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(PART II)

THERMODYNAMIC PROPERTIES OF INDIVIDUAL SUBSTANCES. VOLUME I: CALCULATION OF THE THERMODYNAMIC PROPERTIES. (CHAPTERS 16 THRU 27)

by

A. V. Gurvich, G. A. Khachkuruzov, et al.

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ABSTRACT: Thermodynamic properties for the ideal gas state in table form for 335 gases, 44 liquids, and 45 solids compounded from 33 chemical elements and their isotopes, viz.: H, D, T. He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Br, Kr, Re, Sr, Zr, I, Xe, Cs, Ba, Hg, and Pb. Thermodynamic properties are given for the following 22 gases in the range from room temperature to 20,000°K: H, H^+, H^-, O, O^+, H_2, O_2^+, O_2, OH, OH^+, H_2O, N, N^+, N_2, N_2^+, NO, NO^+, C, C^+, CO, CO^+, and e^-; for the 14 least stable gases up to 4000°K; and for the remaining 299 gases up to 6000°K. Virial coefficients for 34 gases are also given up to 6000°K.

In Vol. I of the Handbook the methods of calculating the thermodynamic properties of individual substances are described, and critical analysis is given of the literature data until 1960, including the constants necessary for the calculation of the tables of the thermodynamic properties (molecular constants, heats of formation and heats of phase transitions, specific heats, dissociation energies, etc.), the choice of the values of these constants accepted in the Handbook is substantiated and their values are estimated for such cases where experimental data are lacking.

Volume II of the Handbook contains tables of the thermodynamic properties of individual substances. All tables were calculated by the authors of the Handbook on the basis of the data accepted in Vol. I. English Translation: 321 tables, 4392 references; 2409 pages.

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→ THIS SECOND PART OF VOLUME I COVERS THE [illegible] AND [illegible] C, CH, C_2H_2, C_2H_4, S, P, Al, Ba, Hg, [illegible]

Partial Listing of Contents.

Part One. Methods of Calculation of Thermodynamic Properties of Individual Substances.

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Chapter 16

CARBON AND ITS COMPOUNDS WITH OXYGEN

(C, C^+, C_2, C_3, CO, CO^+, CO_2, C_3O_2, HCO, H_2CO, FCO, F_2CO,
$HFCO$, $ClCO$, Cl_2CO, $FClCO$)

The thermodynamic properties of a large group of compounds, containing carbon, are treated in the Handbook. Carbon and the compounds of carbon and oxygen, and compounds of carbon with oxygen and hydrogen, oxygen and fluorine or oxygen and chlorine will be discussed in the present chapter. Methane is treated in Chapter 17, ethylene in Chapter 18, acetylene and their halogen derivatives in Chapter 19. Compounds of carbon containing more than two carbon atoms (with the exception of C_3O_2) are not considered in the Handbook. Ethane and its derivatives were also not included in the Handbook, Chapter 20 treats the dissociation products of methane, ethylene and acetylene and their fluorine-chlorine derivatives. The simplest compounds of carbon and sulfur (CS, CS_2, COS), nitrogen (CN, C_2N_2, HCN, FCN) and phosphorus (CP) are treated in Chapter 21.

It should be pointed out that methane, ethylene and acetylene, their halogen derivatives and the compounds of carbon and nitrogen are thermodynamically not very stable and decompose upon heating with separation of carbon in the amorphous state (carbon black). The most stable are the compounds of carbon and oxygen. The high dissociation energy of carbon monoxide (about 255.8 kcal/mole) prevents the dissociation of this compound even at very high temperatures.

The Handbook gives the thermodynamic properties of the two allotropic crystalline modifications of elemental carbon: graphite and diamond. At normal pressure and temperature, graphite is the thermodynamically equilibrated modification of carbon, which is used as the standard state of carbon. However, the transformation of diamond into graphite ("graphitization") begins to take place at a noticeable rate only at temperatures above 1300°K.

In addition to the crystalline modifications, different forms of so-called amorphous carbon are also known, such as carbon black, coke, wood and animal charcoal, etc. The heats of formation of these substances from graphite are 0.5 to 3.4 kcal/g-atom [98, 813]. X-ray studies of "amorphous" carbon showed that it consists mainly of very small graphite crystallites which are arranged without order [306], Upon heating to 2000-300°K, "amorphous" carbon is transformed into graphite. The thermodynamic properties of "amorphous" carbon as well as of other substances in the amorphous state, are not given in the Handbook.

In spite of the fact the long-lasting dispute concerning the heat of sublimation of carbon has now become solved, the composition of the products of evaporation of carbon, particularly at high temperatures,remains as yet unexplained. In addition to the compounds C, C^+, C_2 and C_3, discussed in the Handbook, there are indications concerning the presence of compounds such as C^-, C_4, C_5 [1113, 1405] and even more complex molecules [3256] in saturated carbon vapor. This problem requires further clarification.

The stable compounds of carbon and oxygen are fully presented in the Handbook. In addition to the well-known oxides CO and CO_2, the thermodynamic properties of the under normal conditions comparatively unstable molecule C_3O_2 are also given.

The group of compounds with the formula X_2CO or $XYCO$, where X and

Y are hydrogen, fluorine or chlorine, contains several compounds which are generally not very stable. Under certain conditions, however, these compounds (particularly F_2CO) can be important components of the reaction products. Also included in the Handbook are HCO, FCO and ClCO, the dissociation products of the above-mentioned compounds of the type X_2CO.

On the whole, the thermodynamic data, presented in the present chapter and in other chapters, in which carbon compounds are treated, make it possible to carry out fairly accurate calculations of the compositions and thermodynamic properties of the products of interaction between carbon and oxygen, hydrogen, halogens, sulfur, phosphorus and nitrogen.

§57. MOLECULAR CONSTANTS

C. In the ^3P-ground state, the carbon atom has the electronic configuration $1s^2 2s^2 2p^2$, to which correspond two more states: ^1D and ^1S. When one of the 2p electrons is excited, the group of states $1s^2 2s^2 2p(^2P)n\ell$ arises, whose ionization limit is situated 90,878.3 cm^{-1} above the lower $^3P_0$ substate. This group consists of triplet and singlet terms with $L = 1$ at $\ell = 0$ and $L = \ell, \ell \pm 1$ at $\ell > 0$. Four more groups of terms are connected with the excitation of a single 2s electron: $1s^2 2s^2 p^2(^4P)n\ell'$; $1s^2 2s2p^2(^2D)n\ell''$; $1s^2 2s2p^2(^2S)n\ell'''$; $1s^2 2s2p^2(^2P)n\ell''''$ the terms of the other groups which correspond to an excitation of the 1s electrons or the simultaneous excitation of two electrons with $n = 2$, have an energy over 200,000 cm^{-1} and are not treated in the present Handbook.

Table 124 gives the levels of the carbon atom, corresponding to the electronic configurations $1s^2 2s^2 2p^2$, $1s^2 2s^2 2pn\ell$ and $1s^2 2s2p^2 n\ell$ with values of $n \leq 13$. The excitation energies of these states were adopted on the basis of the figures, recommended by Moore [2941]. The states with similar excitation energies are combined into a single level with a mean energy and a summary statistical weight. It should be pointed out that for the group $1s^22s^22pn\ell$, data are given in the summary [2941] only for the states with $n \leq 11$, mainly for the S and D terms.

TABLE 124

Energy Levels of the Carbon Atom

A Номер уровня	B Состояние		E Статистический вес	F Энергия, $см^{-1}$
	электронная конфигурация C	терм D		
0	$1s^22s^22p^2$	$^3P_0$	1	0
1	$1s^22s^22p^2$	$^3P_1$	3	16,4
2	$1s^22s^22p^2$	$^3P_2$	5	43,5
3	$1s^22s^22p^2$	^1D	5	10193,7
4	$1s^22s^22p^2$	^1S	1	21648,4
5	$1s^22s2p^3$	^5S	5	33735,2
6	$1s^22s^22p\,(^2P)\,3s$	^3P	9	60370
7	$1s^22s^22p(^2P)3s$	^1P	3	61982
8	$1s^22s2p^3$	^3D	15	64090
9	$1s^22s^22p\,(^2P)\,3p$	^1P	3	68858
10	$1s^22s^22p\,(^2P)\,3p$	^3D	15	69720
11	$1s^22s^22p\,(^2P)\,3p$	^3S	3	70744
12	$1s^22s^22p\,(^2P)\,3p$	^3P	9	71375
13	$1s^22s^22p\,(^2P)\,3p$	^1D	5	72611

A Номер уровня	Состояние B		E Статистический вес	F Энергия, см⁻¹
	электронная конфигурация C	терм D		
14	$1s^22s^22p\,(^2P)\,3p$	^1S	1	73976
15	$1s^22s2p^3$	^3P	9	75256
16	$1s^22s^22p\,(^2P)\,3d$	^1D	5	77680
17	$1s^22s^22p\,(^2P)\,4s$ $1s^22s^22p\,(^2P)\,3d$	P $F,\ ^3D,\ ^1P$	58	78300
18	$1s^22s^22p\,(^2P)\,3d$	^3P	9	79320
19	$1s^22s^22p\,(^2P)\,4p$	$^3D,\ ^1P$	18	80260
20	$1s^22s^22p\,(^2P)\,4p$	$^3S,\ ^3P,\ ^1D$	17	81420
21	$1s^22s^22p\,(^2P)\,4p$	^1S	1	82252
22	$1s^22s^22p\,(^2P)\,4d$ $1s^22s^22p\,(^2P)\,5s$	$P,\ D,\ F$ $^1P,\ ^3P^\circ$	72	83850
23	$1s^22s^22p\,(^2P)\,5p$	$^3S^\circ,\ ^1P,\ ^3P^\circ,\ ^3D$	30	84950
24	$1s^22s^22p\,(^2P)\,5p$	$^1D,\ ^1S$	6	85440
25	$1s^22s^22p\,(^2P)\,5d$ $1s^22s^22p\,(^2P)\,6s$	$P,\ D,\ F$ $^1P,\ ^3P^\circ$	72	86380
26	$1s^22s^22p\,(^2P)\,6p$ $1s^22s^22p\,(^2P)\,6d$ $1s^22s^22p\,(^2P)\,7s$	$S^\circ,\ P^\circ,\ D^\circ$ $P,\ D,\ F$ $^1P,\ ^3P^\circ$	108	87720
27	$1s^22s^22p\,(^2P)\,7p$ $1s^22s^22p\,(^2P)\,7d$	$S^\circ,\ P^\circ,\ D^\circ$ $P,\ ^1D^\circ,\ ^3D,\ F$	96	88570
28	$1s^22s^22p\,(^2P)\,8s$ $1s^22s^22p\,(^2P)\,8p$ $1s^22s^22p\,(^2P)\,8d$ $1s^22s^22p\,(^2P)\,9s$ $1s^22s^22p\,(^2P)\,9p$ $1s^22s^22p\,(^2P)\,9d$	P° $S^\circ,\ P^\circ,\ D^\circ$ $^1P^\circ,\ ^3P,\ ^1D^\circ,\ ^3D,\ F$ P° $S^\circ,\ P^\circ,\ D^\circ$ $P^\circ,\ ^1D^\circ,\ ^3D,\ F$	216	89290
29	$1s^22s^22p\,(^2P)\,10s,\ 11s$ $1s^22s^22p\,(^2P)\,10p,\ 11p$ $1s^22s^22p\,(^2P)\,10d,\ 11d$	P° $S^\circ,\ P^\circ,\ D^\circ$ $P^\circ,\ ^1D^\circ,\ ^3D,\ F^\circ$	216	89870
30	$1s^22s^22p\,(^2P),\ 3 \leqslant n \leqslant 13$ $3 \leqslant l \leqslant 12$ $1s^22s^22p\,(^2P),\ n=12,\ 13,\ l=0,1,2$	$L = \lvert l \rvert,\ \lvert l \pm 1 \rvert$	5040[a]	90878
31	$1s^22s2p^3$ $1s^22s2p^2\,(^4P)\,3s$	$^3S,\ ^1P,\ ^1D$ ^5P	26	104600

Номер уровня A	Состояние B		Статистический вес E	Энергия, $см^{-1}$ F
	электронная конфигурация C	терм D		
32	$1s^22s2p^2\,(^4P)\,3p3d$ $1s^22s2p^2\,(^4P), 4 < n < 13$ $0 < l < 12$ $1s^2\,2s2p^2\,(^4P)\,3s$	$L = \lvert l\rvert, \lvert l \pm 1\rvert$ $^3P^{\circ}$	$12009^{б}$ b	133880
33	$1s^22s2p^2(^2D), 3 < n < 13$ $0 < l < 12$	$L = \lvert l\rvert,$ $\lvert l \pm 1\rvert, \lvert l \pm 2\rvert$	$10020^{в}$ c	165809
34	$1s^22s2p^2(^2S), 3 < n < 13$ $0 < l < 12$	$L = \lvert l\rvert$	$2002^{г}$ d	187372
35	$1s^22s2p^2(^2P), 3 < n < 13$ $0 < l < 12$	$L = \lvert l\rvert, \lvert l \pm 1\rvert$	$6012^{д}$ e	201503

* the state has not been observed experimentally.

a) the value of p_M is given for $n \leq 11$; at $n \leq 12$ $p_M = 6768$; at $n \leq 13$ $p_M = 8796$;

b) the value p_M is given for $n \leq 11$; at $n \leq 12$ $p_M = 15465$; at $n \leq 13$ $p_M = 19521$;

c) the value p_M is given for $n \leq 11$; at $n \leq 12$ $p_M = 12900$; at $n \leq 13$ $p_M = 16280$;

d) the value p_M is given for $n \leq 11$; at $n \leq 12$ $p_M = 2580$; at $n \leq 13$ $p_M = 3256$;

e) the value of p_M is given for $n \leq 11$; at $n \leq 12$ $p_M = 7740$; at $n \leq 13$ $p_M = 9768$.

A) Number of level; B) state; C) electronic configuration; D) term; E) statistical weight; F) energy cm^{-1}..

For the states which belong to the other groups, experimental data exist only for the states corresponding to the electronic configurations $1s^22s2p^3$ and $1s^22s2p^2(^4P)3s$. The excitation energies of all the other states are unknown and the figures given for them in Table 124 are based on approximate estimates, carried out in correspondence with the previously formulated rules (see page 55). In particular, in the group $1s^22s^22p(^2P)n\ell$, the excitation energies of the ^3P states with $n = 5$-7 and $\ell = 0$, were assumed to be equal to the excitation energies of the ^1P terms, the excitation energies of the ^1P terms, the excitation energies of the states . . . $5p^3S$ and ... $5p^3P$ were assumed to be equal to the energies of the terms ... $5p^1P$ and ... $5p^3D$, etc. Because the excitation energies of all the states with $\ell \geq 3$ are unknown, they were assumed to be equal to the energy of the ionization limit. The maximum uncertainty in the estimation of the energies of the levels in this group is that for the states with the configuration ... (^2P) 4f and amount to approximately 6000 cm^{-1}, at an energy of about 90,000 cm^{-1}.

The experimentally not observed states, corresponding to the configuration $1s^22s2p^2n\ell$, were also assigned to the ionization limits of the respective groups of terms. The maximum error in the excitation energies of the levels with low principal quantum numbers n adopted on the basis of these estimates can attain 25,000-30,000 cm^{-1} with a magnitude of these energies of about 120,000-170,000 cm^{-1}.

$\underline{C^+}$. In the ground state ^2P, the positive ion of monatomic carbon has the electronic configuration $1s^22s^22p$. When one of the 2p electrons is excited, a group of doublet states appears, having the electronic configuration $1s^22s^2(^1S)n\ell$; the corresponding ionization limit has an energy of 196,658 cm^{-1}. Two other groups of states with the electronic configurations $1s^22s2p(^3P)n\ell$ and $1s^22s2p(^1P)n\ell$ are connected with the excitation of a single 2s electron. The energies of the ionization limits of these groups are unknown, but exceed the energy of the ionization limit of the group $1s^22s^2(^1S)n\ell$. Table 125 gives the energy levels of the ion C^+, corresponding to the electronic configurations $1s^22s^22p$ and $1s^22s2p^2$ with excitation energies of less than 100,000 cm^{-1}. The states with higher excitation energies are not treated in the Handbook, because their contribution to the results of the following calculations is small. The excitation energies, presented in Table 125, were adopted on the basis of the data of Moore

[2941]; for the multiplet states, the mean excitation energies and the summary statistical weight are given.

TABLE 125

Energy Levels of the Ion C^+

Номер уровня A	B Состояние		E Статистический вес	F Энергия, см⁻¹
	электронная конфигурация C	терм D		
0	$1s^22s^22p$	$^2P_{1/2}$	2	0
1	$1s^22s^22p$	$^2P_{3/2}$	4	64,0
2	$1s^22s2p^2$	^4P	12	43 033
3	$1s^22s2p^2$	^2D	10	74 930
4	$1s^22s2p^2$	^2S	2	96 494

A) Number of level; B) state; C) electronic configuration; D) term; E) statistical weight; F) energy, cm^{-1}.

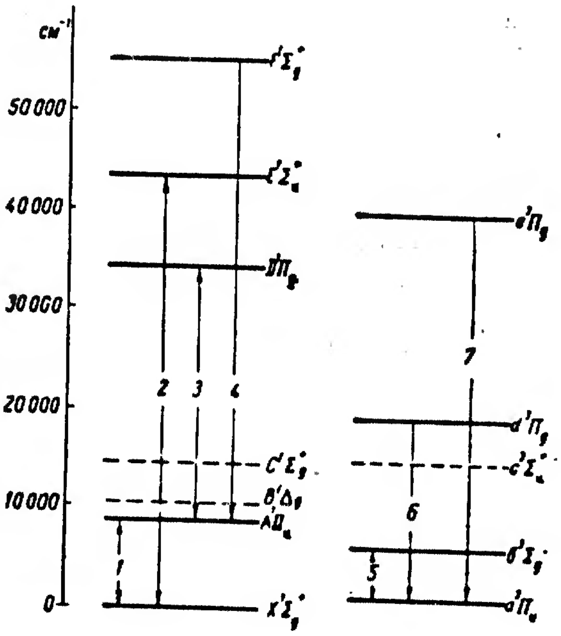

Fig. 15. Scheme of the energy levels of the molecule C_2. The horizontal lines designate the electronic states. The electronic transitions, observed in the spectrum of C_2, are indicated by arrows, where 1) Phillips system ($^1\Pi_u - {}^1\Sigma^+_g$); 2) Milliken system ($^1\Sigma^+_u - {}^1\Sigma^+_g$); 3) Deslandres-Azambia system ($^1\Pi_g - {}^1\Pi_u$); 4) Freimark system ($^1\Sigma^+_g - {}^1\Pi_u$) 5) Ballik-Ramsay system ($^3\Sigma^-_g - {}^3\Pi_u$); 6) Swan system ($^3\Pi_g - {}^3\Pi_u$); 7) Fox-Herzberg system ($^3\Pi_g - {}^3\Pi_u$); intercombination transitions have not been observed in the spectrum of C_2. The existence of the state

$^3\Sigma^+_u$ and its excitation energy is reported in the work [527] with a reference to a private communication by Ballik and Ramsay.

C_2. Three systems of bands were observed in the emission spectrum of the C_2 molecule connected with the transitions between the triplet states: Swan ($^3\Pi_g - {}^3\Pi_u$); Fox - Herzberg ($^3\Pi_g - {}^3\Pi_u$); and Ballik and Ramsay ($^3\Sigma^-_g - {}^3\Pi_u$) and four systems, due to transitions between the singlet states: Phillips ($^1\Pi_u - {}^1\Sigma^+_g$); Deslandres - Azambia ($^1\Pi_g - {}^1\Pi_u$), Mulliken ($^1\Sigma^+_u - {}^1\Sigma^-_g$) and Freimark ($^1\Sigma^+_g - {}^1\Pi_u$). The systems of Swan [3234], Phillips [3233], Deslandres - Azambia [2049], Mulliken [2556] and Ballik and Ramsay [629] were also observed in the absorption spectrum (see Fig. 15). On the basis of the method of molecular orbits, Mulliken [2983, 2997] showed that in addition to the states, observed experimentally and given in Fig. 15, the existence of several more stable electronic states is possible, which have relatively low excitation energies, in particularly the states $^1\Delta_g$ and $^3\Sigma^-_g$. From the theoretical analysis, carried out by Mulliken [2997] followed that the electronic ground state of the C_2 molecule may be the states $^1\Sigma^+_g$, $^3\Pi_u$, $^3\Sigma^-_g$ and $^1\Delta_g$.

Up to 1959, the lower triplet state, namely the state $^3\Pi_u$, had been taken for the electronic ground state of C_2. This assignment was based on the fact that the system of Swan is easily observed in the absorption spectra. This was also confirmed by the experiments of Robinson and MacCarty [3459a], in which C_2 molecules were frozen in an inert gas matrix at a temperature of 4.2°K and Swan bands with constant intensity appeared in the absorption spectrum for several hours. The Swan bands were also observed in the emission spectrum of comets [3909a], and were connected with the process of resonance fluorescence. Moreover, Hicks [2068] measured the temperature coefficient of the intensity of the Swan and Phillips bands in the emission spectrum of a

King furnace and arrived at the conclusion that the state $^1\Sigma^+_g$ should be situated 2800 ± 1400 cm^{-1} above the state $^3\Pi_u$.

TABLE 126

Adopted Values of the Molecular Constants of C_2

Состояние A	T_e	ω_e	$\omega_e x_e$	B_e	$\alpha_1 \cdot 10^2$	$D_e \cdot 10^6$	$\beta_1 \cdot 10^6$	r_e
	см⁻¹ B							Å
$X^1\Sigma^+_g$ ^{a}	0	1855,18	13,71^b	1,82052	1,832	6,36	0,41	1,2422
$a^3\Pi_u$	717^c	1641,328	11,625^d	1,6326	1,683	7,02	0,15	1,3117
$b^3\Sigma^-_g$	6243,5^e	1470,438	11,166^f	1,49852	1,634	6,23	—	1,3631
$A^1\Pi_u$	8391,66	1608,284	12,047^g	1,61700	1,720	6,35	—0,12	1,3180
$B^1\Delta_g$ ^{h}	10000^e	1481^i	11,14^i	1,486^n	1,5^i	5,98^k	—	1,375^i
$C^1\Sigma^+_g$ ^{h}	14000^e	1470^i	10,06^i	1,475^i	1,3^i	5,94^k	—	1,380^i
$c^3\Sigma^+_u$ ^{h}	14300^e	1891^i	14,23^i	1,897^i	1,8^i	7,64^k	—	1,217^i
$d^3\Pi_g$	19923,0	1788,22^l	16,44^m	1,7527	1,608^n	6,74	—0,103^o	1,2660
$D^1\Pi_g$	34261,9	1809,1	15,81	1,7834	—	6,8	—	1,255
$e^3\Pi_g$	40523,4	1106,56	39,26	1,1922	2,42	6,3	—	1,5350
$E^1\Sigma^+_u$	43240,23	1829,57	13,97	1,8334	2,04	7,89	0,7	1,2378
$F^1\Sigma^+_g$	55035,4	1671,5	40,02	1,7930	1,21	—	—	1,25

a) in the work of Altman [527] reference is made to a private communication by Ballik and Ramsay and the following constants (in cm^{-1}) are given for this state: $\omega_e = 1854.72$; $\omega_e x_e = 13.34$; $\omega_e y_e = -0.17$; $B_e = 1.81984$; $\alpha_1 = 0.01765$; $\alpha_2 = -0.00023$; b) $\omega_e y_e = -0.06$ cm^{-1}; c) A = -16.4 cm^{-1}; d) $\omega_e y_e = -0.0298$ cm^{-1}; e) the value T_0 is given; f) $\omega_e y_e =$ $= -0.016$ cm^{-1}; g) $\omega_e y_e = -0.062$ cm^{-1}; h) this state has not been observed experimentally (see page 870); i) the values estimated by Clementi [1128b] are given; k) calculated on the basis of the relation (1.36); l) the vibrational constants for the state $d^3\Pi_g$, given in the Table, are the coefficients of the equation which holds for v ≤ 3 (see page 869); m) $\omega_e y_e = -0.5067$ cm^{-1}; n) $\alpha_2 = -0.001274$ cm^{-1}; o) $\beta_2 =$ $= -0.0442 \cdot 10^{-6} cm^{-1}$. A) State; B) cm^{-1}.

It was found, however [630] during the analysis of the vibrational and rotational structure of the bands of the infrared system $^3\Sigma^-_g - {}^3\Pi_u$, first detected by Ballik and Ramsay [629] in the emission spectrum of a carbon furnace, that certain rotational levels of the

$^3\Sigma^-_g$ state are subjected to perturbations. Because Ballik and Ramsay [630] found the corresponding perturbations in the bans of the Phillips system, they arrived at the conclusion that the states $^3\Sigma^-_g$ and $^1\Sigma^+_g$ perturb each other. Analysis of the perturbations showed that the zero rotational level of the state $^1\Sigma^+_g$ is 610 cm^{-1} below the zero vibrational level of the state $^3\Pi^+_u$.* Thus it has been proved indisputably that the electronic ground state of the molecule C_2 is the singlet state $^1\Sigma^+_g$.** On the basis of the work of Ballik and Ramsay [630], the state $^1\Sigma^+_g$ has been adopted in the present Handbook as the ground state of C_2. In this connection, the designations of the states (X, A, B, ...) given in Table 126 and used in the present Handbook, differ essentially from the corresponding designations, used by Herzberg [2020] and Rosen [649] and which have been widely adopted in the spectroscopical literature.

The molecular constants of C_2 in the ground state $X^1\Sigma^+_g$ were found by Landsvert [2556] and Phillips [3233] as a result of an analysis of the bands in the systems $E^1\Sigma^+_u \rightarrow X^1\Sigma^+_g$ and $A^1\Pi^+_u \rightarrow X^1\Sigma^+_g$, respectively.

Landsverk [2556] studied the bands of the sequence $\Delta v = 0$ with $v \leq 3$ in the system $E^1\Sigma^+_u \rightarrow X^1\Sigma^+_g$. A carbon arc, which burned in a helium atmosphere, served as the radiation source. The bands were photographed on a spectrograph with a lattice which had a dispersion of 0.25 A/mm in the third order. As a result of the analysis carried out by him, Landsverk found the following values of the rotational constants of C_2 in the state $X^1\Sigma^+_g$ (in cm^{-1}): $B_e = 1.8223$; $\alpha_1 = 0.0195$; $D_e = 7.86 \cdot 10^{-6}$; $\beta_1 = 9.4 \cdot 10^{-7}$ and estimated the value of $\omega_e = 1774$ cm^{-1}. For the state $E^1\Sigma^+_u$ he found the values $B_e = 1.8334$; $\alpha_1 = 0.0204$; $D_e = 7.89 \cdot 10^{-6}$; $\beta_1 = 7.0 \cdot 10^{-7}$; and $\omega_e = 1767$ cm^{-1}.

Phillips [3233] investigated the bands of the system $^1\Pi_u - {}^1\Sigma^+_g$

during excitation in a discharge tube, filled with a mixture of benzene and argon. The spectrum, situated in the region from 7500 to 9000 A, was recorded in the first order of a 21 foot grating with a dispersion of 2.5 A/mm. Phillips measured the rotational structure and determined the positions of the zero lines of five bands ($v' = 2, 3, 4$ and 5 and $v'' \leq 2$). On the basis of the analysis carried out by him, he recommended the following values for the molecular constants of C_2 in the state $X^1\Sigma^+_g$: $\omega_e = 1855.68$; $\omega_e x_e = 14.08$; $B_e = 1{,}82052$, $\alpha_1 = 0{,}01832$, $D_e = 7{,}36 \cdot 10^{-6}$, $\beta_1 = +0{,}41 \cdot 10^{-6}$ $см^{-1}$ and correspondingly for the upperstate of the observed transition ($A^1\Pi_u$): $\omega_e = 1608.33$; $\omega_e x_e = 12.14$; $B_e = 1.61700$; $\alpha_1 = 0.01720$; $D_e = 6.35 \cdot 10^{-6}$ and $\beta_1 = -0.12 \cdot 10^{-6}$ cm^{-1}.

Extrapolation of the vibrational levels of the state $X^1\Sigma$ on the basis of the constants, found by Phillips [3233], leads to a dissociation limit at 60,212 cm^{-1}, which exceeds considerably the value D_0 (C_2), adopted in the present Handbook (see page 952). Hence, when the Handbook was prepared, the values of the vibrational constants of C_2 in the state $X^1\Sigma^+_g$ were calculated again on the basis of the values $\Delta G_{1/2}$ and $\Delta G_{3/2}$, found by Phillips [3233], the value of D_0 (C_2) = 50,072 cm^{-1} (see page 952) and the relations (1.14a) and (1.14b). The vibrational constants thus obtained are given in Table 126 and were adopted in the Handbook.

Analogously, extrapolation of the vibrational levels of the state $A^1\Pi$ on the basis of the constants, found by Phillips [3233] leads to a dissociation limit at 52,465 cm^{-1} which is approximately 10,000 cm^{-1} higher than the value, calculated on the basis of the adopted dissociation energy of C_2 in the state $X^1\Sigma^+_g$ and the excitation energy of the state $A^1\Pi$. Hence the vibrational constants of C_2 in the state $A^1\Pi$, given in Table 126 and adopted in the present Handbook, differ slightly from the constants, recommended by Phillips. They were calculated on the basis of the experimental data, given in the work of Phillips, taking into account the dissociation energy of C_2, adopted in the Handbook. The values of the rotational constants of C_2 in the states $X^1\Sigma$ and $A^1\Pi$ given in Table 126, were taken from the work of Phillips [3233].

As has been pointed out earlier, the state $a^3\Pi_u$ (excitation energy 717 cm^{-1}) which is the lower state of the wellknown Swan system ($d^3\Pi_g - a^3\Pi_u$) is directly adjacent to the electronic ground state $X^1\Sigma^+_g$. An analysis of the vibrational and rotational structure of the bands in the Swan system has been carried out by many authors [2261, 3697, 1006, 1589, 3234, 2019]. In order to obtain more accurate molecular constants of C_2, Phillips [3234] carried out an analysis of the vibrational structure of the band systems, found by various authors and connected with the state $^3\Pi_u$ [1589, 3234, 2019] and showed that the binomial formula with the constants $\omega_e = 1641.35$ cm^{-1} and $\omega_e x_e = 11.67$ cm^{-1} describes the energy of the vibrational levels of the state $^3\Pi_u$ satisfactorily up to $v = 11$. However, Phillips [3234] did not succeed in finding an equation which describes sufficiently accurately the experimental data on the energy of the vibrational levels of C_2 in the state $^3\Pi_g$. This is due to the fact that the dependence of ΔG on $\underline{v}$ for the lower vibrational levels is practically linear, while for the high vibrational levels there is a considerable deviation from linearity. Hence, Phillips [3234] used two third power equations to describe the vibrational levels of the state $^3\Pi_g$. The first equation has the form $G_0(v) = 1771.40v - 17.200v^2 - 0.5067v^3$ at $v > 5$, it already gives a considerable error (the difference between the observed and calculated values of $G_0(10)$ is 239 cm^{-1}). The second equation $G_0(v) = 1767.51v - 13.900v^2 - 1.0345v^3$, obtained by using all observed vibrational terms, is only approximate, because the differences between the observed and calculated values of G_0 (v) attain ±4 cm^{-1} for the low as well as the high levels. The use of a fourth power equation does not give a greatly improved accuracy of the description of the vibrational levels. The vibrational constants of C_2 in the state $d^3\Pi_g$, adopted in the present Handbook, are given in Table 126.

The values of the vibrational constants of C_2 in the state $a^3\Pi_u$, adopted in the Handbook, were calculated on the basis of the data given in the work of Phillips [3234], taking into account the adopted value of the dissociation energy of C_2.

The values of the rotational constants for the electronic states $a^3\Pi_u$ and $d^3\Pi_g$, found by Phillips [3234] and in the works of other authors [1006, 1589], agree well with each other. Because there was no reason for giving preference to any single value, Phillips [3234] recommends as the most probable values of the constants the averages of those obtained in the works [1006, 1589, 3234]. These values are given in Table 126 and were adopted in the Handbook.

Presented in the same Table are the molecular constants of C_2 in the state $b^3\Sigma^-_g$, first observed by Ballik and Ramsay [629]. The vibrational constants of C_2 in this state were calculated on the basis of the data, given in the work [527] and the adopted value of the dissociation energy of C_2; the values of the rotational constants were borrowed from the work of Altman [527] who refers to a private communication from Ballik and Ramsay.

The molecular constants of C_2 in the singlet states $D^1\Pi_g$, $E^1\Sigma^+_u$, and $F^1\Sigma^+_g$, adopted in the Handbook, were obtained in the works [3233, 2049, 2556, 1611] as a result of an analysis of the bands in the system of Deslandres - Azambia, Mulliken and Freimark.

The values of the molecular constants of C_2 in the state $e^3\Pi_g$, adopted in the Handbook (see Table 126), were found in the work [3235] on the basis of an analysis of the band system of Fox – Herzberg.

Clementi [1128b], in accordance with the results of the theoretical calculations of Mulliken [2983, 2997] and Pitzer and Clementi [3256, 1128c] proposed that in addition to the experimentally observed states, the stable states $^1\Delta_g$, $^1\Sigma^+_g$ and $^3\Sigma^+_u$ with low excitation energies (10,000-14,000 cm^{-1}) should exist in the molecule C_2. The values of the molecular constants of C_2 under these conditions, found in the work [1128b], obtained on the basis of approximate estimates, are given in Table 126 and were adopted in the present Handbook. Because the analogous estimate of the molecular constants of C_2 in the investigated experimental states ($^1\Sigma^+_g$, $^3\Pi_u$, $^1\Pi_u$, $^3\Sigma^-_g$, etc.) carried out by Clementi, leads to values which differ from the experimentally found values by not more than 3-5%, it may be expected that the error in the constants of C_2 in the states $^1\Delta_g$, $^1\Sigma^+_g$ and $^3\Sigma^+_u$, estimated by Clementi, does not exceed 3-5%.

It should be pointed out that linear extrapolation of the vibrational levels of the states $B^1\Delta_g$, $C^1\Sigma^+_g$ and $c^3\Sigma^+_u$ on the basis of the constants, recommended by Clementi [1128b], leads to dissociation limits, whose energy is considerably higher (by 8000, 17,000 and 26,000 cm^{-1}, respectively) than the excitation energies of these states calculated on the basis of the adopted values and the dissociation energy of the C_2 molecule.*

<u>CO</u>. The molecule of carbon monoxide has the ground state $^1\Sigma^+$ and several triplet and singlet excited states. The spectra of the CO molecule have been studied more intensively to date than the spectra of most other diatomic molecules. Figure 16 shows a scheme of the known electronic states of the molecule CO, whose excitation energies

do not exceed 100,000 cm^{-1} and indicates the observed transitions between these states. In addition to the electronic spectra, situated in the ultraviolet, visible and near infrared regions, the vibrational - rotational and rotational spectra of CO in the infrared and microwave regions have also been studied.

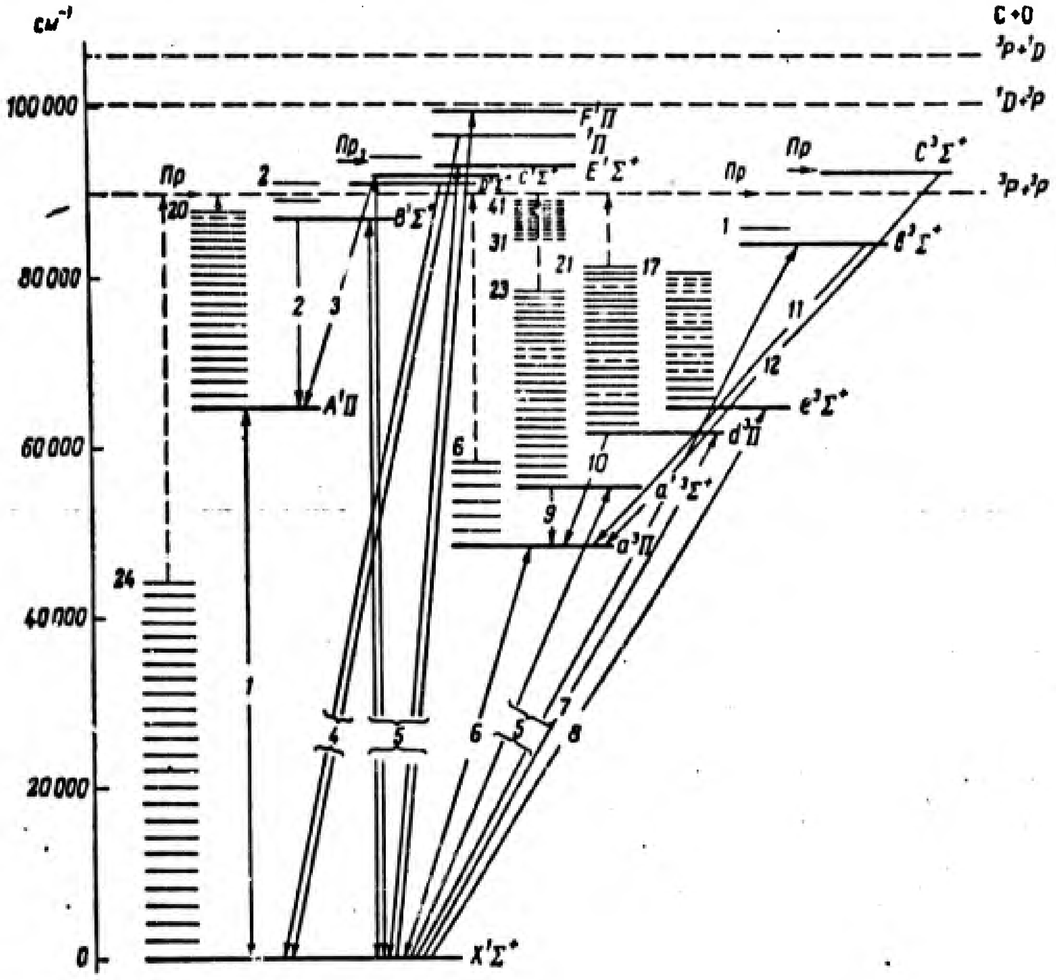

Fig. 16. Scheme of the energy levels of the CO molecule. The thick horizontal lines indicate the electronic states. The finer lines correspond to the vibrational levels. The figure at left indicate the number of observed vibrational levels in the given state. The dotted arrows indicate the dissociation limits of the electronic states. These limits are marked by dotted horizontal lines. The horizontal arrows (Пр) indicate the predissociations. The electronic transitions, observed in the spectrum of CO, are indicated by thick arrows, where 1) band system $A^1\Pi - X^1\Sigma^+$ (fourth positive band system); 2) $B^1\Sigma^+ - A^1\Pi$ (Angstrom band); 3) $C^1\Sigma^+ - A^1\Pi$ (Herzberg bands); 4) $D^1\Sigma^+ - X^1\Sigma^+$ (Chulanovskiy band); 5) Hopfield - Birge bands with the lower state $X^1\Sigma^+$; 6) $a^3\Pi - X^1\Sigma^+$ (Cameron band); 7) $d^3\Pi - X^1\Sigma^+$ (Tanaka band);

8) $B^3\Sigma^+ - X^1\Sigma^+$ (Herzberg - Hugo band); 9) $a'^3\Sigma^+ - a^3\Pi$ (Asundi band); 10) $d^3\Pi - a^3\Pi$ ("triplet" band system); 11) $b^3\Sigma^+ - a^3\Pi$ (third positive band system); 12) $c^3\Sigma^+ - a^3\Pi$ (band system "3A").

Basic information on the molecular constants of CO in the $X^1\Sigma^+$ state was obtained as a result of a study of the fourth positive band system; situated in the region 1300-2700 A and corresponding to the transition $A^1\Pi - X^1\Sigma^+$ and also the vibrational-rotational spectra of this molecule. The most detailed investigation of the system $A^1\Pi - X^1\Sigma$ has been carried out by Gero [1688, 1689] and Schmid and Gero [3635] who obtained on a spectograph with a dispersion of 1.2 A/mm, a large number of bands, connected with transitions to different vibrational levels of the ground state with values of v" from 8 to 24, and who carried out an analysis of their rotational structure. The bands corresponding to the transitions to the lower vibrational levels of the state $X^1\Sigma^+$ were studied by Read [3405, 3406] (v" from 0 to 10), and Chulanovskiy and Stepanov [459] (v" from 5 to 8). Read [3406] and Schmid and Gero [3635] calculated on the basis of the results of investigation of the band system $A^1\Pi - X^1\Sigma^+$ the constants in the equations for the vibrational and rotational energies, which describe the experimental data satisfactorily. The other band systems of CO were observed in absorption or were obtained on low dispersion devices. The results of the investigations on these systems did not permit the introduction of improvements into the values of the constants for the state $X^1\Sigma^+$, found on the basis of an analysis of the system $A^1\Pi - X^1\Sigma^+$. The sole exception is the investigation of the band system $a^3\Pi - X^1\Sigma^+$ (Cameron band), carried out by Gero [1691], Gero, Herzberg and Schmid [1697], Rao [3390] and McCulloh and Glockler [2697], in which the structure of the bands, corresponding to values of v" ≤ 5, was studied.

In order to define the energies of the first vibrational levels of the $X^1\Sigma^+$ state more accurately, careful investigations of the vibrational-rotational spectrum of CO were carried out in several works. In the works of Lagemann and coauthors [4243, 2515], G. Herzberg and Rao [2043], Rao [3391] and Rank and coauthors [3375] the infrared absorption spectra of CO were studied in the range of 1.2-5 microns (8300-2000 cm^{-1}) and an analysis of the bands 1-0, 2-0, 3-0 and 4-0 was carried out. Plyler and coworkers [3279, 3274, 3280, 3281, 3273] investigated the infrared emission and absorption spectra of CO containing flames and carried out an analysis of the bands, corresponding to the transitions with $\Delta v = 1$ and $\Delta v = 2$ for values $v \leq 5$. Finally, Goldberg and Muller [1791], as a result of an analysis of the infrared spectrum of the sun in the region 2.5 microns (4000 cm^{-1}), investigated six CO bands, corresponding to the transitions with $\Delta v = 2$ fcr $v \leq 7$. The data obtained as a result of the investigations on the vibrational-rotational spectrum of CO enabled the values of $G_0(v)$ and B_v for v from 0 to 7 to be considerably improved. The rotational constants of CO (B_0, α_1, D_0) determined in these studies, agree well with those obtained from the purely rotational spectra, situated in the far infrared [3167] and microwave [1750] regions.

On the basis of the investigations of the infrared spectrum and also the results of earlier investigations of the bands $A^1\Pi - X^1\Sigma^+$ and $a^3\Pi - X^1\Sigma^+$ of carbon monoxide in the works [4243, 2515, 2043, 3375, 3279, 3281, 2697, 836, 1791], values were proposed for the constants in the equations for the vibrational and rotational energies of the molecule CO in the $X^1\Sigma^+$ state. As can be seen from Table 127 the values of $G_0(v)$, calculated on the basis of the constants, proposed by various authors, and the values, found experimentally, agree well with each other. However, the levels of the vibrational energies, calculated on the basis of these constants, converge in the region of 95,000-96,000 cm^{-1}, i.e., considerably above the dissociation limit of the $X^1\Sigma^+$ state (see page 950).

TABLE 127

Energies of the Vibrational Levels $G_0(v)$ of the Molecule CO in the State $X^1\Sigma^+$ (in cm^{-1})

v	Experimental data	calculated on the basis of the constants			
		[2697][а]	[836,1791][б] b	[3375][в] c	табл. 128
1	2143,274 [3281]	2143,28	2143,274	2143,276	2143,317
2	4260,06 [3279]	4260,05	4260,05	4260,07	4260,06
3	6350,42 [836]	6350,42	6350,41	6350,44	6350,33
4	8414,42 [3273]	8414,42	8414,42	8414,47	8414,22
5	10452,18 [3273]	10452,20	10452,11	10451,21	10451,83
10	20249,2 [1689]	20249,4	20248,9	20249,1	20248,9
15	29401,2 [1689]	29401,0	29398,9	29399,5	29401,2
20	37916,2 [1689]	37916,1	37910,9	37911,9	37916,1
24	44273,1 [1689]	44276,2	44266,8	44268,1	44272,6
v_{max}	89595 ± 30	94230	94960	94970	89615[г] a

a $G_0(v) = 2156,539\ v - 13,2826\ v^2 + 0,0123\ v^3$; $v_{max} = 105$.

b $G_0(v) = 2156,533\ v - 13,2797\ v^2 + 0,01150\ v^3$; $v_{max} = 92$.

c $G_0(v) = 2156,543\ v - 13,2777\ v^2 + 0,01150\ v^3$; $v_{max} = 92$.

d $v_{max} = 81$.

In view of this the authors of the Handbook calculated the values of the constants in the fourth power equation (previously the constants had been determined only in second and third power equations). The calculation was carried out on the basis of the experimentally obtained values of $G_0(v)$ for $v \leq 24$ (see Table 127), under the assumption that $G_0(v_{max}) = D_0(CO) = 89595$ cm^{-1}. As is evident from the Table, the constants thus obtained describe the experimental values of $G_0(v)$ well and satisfy the requirement for the convergence of the levels near the dissociation limit.

These values of the vibrational constants were adopted in the present Handbook and are given in Table 128. The values of the rotational constants of CO in the $X^1\Sigma^+$ state, adopted on the basis of the work [836] can also to be found there.

The first excited state of CO, the state $a^3\Pi$, has an energy of 48473.97 cm^{-1} [3390] and a general dissociation limit with the state $X^1\Sigma^+$. The molecular constants of CO in the $a^3\Pi$ state can be determined on the basis of an analysis of the Cameron bands ($a^3\Pi - X^1\Sigma^+$), Asundi ($a'^3\Sigma^+ - a^3\Pi$), the triplet system ($d^3\Pi - a^3\Pi$), the third positive system ($b^3\Sigma^+ - a^3\Pi$) and the system "3A" ($c^3\Sigma^+ - a^3\Pi$). The Cameron bands were obtained in the emission as well as the absorption spectra of CO, the other systems were observed only in emission. In most works, carried out on low dispersion apparatus, only the band edges could be observed. An analysis of the rotational structure of the Cameron bands was carried out in the works of Gero, Herzberg and Schmid [1697] and Rao [3390], of the Asundi bands in the work of Gero and Lorinczi [1698], of the triplet system, in the work of Gero and Szabo [1702], of the third positive system in the work of Dieke and Mauchly [1344, 1345, 1346], Schmid and Gero [3633, 3636, 1690], Beer [715] and for the system "3A" by Gero [1692]. The results of the analysis had shown that the $a^3\Pi$ state is a normal $^3\Pi$ state. The rotational constants of CO in the $^3\Pi$ state had been calculated by Dieke and Mauchly [1346], Beer [715] and Budo [1006]. The values of the rotational constants given in Table 128 were taken from the works [1346, 1006].

In all band systems connected with transitions to the $a^3\Pi$ state, bands were observed which correspond to transitions only to several of the first vibrational levels ($v \leq 5$) of this state. The vibrational constants of CO in the $a^3\Pi$ state, calculated in the works of Birge [824], Garg [1650] and those adopted in the handbook [649] and the monographs of Herzberg [2020], describe the experimental values of $G_0(v)$ with insufficient accuracy. Moreover, the levels of the vibrational energies calculated on the basis of these constants, converge about 10,000 cm^{-1} above the dissociation limit of the state $X^1\Sigma^+$, which should be the same as for the $a^3\Pi$ state. Hence the authors of the Handbook calculated new values for the constants in third power equations on the basis of the known values $G_0(v)$, assuming, that the states $X^1\Sigma^+$ and $a^3\Pi$ have the same dissociation limit, and for the state $a^3\Pi$ $G_0(v_{max}) = D_0(CO) - \nu_{00}(a^3\Pi) = 89,595 - 48,474 = 41,121$ cm^{-1}. The constants thus determined are given in Table 128. They describe the experimental data much better and lead to a convergence of the levels at $v_{max} = 44$ and $G_0(44) = 41,126$ cm^{-1}.

The molecular constants of CO in the second excited state $a'^3\Sigma^+$ were determined on the basis of an analysis of the band system of Asundi ($a'^3\Sigma^+ - a^3\Pi$) and Hopfield - Birge ($a'^3\Sigma^+ - X^1\Sigma^+$). The first system was obtained in emission by Asundi [577], Vaydya [4047], Gero [1693], Gero and Lorinczi [1698] and Garg [1650], bands corresponding to $v' \leq 25$ being observed in the work [1650]. On the basis of these research results Garg [1650] recommended the values of the constants of CO in the $a'^3\Sigma^+$ state, which were adopted in the Handbook [649] and the monographs [2020]. More accurate values of the constants if this state were found by Herzberg and Hugo [2033] during an investigation of the band system of Hopfield - Birge on a vacuum device with high dispersion. The authors of the work [2033] carried out an analysis of the rotational structure of all observed bands ($v' \leq 23$), determined the excitation energy of the state $a'^3\Sigma^+$ more precisely and determined the constants of CO in this state (given in Table 128). These constants describe well all the experimental data with the exception of the levels, found by Schmid and Gero [3636] in their analysis of the perturbations of the bands in the third positive system. The differences in the values of $G_0(v)$, calculated by means of the adopted constants and those found experimentally, attain several hundred cm^{-1} in this case. These differences are possibly due to the inaccuracy of the method, used in the work [3636] during the analysis of the perturbations (see [390]).

TABLE 128

Adopted Values of the Molecular Constants of CO

State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_1	α_2	D_e	r_e
	cm^{-1}								Å
$X^1\Sigma^+$	0	2169,999	13,371	0,01884[a]	1,93130	0,017520	$4,5\cdot10^{-6}$	$6,26\cdot10^{-6}$[b]	1,1282
$a^3\Pi$[c]	48687,52	1743,40	14,31	—0,0824[e]	1,6810	0,0193	—[f]	$6,1\cdot10^{-6}$	1,2093
$a'^3\Sigma$[d]	55823,07	1230,651	11,0130	0,07378[a]	1,3453	0,1872	$2,05\cdot10^{-4}$[e]	$6,5\cdot10^{-6}$	1,3518
$d^3\Pi$[g]	62300,4	1137,79	7,624	—0,1125	1,2615	0,0170	—	—	1,3960
$A^1\Pi$[h]	65075,6	1515,61	17,250	—	1,6116[b]	0,02229	$-1,05\cdot10^{-4}$	—	1,2351
$e^3\Sigma$	65340,05	1093,993	9,578	0,00587	1,2663[b]	0,0179	$1,10^{-4}$	$6,5\cdot10^{-6}$	1,3933
$b^3\Sigma$	83816	2198[i]	—	—	2,075	0,033	—	—	1,088
$B^1\Sigma$[k]	86927,6	2160,7	39,3	—	1,961[ℓ]	0,027	—	$6,1\cdot10^{-6}$	1,120
$^1\Sigma$[k]	91947,9	—	—	—	1,1764[ℓ]	—	—	—	—
$C^1\Sigma$	91937	2133[i]	—	—	1,9422[ℓ]	—	—	—	1,1250
$c^3\Sigma$	93158,0	—	—	—	1,9563[ℓ]	—	—	—	1,1210
$E^1\Sigma$[k]	92938	2134[i]	—	—	—[ℓ]	—	—	—	—
$^1\Pi$[k]	97730,0	—	—	—	1,134[ℓ]	—	—	—	—
$F^1\Pi$	99806	2112	198	—	—	—	—	—	—

a $\omega_e z_e = 0,000171$ см$^{-1}$.

b $\beta = -2,99\cdot10^{-9}$ см$^{-1}$.

c $A = 41,5$, $y = 24,7$ см$^{-1}$.

d $\lambda + \frac{\mu}{2} = -1,13$ см$^{-1}$.

e $\omega_e z_e = 0,00115$ см$^{-1}$.

f $\alpha_3 = 5,1\cdot10^{-6}$ см$^{-1}$.

g $A = -34,6$ см$^{-1}$, $y = -27,63$ см$^{-1}$.

h $\lambda + \frac{\mu}{2} = +0,84$ см$^{-1}$.

i ω_0.

k По ccording to Chulanovskiy; [58]

ℓ B_0.

The vibrational levels of the $a'^3\Sigma^+$ state, calculated by means of the adopted values of the constants, converge in the region of 90,900 cm^{-1} which compels us to assume that this state has the same dissociation limit as the $X^1\Sigma^+$ state. The authors of the work [3991a] arrived at an analogous conclusion on the basis of a calculation of the potential energy curve of CO in the state $a'^3\Sigma$.

The molecular constants of CO in the $d^3\Pi$ state were determined as a result of investigations of the triplet band system $d^3\Pi - a^3\Pi$ in the emission spectrum of this molecule. An analysis of the rotational structure of individual bands of the system was carried out in the work of Gero and Szabo [1702], who showed that the $d^3\Pi$ state is reversed and who determined the values of B_v for several vibrational levels. The most accurate values of the vibrational constants of CO in the $d^3\Pi$ state were calculated by Asundi [578] who obtained two new bands of the triplet system and improved the numbering of the bands. The constants found by Asundi were confirmed by Tanaka and coauthors [3935] who studied the band system $d^3\Pi - X^1\Sigma^+$ in absorption. The highest vibrational level of the $d^3\Pi$ state, observed in the absorption spectrum of CO (v = 21), has an energy of about 81,150 cm^{-1} while extrapolation on the basis of the values of ΔG leads to their convergence in the region of 90,000 cm^{-1}. The rotational constants of CO in the $d^3\Pi$ state, given in Table 128, were adopted on the basis of the data [1702], the vibrational constants on the basis of the work [578]; the same values are recommended in the Handbook [649] and the monographs [2020].*

The existence of the $e^3\Sigma^-$ state of CO had been predicted by Coster and Brons [1188] and Schmid and Gero [3637] on the basis of observations of perturbations in the $A^1\Pi$ state. A detailed investigation of the constants of this state has been carried out by Herzberg and Hugo [2033] during a study of the absorption spectrum of CO in the vacuum ultraviolet on a high-dispersion apparatus. The authors of this work carried out an analysis of the rotational structure of several bands in the system $e^3\Sigma^- - X^1\Sigma^+$ and found the constants, given in Table 128. In the work of Tanaka and coauthors [3935] it is pointed out that the data obtained by them during the study of the system $e^3\Sigma^- - X^1\Sigma^+$ on an apparatus with lower dispersion, agree well with the results of the analysis by Herzberg and Hugo [2033].

The highest vibrational level (v = 17) of the state $e^3\Sigma^-$, observed experimentally, has an energy of approximately 80,500 cm^{-1} relative to the v = 0 level of the state $X^1\Sigma^+$. Extrapolation of the levels on the basis of the constants proposed in the work [2033], leads to a dissociation limit in the region of 96,000 cm^{-1}. If a more rapid convergence of the levels is assumed, this state could have a common dissociation limit with the state $X^1\Sigma^+$. However, the existing experimental data are insufficient for a verification of this hypothesis.*

The molecular constants of CO in the $b^3\Sigma^+$ state can be determined by means of an analysis of the third positive system of bands ($b^3\Sigma^+ - a^3\Pi$), to which belong also the bands , designated previously as the system "5B", and also from an analysis of the system of Hopfield-Birge ($b^3\Sigma^+ - X^1\Sigma^+$). The third positive system in the emission spectrum of CO has been investigated repeatedly by several authors. An analysis of the rotational structure of the bands in this system was carried out in the works [1346, 3633, 1690, 715]. The system of Hopfield-Birge was studied in the works [3634, 1188]. The constants of CO in the $b^3\Sigma^+$ state were adopted on the basis of the data [3633, 1690]. A typical feature of the $b^3\Sigma^+$ state of CO is the presence of predissociation in the region of 89,500 cm^{-1} on levels with the values v = 0 and v = 1. Until recently it has not been possible to observe the bands, connected with the second vibrational level of this state, which should have an energy of approximately 88,200 cm^{-1}. However, in the work of Tanaka et al [3935], a band was found in the absorption spectrum of CO whose wavelength $\lambda = 1133.4$ A practically coincides with that calculated for the band 2-0 in the system $b^2\Sigma^+ - X^1\Sigma^+$.

The molecular constants of CO in the first excited singlet state were determined by means of an analysis of the fourth positive band system $A^1\Pi - X^1\Sigma^+$, which has been investigated in emission as well as absorption, and also the Angstrom bands $B^1\Sigma - X^1\Sigma^+$. In the absorption spectrum of CO, the band system $A^1\Pi - X^1\Sigma^+$ is developed to v' = 20 [3935], the energy of the last observed level of the $A^1\Pi$ state being 87,742 cm^{-1}. A brief extrapolation of the curve $\Delta G_{v+1/2}$ for the $A^1\Pi$ state leads to a dissociation limit* in the region of 90,000 cm^{-1}. It should be pointed out that Gero [1688, 1689] and Schmid and Gero [3634] advanced a hypothesis concerning the presence of a predissociation at several vibrational levels (v = 4, 7, 8, 9) of the $A^1\Pi$ state on the basis of an analysis of the spectra of the $A^1\Pi - X^1\Sigma^+$ and $B^1\Sigma - X^1\Sigma^+$ systems of CO. However, careful investigations of these two band systems in the works of Douglas and Moller [1378] and Tanaka et al [3935] showed convincingly that anomalies attesting to the presence of predissociation are absent in the intensity and position of the levels of the $A^1\Pi$ state. The most accurate values of the vibrational constants of CO in the $A^1\Pi$ state, given in Table 128, were determined by Read [3405, 3406] during an analysis of the bands of the system $A^1\Pi - X^1\Sigma^+$. It has been shown in the work [2697] that these constants agree well with the magnitudes, obtained during the analysis of the bands $A^1\Pi - X^1\Sigma^+$ and $B^1\Sigma - A^1\Pi$ for the molecule $C^{13}O$. The rotational constants were adopted on the basis of the data of Schmid and Gero [3635]. The same values of the constants are recommended by Herzberg [2020] and in the Handbook [649].

Two systems are connected with the second excited singlet state $B^1\Sigma$: the Angstrom bands $B^1\Sigma - A^1\Pi$, observed only in emission and the Hopfield-Birge bands $B^1\Sigma - X^1\Sigma^+$, which were studied in emission and absorption. An analysis of these two systems was carried out by Read [3405, 3406] and of the Angstrom bands by Schmid and Gero [3632]. A typical feature of the $B^1\Sigma$ state of CO is the presence of predissociation at the levels v = 0, K = 38 and v = 1, K = 18 in the region 90,700 cm^{-1}. Until recently, the levels of the $B^1\Sigma^+$ state with $v > 1$

have not been observed in the spectrum of CO, in consequence of which the vibrational constants in this state could not be determined. However, the 2-0 band was detected in the work of Tanaka et al [3935] during an investigation of the system $B^1\Sigma - X^1$ and the energy of the level v = 2 relative to v = 0 of the state $X^1\Sigma^+$ has been determined as 91,000 cm^{-1}. The vibrational constants, given in Table 128, were found by McCulloh and Glocklet [2697] on the basis of a simultaneous analysis of the Angstrom bands in the spectra of $C^{12}O$ and $C^{13}O$. These agree well with the values calculated on the basis of the data in the work [3935] (ω_e = 2148 and $\omega_e x_e$ = 37 cm^{-1}).

The rotational constants of CO in the $B^1\Sigma$ state, given in Table 128, were found by Schmid and Gero [3632].

In addition to the eight above discussed electronic states of CO, transitions were also observed in the electronic spectra of this molecule in one triplet state $c^3\Sigma$ and a number of singlet states. Table 128 shows the excitation energies and the molecular constants of CO in these states, having excitation energies under 100,000 cm^{-1}, which were adopted in correspondence with the values recommended by Herzberg [2020] and in the Handbook [649].

The singlet electronic states of CO which form three Rydberg series and have excitation energies over 100,000 cm^{-1}, are not presented in the Table. The research results on these states are described in the works of Tanaka [3918, 3926].

<u>CO^+</u>. The electronic ground state of the molecule CO^+ is the state $^2\Sigma$. Three band systems are observed in the spectra of the molecule CO^+ which are connected with transitions between the three electronic states: $A^2\Pi - X^2\Sigma$, $B^2\Sigma - X^2\Sigma$ and $B^2\Sigma - A^2\Pi$.

The first investigations on the band systems $A^2\Pi - X^2\Sigma$ and $B^2\Sigma - X^2\Sigma$ on an apparatus with high dispersion were carried out by

Blackburn [833, 834], who determined the values of the constants of CO$^+$ in two electronic states as a result of an analysis of the structure of the bands $B^2\Sigma - X^2\Sigma$. Later on, the band system $B^2\Sigma - X^2\Sigma$ was again studied by Coster, Brons and Bulthuis [1189] and Schmid [3630] (errors committed by Blackburn in the determination of the rotational constants were detected in the work [3630] and also by Biskamp [831] (up to $v' = 12$ and $v'' = 8$) and Schmid and Gero [3631] and the band system $A^2\Pi - X^2\Sigma$ by Coster and coauthors [1189] and Schmid and Gero [3631].

The third band system of CO$^+$, situated in the region 3300-4845 A, was studied by Bulthuis [1015] who showed on the basis of the values of the Raman differences that this system is connected with a transition between the states $B^2\Sigma$ and $A^2\Pi$. Bulthuis also carried out detailed investigations on two other band systems of CO$^+$, the results of which were described in his doctoral thesis [1016] which the author of the present Handbook was unable to obtain.

The most complete analysis of the bands of the systems $A^2\Pi - X^2\Sigma$ and $B^2\Sigma - X^2\Sigma$ was carried out in 1950 by Rao [3392, 3393] who used a discharge tube with hollow water-cooled graphite cathode as a radiation source. As a result of the analysis which he had carried out, Rao gave more accurate values of the rotational constants in the states $X^2\Sigma$ ($v \leq 7$) and $A^2\Pi$ ($v \leq 11$) and showed also that the state $A^2\Pi$ is reversed. The values of the constants of the molecule CO$^+$, obtained in the works of Rao [3392, 3393] are recommended in the Handbook [649] and the monographs [2020]. However, the values of the vibrational constants of the state $X^2\Sigma$ of the molecule CO$^+$, found by Rao [3392], evidently do not describe satisfactorily the energy of the high vibrational levels of this state because the levels, calculated on the basis of these constants, converge at 79,457 cm^{-1}, while the dissociation energy of CO^+ is 67,140 ± 150 cm^{-1} (see page 954). In view of this, new values of the vibrational constants of CO^+ in the state $X^2\Sigma$ were calculated in the work [173], which lead to the convergence of the vibrational levels in the region of the dissociation energy. Table 129 gives a comparison of the values of $\Delta G_{v+1/2}$, calculated on the basis of the constants proposed by Rao and in the work [173] for $v \leq 12$, with the experimental data. It can be seen from this Table that although for $v \leq 6$ the constants proposed by Rao, describe the data better, at high values of v they lead to considerable divergences from the experimental data.

TABLE 129

Values of $\Delta G_{v+1/2}$ of the state $X^2\Sigma$ of the Molecule CO^+ (in cm^{-1})

v	Экспериментальные значения [3393, 831] A	Расчет по постоянным B		v	Экспериментальные значения [3393, 831] A	B Расчет по постоянным	
		[3392,3393]ª	табл. 130			[3392,3393]ª	табл. 130
0	2183,89	2183,91	2184,3	7	1968,9	1971,48	1970,1
1	2153,58	2153,58	2253,6	8	1939,4	1941,13	1939,5
2	2123,21	2123,29	2122,9	9	1907,6	1910,75	1908,6
3	2092,93	2092,90	2092,4	10	1879,0	1880,38	1877,7
4	2062,53	2062,55	2061,9	11	1849,2	1850,01	1846,6
5	2032,16	2032,20	2031,4	12	1790,3	1819,63	1814,1
6	1999,0	2001,85	2003,8				

A) Experimental values; B) calculated on the basis of the constants.
a) $\Delta G_{v+1/2} = 2183.917 - 30,326v + 0.0021\ v^2$.

Table 130 gives the constants of the molecule CO^+, adopted in the present Handbook; all values of the constants, with the exception of the vibrational constants of the state $X^2\Sigma$, adopted on the basis of the works of Rao [3392, 3393],* and the vibrational constants of the state $X^2\Sigma$ on the basis of the work [173].

$\underline{C_3}$. A group of bands, known in the literature as the "band group 4050" is connected with the molecule C_3. The bands λ 4050 A were first observed in the radiation spectra of comets [2309] and in the absorption spectra of stars [2716, 3910]. These bands were later found under laboratory conditions during investigations on the emission spectra of electrical discharges [2017, 1834, 1133, 2004], hydrocarbon flames [2393, 1425, 1673, 2395, 2396, 2780, 1038, 2781], carbon furnaces [1655, 3236] and in the absorption spectra obtained during impulse photolysis of various hydrocarbon compounds [3104, 1048, 2449]. The most comprehensive review of the research results on the conditions of appearance and structure of the bands has been given in the works of Rosen and Swings [3485] and Herzberg [2025]. Douglas was the first to advance the hypothesis that the source of the bands is the molecule C_3 [1368]. He obtained bands with a wavelength of λ 4050 A in the discharge spectrum of a mixture of xenon and hydrogen between carbon electrodes. The spectrum was photographed in the third order of a six-meter concave grating with a resolution of approximately 200,000. An analysis of the bands, carried out under the assumption, that they are connected with the transition $^1\Pi - {}^1\Sigma$ of the linear triatomic molecule C_3, made it possible to obtain the rotational constants which lead to a value of the interatomic distance in the electronic ground state of the molecule C_3 ($r_{C=C}$ = 1.28 A) which is entirely reasonable for a carbon double bond and agrees well with the bond length $C = C$ in hydrocarbons of the allene type. The data on the isotope shift of the band edges obtained in the study of the spectrum of a mixture containing 50% of the isotope C^{13} and also the results of the investigations of the spectra appearing only in presence of the isotope C^{13} [1133, 1368] do not leave any doubt that the linear triatomic molecule C_3 is the source of the bands.

The molecule C_3 belongs to the symmetry class $D_{\infty h}$ and should have three fundamental frequencies: two frequencies, due to the valency vibrations (ν_1 and ν_3) and one (ν_2) due to the deformation vibrations.

It has not been possible to date to carry out an analysis of the vibrational structure of the electronic spectrum of the molecule C_3. Attempts to carry out such an analysis, undertaken in the works of Herman [1998], Goupil and Herman [1834], Rosen and Swings [3485], Keiss and Broida [2395, 2396], and Tatevskiy Mal'tsev and Shevel'kov [55] were not crowned with success. As the infrared spectrum and the Raman spectrum of C_3 have not been obtained, the vibrational frequencies of the molecule C_3 were estimated by several researchers on the basis of theoretical calculations.

TABLE 130

Adopted Values of the Molecular Constants of CO^+

Состояние A	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_1	D_e	r_e
	см⁻¹							Å
$X^2\Sigma^+$	0	2215,10	15,445	0,0237[a]	1,97720	0,01896[b]	$6,37\cdot10^{-6}$[c]	1,11506
$A^2\Pi_i$	20733,19[d]	1562,06	13,532	0,0131	1,58940	0,01942	$6,60\cdot10^{-6}$	1,24367
$B^2\Sigma$	45876,70	1734,18	27,927	0,3283	1,79992	0,03025	$7,75\cdot10^{-6}$[e]	1,16868

[a] $\omega_e z_e = 0{,}00118$ см⁻¹.

[b] $\alpha_2 = -0{,}000037$ см⁻¹.

[c] $\beta_1 = 1\cdot10^{-8}$ см⁻¹.

[d] $A = 117{,}5$ см⁻¹.

[e] $\beta_1 = 2{,}2\cdot10^{-7}$ см⁻¹.

Tatevskiy, Mal'tsev and Shevel'kov [55] and the authors of the present Handbook calculated the vibrational frequencies of C_3 by means of Eqs. (P4.31) after an estimate of the force constants of this molecule had been made. The force constants of C_3 were estimated on the basis of a comparison between the force constants of the molecules C_2H_4, C_2 and C_3H_4. Upon transition from the ethylene molecule to the radical C_2 the quasi-elastic coupling constant of the C = C bond varies from $9.04\cdot10^5$ [366] to $9.53\cdot10^5$ dyne·cm^{-1} [3234] and the interatomic distance $r_{C=C}$ from 1.33 [3876] to 1.31 A [3234]. The assumption is natural that upon transition from the allene molecule C_3H_4 with its interatomic distance of $r_{C=C}$ = 1.308 A [3874] to the radical C_3, in which

$r_{C=C}$ = 1.28 A, the relations of the force constants will be approximately the same as upon transition from C_2H_4 to C_2. On the basis of these conceptions and the force constants of the allene molecule, calculated by Sverdlov [364] on the basis of the results of the most recent studies on the spectrum of C_3H_4 [2651, 3181, 2652], the value of the quasi-elastic coupling constant C = C of the molecule C_3 was assumed to be $f_d = 10.1 \cdot 10^5$ dyne·cm^{-1}. The bond interaction constant and the deformation constant of C_3 were taken as being the same as in the allene molecule: $f_{dd} = 0.10 \cdot 10^5$ dyne·cm^{-1}, $f_\alpha/d^2 = 0.29 \cdot 10^5$ dyne··cm^{-1}. The values of the basic frequencies of C_3 calculated by means of Eqs. (P4.31) are (in cm^{-1}): $\nu_1 = 1160$, $\nu_2 = 480$, $\nu_3 = 1980$. The following frequencies were obtained in the work [55] on the basis of analogous calculations (in cm^{-1}): $\nu_1 = 1171$, $\nu_2 = 496$, and $\nu_3 = 2004$, and the following frequencies were recommended as the most probable (in cm^{-1}): $\nu_1 = 1200$, $\nu_2 = 500$ and $\nu_3 = 1970$.

The value of the frequency ν_2 calculated in this manner agrees satisfactorily with the magnitude of the constant for the difference (523 cm^{-1}) between the positions of the band edges of the progression obtained by Kiess and Broida [2395, 2396] in the spectrum of C_3. The authors of the works [2395, 2396] pointed out that the value of this difference is close to the frequency which one would expect for the deformation vibrations of the carbon double bond. The calculated value of the frequency ν_3 practically coincides with the corresponding frequency in the molecule of allene (1960 cm^{-1}) and the value ν_1 exceeds the frequency of the valency vibration of the C = C bond in the molecule C_3H_4 (1080 cm^{-1}) by about 90 cm^{-1}. Values of the basic frequencies of the molecule C_3, fairly close to those given above, were estimated by Goupil and Herman [1834] ($\nu_1 = 1263$ and $\nu_3 = 1947$ cm^{-1}) and Glockler [1766] ($\nu_1 = 1070$, $\nu_2 = 355$ and $\nu_3 = 1980$ cm^{-1}). Because, however, the details of these calculations are not reported, a discussion of the results thus obtained is made more difficult.

The values, recommended in the work [55] and given in Table 131,* which are close to the averages of the above listed values, have been adopted in the present Handbook for the fundamental frequencies of the molecule C_3. It must be pointed out that these values may only be regarded as approximate, containing an uncertainty of 10-15%.

An analysis of the rotational structure of the bands with λ 4050 and λ 4072A, appertaining to the molecule C_3, has been carried out by Douglas [1368], Kiess and Bass [2393] and Kiess and Broida [2395]. The values of the rotational constants B" and D" found by these authors, practically coincide.** Table 131 presents the values of the rotational constants of the molecule C_3, obtained in the work [2395].

TABLE 131

Adopted Values of the Molecular Constants of C_3 in the Electronic Ground State

ν_1	ν_2 (2)	ν_3	B	D	σ
cm^{-1}					
1200	500	1970	0,4280	$0,46\cdot10^{-6}$	2

Experimental data which would enable the problem of the type of ground state of the radical C_3 to be decided unequivocally are lacking at the present time. In the analysis of the electronic spectrum of C_3 in the works [1368, 2393, 2395] it was assumed that the observed bands are connected with transitions of the type $^1\Pi - {}^1\Sigma$. This hypothesis was supported by the absence of any splitting of the rotational lines in the spectrum but because of the small rotational constant of this molecule such an effect may also be caused by insufficient resolution of the rotational structure of the bands and the low value of the coupling constant. Glockler [1766] assumed in the estimation of the constants of C_3 that the ground state of C_3 is a quintet. Because this assumption is not substantiated in any way in the work [1766] and it is difficult to account for the presence of two unpaired electrons in each of the outer carbon atoms, the hypothesis that the ground state of C_3 is the state $^1\Sigma$ appears to be more justified. This hypothesis has been adopted in the present Handbook.*

The energy of the excited state of C_3 with which the band λ 4050 A are connected, is about 25,000 cm^{-1}.

$\underline{CO_2}$. The molecule CO_2 has a linear symmetrical structure and belongs to the point group $D_{\infty h}$. Two fundamental frequencies of CO_2(ν_2 and ν_3) are active in the infrared spectrum, the third one (ν_1) in the Raman spectrum. The infrared spectrum and the Raman spectrum of carbon dioxide have been studied in dozens of works and have been investigated better to date than for any other polyatomic molecule. Herzberg [152], on the basis of an analysis of the data, published prior to the year 1944, recommends for the molecule CO_2 the values of the vibrational constants, determined by Dennison [1314] and the rotational constants, obtained by Adel and Dennison [490] (see Table 132).

It should be pointed out that a strong perturbation of the energy levels occurs in the molecule CO_2 owing to the Fermi resonance between the vibrational states (v_1, v_2, v_3) and ($v_1 - 1$, $v_2 + 2$, v_3). This circumstances make an analysis and the determination of the molecular constants of CO_2 of the spectrum considerably more difficult. In the calculation of the values of the vibrational constants of CO_2 in the work [1314] the assumption was made that the constant of the resonance interaction W is independent of the vibrational quantum numbers.

During the Fifties, the spectrum of CO_2 was again studied in several works. Individual bands in the infrared spectrum were obtained on apparatus with great resolving power. Nielsen and Yao [3079] (ν_3); Benedict, Herman and Silverman [729] (six bands with $\Delta\nu_3 = 1$); Benedict and Plyler [730] ($2\nu_2$ and $\nu_1 + \nu_3$); Plyler and Ball [3274] (ν_3 and $\nu_2 + \nu_3 - \nu_2$); A. Nielsen and Lagemann [3074]; Gailar and Plyler [1639] ($3\nu_3$); Rosman, Rao and H. Nielsen [3511] (ν_2); Rossmann, France, Rao and H. Nielsen [3510] ($\nu_3 - \nu_1$ and $\nu_3 - 2\nu_2$) and Blaine, Plyler and Tidwell [836] (ν_3). In some of these works [3074, 3079, 729] and also in the work of Goldberg and coauthors [1790] who investigated the rotational structure of 13 CO_2 bands in the region 1.5-8.1 mk (6670--1250 cm^{-1}) in the emission spectrum of the sun, gave more accurate values for the individual constants of the CO_2 molecule.

Detailed investigations of the infrared spectrum of CO_2 were carried out by Taylor, Benedict and Strong [3951], G. Herzberg and L. Herzberg [2030] and Courtoy [1199]. Taylor et al. [3951] studied the absorption spectrum of carbon dioxide gas heated to 500°C within the range of 5 microns (2000 cm^{-1}) on a prism spectrometer and in the range of 15 microns (670 cm^{-1}) on an apparatus with a diffraction grid. By an investigation of the spectrum of the hot gas, the authors of the work [3951] obtained 22 new CO_2 bands, connected with transitions between energyblevels with the values $v_1 \leq 3$ and $v_2 < 5$, most of which were perturbed by a Fermi resonance, and also to determine more precisely the frequency of the band $2\nu_1 - \nu_2$. In the work [3951] it was found for the first time that the interaction of the Fermi resonance in CO_2 is not constant but depends on the vibrational quantum numbers. On the basis of the experimental data thus obtained, the authors [3951] determined the vibrational constants of CO_2 with greater precision (see Table 132) and also determed W as a function of the values of v_1, v_2 and v_3.*

G. Herzberg and L. Herzberg [2030] investigated the spectrum of CO_2 in the range 0.8-1.25 microns (12,500-8000 cm^{-1}) on a large dispersion apparatus (1.25 and 2.5 A/mm) using thick layers of the absorbing gas (from 530 to 5500 m). 13 new composite and difference bands of CO_2 were discovered in this work, corresponding to the values $v_2 \leq 4$ and $v_3 \leq 5$, and an analysis of the rotational structure of 11 bands was carried out. By means of an investigation in the photographic range, the authors of [2030] determined the wave numbers of the lines with an accuracy of ± 0.02 cm^{-1} which made it possible to increase considerably the accuracy of the determination of the rotational constants. Their combination differences obtained in the analysi of six bands, were found to be $B_{000} = 0.39020 \pm 0.00010$ cm^{-1} and $D_0 = (12 \pm 4) \cdot 10^{-8}$ cm^{-1}. On the basis of the magnitudes of $B_{v_1 v_2 v_3}$, which had been found and also the data obtained in the works [1790, 730, 3079], G. Herzberg and L. Herzberg determined the values of the rotational constants of CO_2 given in Table 132 and showed that the usual formula (1.56) with these constants describes the values of $B_{v_1 v_2 v_3}$ for the unperturbed states with an accuracy of ± 0.00003 cm^{-1} and the mean values of the constants $B_{v_1 v_2 v_3}$ for the polyads, connected with the Fermi resonance, with an accuracy of ± 0.0002 cm^{-1}.

The most accurate values of the constants of CO_2 were obtained in the work of Courtoy [1199] which was essentially a continuation of the work of G. Herzberg and L. Herzberg. Courtoy investigated the absorption spectrum of carbon dioxide gas in the range 1.25-2.85 microns (8000-3500 cm^{-1}) on a high-dispersion apparatus. In order to increase the accuracy of determination of the wavelengths of the lines, a Fabry-Perot interferometer was used. Courtoy obtained 27 composite and different bands, including the bands corresponding to the transitions between the states with $\ell = 1$ and $\ell = 2$ and carried out an analysis of the rotational structure of these bands. In order to determine the vibrational constants of CO_2, Courtoy used, in addition to his own data, the results of at the time unpublished investigations on the infrared spectrum of CO_2, including the data of Benedict for the states 03^10 and 02^20 and the Raman spectrum) data of Stoicheff for the v_1 bands, see [3877] and also the data [3511, 836, 3951, 2030]. Courtoy proposed the expression

$$W = (W_0 - \lambda_1 v_1 - \lambda_2 v_2 - \lambda_3 v_3 - \lambda_l l).$$

for the dependence of the constant interaction of the Fermi resonance W on the vibrational quantum numbers. This expression agrees with the formula obtained by Amat and Goldsmith [536] on the basis of the general perturbation theory.

The constants found by Courtoy in the cubic equation for the energies of the unperturbed vibrational levels of CO_2 and also the constants in the expression for W, are given in Table 132. The values of $G_0(v_1v_2v_3\ell)$ for 55 vibrational levels of CO_2 corresponding to the values $v_1 \leq 4$, $v_2 \leq 8$, $v_3 \leq 5$ and $\ell \leq 5$, calculated on the basis of these constants, agree with those found experimentally within the limits of ± 0.5 cm^{-1}.

The rotational constants of CO_2 in the ground state were determined by Courtoy on the basis of the combination differences, obtained in the analysis of 14 bands and found to be equal to $B_{000} = 0.39021 \pm 0.00004$ cm^{-1} and $D_0 = (13.5 \pm 0.5) \cdot 10^{-8}$ cm^{-1}. To this value of B_{000} corresponds r_{000} (CO) = 1.16213 ± 0.00012 A. On the basis of the discovered values of $B_{v_1v_2v_3}$ and also the data obtained in the works [3510, 836, 3951], Courtoy calculated the values of the rotational constants in the second-order equation

$$B_{v_1v_2v_3} = B_e - \sum_n \alpha_n \left(v_n + \frac{d_n}{2}\right) + \sum_n \sum_m \gamma_{nm} \left(v_n + \frac{d_n}{2}\right)\left(v_m + \frac{d_m}{2}\right).$$

given in Table 132. It should be pointed out that if one calculates on the basis of these constants the unperturbed values of $B_{v_1v_2v_3}$ and then calculates by means of the constants which characterize the proportion of the unperturbed vibrational eigenfunctions in the perturbed functions, the values of $B_{v_1v_2v_3}$ for the perturbed states, the corresponding magnitudes agree with those found experimentally within $1 \cdot 10^{-5}$ cm^{-1}.*

TABLE 132

Molecular Constants of CO_2 (in cm^{-1})

Постоянная A	[152]	[3951]	[2030]	[1199]^{а,б,в} abc
ω_1	1351,2	1354,42	—	1354,94
ω_2 (2)	672,2	672,43	—	673,02
ω_3	2396,4	2396,80	2396,31	2396,40
x_{11}	−0,3	−2,20	−2,61	−3,75
x_{22}	−1,3	−0,75	—	−0,63
x_{33}	−12,5	−12,50	−12,50	−12,63
x_{12}	5,7	+3,76	—	3,62
x_{13}	−21,9	−21,84	−19,17	−19,37
x_{23}	−11,0	−11,58	−12,42	−12,53^{г} d
g_{22}	1,7	1,03 e	—	0,775 f
W_e	50,4	51,01^{д}	—	51,31^{е}
B_e	0,3906	—	0,3915	0,39162^{ж} g
α_1	0,00056	—	0,00109	0,00126
α_2	−0,00062	—	−0,00073	−0,00076
α_3	0,0029	—	0,00307	0,0030875
$D_e \cdot 10^6$	—	—	12	12,5

A) constant;
a) several different values for the vibrational constants obtained without taking into account the data of several preceding works are given in the work of Courtoy [1200].
b) practically the same values for the constants of $C^{12}O_2$ are given in the work of Courtoy [1201].
c) the basic frequencies $\nu_1 = 1388.15$, $\nu_2 = 667.40$, $\nu_3 = 2349.16$ cm^{-1}, correspond to the presented values of the vibrational constants.
d) $y_{111} = 0.13$, $y_{222} = 0.01$, $y_{333} = 0.015$, $y_{112} = -0.08$, $y_{122} = -0.07$, $y_{133} = 0.07$, $y_{113} = y_{223} = 0$, $y_{233} = 0.01$, $y_{123} = 0.02$ cm^{-1}.
e) $\beta_2 = 0.025$, $\beta_3 = 0.0095$ cm^{-1}.
f) $\lambda_1 = 0.15$, $\lambda_2 = 0.41$, $\lambda_3 = 0.78$, cm^{-1}, $\lambda_\ell = 0$.

g) $\gamma_{11} = \gamma_{22} = 0$, $\gamma_{33} = 3.5\cdot10^{-6}$, $\gamma_{12} = -3.5\cdot10^{-5}$, $\gamma_{13} = 1.4\cdot10^{-5}$, $\gamma_{23} = 1\cdot10^{-5}$ cm^{-1}.

The constants found by Courtoy for the centrifugal stretching D_v in the perturbed states of CO_2 differ considerably from the magnitude of this constant in the ground state [1204]. However, owing to the fact that the mean values of D_v for each group of interacting levels is close to the value of D_0, this is of no importance for the subsequent calculation of the thermodynamic functions. In the work [1201] Courtoy investigated the infrared spectrum of $C^{13}O_2$ in the region 5440-8000 cm^{-1}, determined the molecular constants of this isotope modification of CO_2 and calculated also the values of the molecular constants of its other isotope modifications. Practically the same values of the constants are recommended in the work [1201] for $C^{12}O_2$ as those found in the work [1199].

According to the present theoretical concepts, the molecule CO_2 should have several electronic states with relatively low excitation energies. Experimental studies of the absorption spectra of CO_2 showed that the gas is transparent up to λ 1700 A and that the excitation energy of the lower electronic ground state of CO_2 should exceed 58,000 cm^{-1}. This inference has been confirmed by the theoretical calculations of Mulligan [2971] according to whom the first excited state of CO_2 should have an energy of about 7.6 ev (61,000 cm^{-1}).

It should be pointed out that a system of bands can be observed in the emission spectrum of carbon monoxide flames in the region 3000-5500 A, which several authors relate to the molecule CO_2 (see [142]). Gaydon [142] identified this band system with the system which is present in the emission spectrum in the region below 1700 A and which is connected with a transition between the triplet state of CO_2 (in which the molecule CO_2 is bent) and the singlet ground state. The fact that the bands of this system, observed in emission, lie in the region of longer wavelengths, than in absorption, Gaydon explains by the different configuration and dimensions of the molecule in the excited and ground states.* Walsh [4140] proposed a different interpretation of the bands of CO flames, assuming that they are connected with a transition between two excited triplet states of this molecule the lower of which ($^3B_2$ state), in his opinion, should have an excitation energy of about 20,000-25,000 cm^{-1}. The absence of transitions between this $^3B_2$ and the $^1\Sigma$ ground state of CO_2 in the spectrum of carbon dioxide Walsh explained by the fact that the respective transitions are forbidden by the selection rules.

The erroneous nature of the hypotheses of Walsh in the interpretation of the bands of carbon monoxide flames has been demonstrated in detail by Gaydon (see [142]). In particular, the calculations of Mulligan [2971] showed that the lower triplet state of CO_2 should have an energy over 60,000 cm^{-1} and that in the absorption spectra of CO_2, obtained in large absorbing layers, bands which could be related to transitions between the lower triplet states, are absent.

In agreement with this, it has been assumed in the present Handbook that the molecule CO_2 has excited states with energies in excess of 58,000 cm^{-1}, which cannot be taken into account in the calculations of the thermodynamic functions of carbon dioxide.

$\underline{C_3O_2}$. The first investigations on the structure and basic frequencies of the molecule C_3O_2 were carried out in the Thirties [857, 962, 963, 1485, 2653]. The problem of the possible structure of the molecule and the problem of the basic frequencies of C_3O_2 connected with it, are examined in fairly great detail in the monograph of Herzberg [152]. However, because of the equivocal interpretations of the experimental data, the problem of the structure of the molecule C_3O_2 could not be considered to have been solved until recently.

On the basis of the general concepts concerning the directions of the valencies, the hypothesis of the linear symmetrical model for C_3O_2 is the most probable. The electron diffraction measurements, carried out by Brockway and Pauling [962, 963] and Boersch [857], confirmed this hypothesis. These authors found $r_{C=C} = 1.30 \pm 0.02$ A and $r_{C=O} = 1.20 \pm 0.02$ A. S. Lefebre and D. Lefebre [2586] found, however, that the molecule C_2O_2 has a dipole moment of 0.7 D, which contradicts the hypothesis of its symmetrical structure.

The results of the first spectroscopic studies proved to be contradictory. An investigation of the infrared absorption spectrum [2653] made it possible to give preference to the linear model of C_3O_2 belonging to the point group symmetry $D_{\infty h}$, while an investigation of the Raman spectrum [1485] attested to the nonlinear structure of C_3O_2 (point group symmetry C_{2v}).

In 1951, Mackle and Sutton [2720] again carried out electron diffraction measurements on an apparatus which was improved as compared with that used in the works [962, 963, 857]. The detailed analysis of the electron diffraction patterns thus obtained by the authors of [2720] showed that the best agreement between theory and experiment can be obtained only for the linear model at $r_{C=O} = 1.19 \pm 0.03$ A and $r_{C=C} = 1.28 \pm 0.03$ A. The hypothesis that the disagreement between the earlier experimental data had been due to the presence of various impurities in the investigated samples of C_3O_2, connected with the process of production of C_3O_2, and, in particular, the presence of ketene, was expressed for the first time in the work of Mackle and Sutton [2720]. This hypothesis was confirmed by O'Loane [3133], who detected the ketene bands in the infrared spectrum of C_3O_2. The presence of Ketene obviously accounts for the appearance of the dipole moment, found in the work [2586] and the presence of several bands in the Raman spectrum and in the infrared absorption spectrum of C_3O_2.*

The doubts with regard to the structure of the molecule were mainly due to the incompleteness of the spectral data [1485, 2653]. Because of this, Long, Murfin and Williams [2640] and Rix [3446] repeated the investigation of the infrared absorption spectrum and the Raman spectrum of C_3O_2. The authors of the work [2640] paid special attention to the process of the synthesis and purification of the investigated compounds. The Raman spectrum of the liquid was recorded on a two-prism photoelectric spectrometer. The accuracy of the determination of the wavelengths of the Raman lines was ± 3 cm^{-1}. The infrared spectrum of gaseous carbon suboxide in the region from 275 to 4600 cm^{-1} was recorded in the work [2640] on a Perkon-Elmer spectrometer. The authors of [2640] recorded the absorption spectrum of different fractions of C_3O_2 at different stages of purification which enabled them to detect changes in the spectrum due to the presence of impurities. The detailed analysis of the observed spectra and the comparison with the spectra obtained in the previous works [1485, 2653] and also the calculation of the force constants of C_3O_2, carried out by the authors of the work [2640] to select the basic frequencies of the molecule and to give an interpretation of the infrared bands and the Raman spectrum on the basis of the hypothesis that the molecule C_3O_2 is linear and belongs to the point group symmetry $D_{\infty h}$.** This involved postulating the existence of the frequency $\nu_7 = 198$ cm^{-1} which is active in the infrared spectrum. Having investigated the spectra of different compounds in the far infrared region, O'Loane [3133] really found this frequency in the spectrum of C_3O_2, which confirmed the correctness of the assignment of the frequencies of C_3O_2, proposed in the work [2640].

Table 133 presents the values of the fundamental frequencies of the molecule C_3O_2 found by the authors of the work [2640] and the value of the moment of inertia calculated on the basis of the results of the electron diffraction measurements of Mackle and Sutton [2720] on the basis of the assumption that the molecule has a linear structure.

TABLE 133

Adopted Values of the Molecular Constants of C_3O_2

ν_1	ν_2	ν_3	ν_4	$\nu_5(2)$	$\nu_6(2)$	$\nu_7(2)$	I	σ
$см^{-1}$							10^{-39} $г \cdot см^{2}$	
2200^a	832^a	2258	1575	578^a	549	198	38,9	2

a) the frequencies ν_1, ν_2 and ν_5 were found as a result of a study of the Raman spectrum of liquid C_3O_2.

The investigation of the vibrational spectra of C_3O_2, carried out by Rix [3446] led to a different conclusion. Although the results of the measurements of the polarization of the lines in the Raman spectrum indicated a linear structure of the molecule C_3O_2, the analysis of the form and structure of the infrared absorption bands led Rix to the cohclusion that a zigzag of the C_3O_2 molecule is the most probable.* However, the author of the work [3446] himself does not consider this conclusion to have been completely substantiated. It should be pointed out that the concept of the zigzag structure of the C_3O_2 molecule does not agree with the theoretical ideas on the direction of the valencies of the carbon atom and has not been confirmed by the results of later studies.**

HCO. The molecule HCO is nonlinear, unsymmetrical and belongs to the point group symmetry C_{1v}. The bands of the molecule HCO, situated in the region 2500-4200 A and having a very complex structure, were first observed in the emission spectrum of different hydrocarbon flames by Vaidya [4048] and later by several other researchers [2126, 3008, 1666, 1672]. This group of bands was obtained in the emission spectrum during the photochemical decomposition of formic acid [419] and also in the fluorescence spectrum of formaldehyde [1437]. Vaidya [4048] first advanced the hypothesis that the radical HCO is the emitter of these bands, known in the literature as "hydrocarbon flame bands". The hypothesis of Vaidya was confirmed by the observation of the isotope displacement of the edges of the bands ccurring when the spectrum is excited in flames of $C_2H_2 + O_2$ and $C_2D_2 + O_2$ [2126, 3008, 4052] and the analogy between the vibrational structure of the observed bands and the structure of the β bands of the molecule NO, which is isoelectronic with the molecule HCO.

With the aim of obtaining the hydrocarbon flame bands in the absorption spectrum, Ramsay [3357] studied the absorption spectra which are observed during impulse photolysis of various compounds (H_2CO, CH_3CHO, $(HCO)_2$) but did not detect any absorption in the region 2600--4100 A, where these bands are situated in the emission spectrum. However, he found extremely weak series of bands with a very simple structure and maxima at 6138.8 and 5624.1 A in the red and green region of the spectrum. An analysis of the rotational structure of the P-, Q- and R- branches of these bands showed that they are connected with an electronic transition from a higher state in which the HCO molecule is bent, to a higher state in which the molecule is linear. The following rotational constants for the lower state were found: $B_{000} = 1.496$, $C_{000} = 1.403$ cm^{-1}. Later on, Herzberg and Ramsay [2042], using the method of impulse spectroscopy during the photochemical decomposition of acetaldehyde and CH_3CDO, obtained 9 HCO bands and 10 DCO bands in the absorption spectrum. The spectra were photographed in the first and second order of a 21-foot spectrograph with curved grid. The relative accuracy of determination of the wave numbers of the lines was ±0.02 cm^{-1}. The results of an analysis of the rotational structure of the bands of the molecules HCO and DCO confirmed the conclusions of Ramsay [3357] to the effect that their emitter is formyl. On the basis of a study of a large number of bands, the authors of the work [2042] improved the values of the rotational constants of HCO slightly and found $B_{000} = 1.4944$ and $C_{000} = 1.4008$ cm^{-1}. Assuming that the inertial defect in the vibrational ground state is negligibly small, Herzberg and Ramsay obtained $A_{000} = 22.365$ cm^{-1}. The values recommended in the work [2042] for the rotational constants and also the value of the centrifugal stretching constant $D_{000} = 9.6 \cdot 10^{-6}$ cm^{-1} were adopted in the present Handbook and are given in Table 134. An analysis of the rotational structure of the bands of HCO and DCO enabled Herzberg and Ramsay [2042] to suggest that $r_{C-H} = 1.08 \pm 0.02$ A, and to determine the values of the structural parameters of the radical HCO in the lower electronic state: $r_{C=O} = 1.198$ A and $\angle HCO = 119°30'$ (these values are close to the analogous magnitudes in H_2CO [see further on, page 907]).

The vibrational structure of the band system of HCO has been studied in the works [4048, 3008, 2128].

Murphy and Schoen [3008] showed on the basis of an analysis of the spectrograms obtained by Baidya [4048], that the bands of HCO can be interpreted as being connected with the two vibrations: $\nu'_1 = 1229$ and $\nu'_2 = 1070$ cm^{-1} in the upper state and $\nu''_1 = 1880$ and $\nu''_2 = 1538$ cm^{-1} in the lower state. These values enabled the authors of [3008] to regard these vibrations as a valency vibration of the C = O bond and a deformation vibration of the molecule HCO. Comparison of the basic frequencies in the lower state with the frequencies of the corresponding vibrations of the formaldehyde molecule (1744 and 1503 cm^{-1}) provided additional confirmation for the hypothesis that the investigated spectrum appertains to the molecule HCO.

TABLE 134

Adopted Values of the Molecular Constants of HCO, H_2CO and Cl_2CO

Молекула A	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	A_{000}	B_{000}	C_{000}	σ
	$см^{-1}$									
HCO[a]	1830	1538	2850	—	—	—	22,365	1,4944	1,4008	1
H_2CO	2766,4	1746,07	1500,6	2843,4	1247,4	1169,5	9,41003 b	1,29536 b	1,13425 b	2
Cl_2CO	570	1827	285	849	440	585	0,264141[6]	0,115913[6]	0,080464[6]	2

A) molecule; a) an excited state $^2\Sigma^+$ with an energy of 8468.13 cm^{-1} is known.
b) the values for the rotational constants for $Cl_2^{35}CO$ have been given.

In order to obtain intense HCO bands free of overlapping by bands of diatomic molecules, normally present in hydrocarbon flames, Hornbeck and Herman [2128] used a special burner which made it possible to obtain a stable flame, fed by a very lean hot mixture (the ratio of fuel to oxidant was varied from 0.01 to 0.05). The high dispersion of the apparatus, by means of which the spectrum was photographed (4 A/mm) and the low temperature of the excitation source enabled Hornbeck and Herman [2128] to obtain a larger number of bands and to carry out more accurate measurements than in the work of Vaidya [4048]. Although the presence of only two progressions in the spectrum of HCO provided little scope for carrying out a vibrational analysis of the spectrum of the polyatomic molecule, the smoothly varying horizontal and vertical differences between the edges of the bands, measured in the work [2128], led to two frequency values: about 1782 and 2851 cm^{-1}. The first frequency proved to be close to the characteristic frequency of the C = O bond and was identified in the work [2128] with the frequency ν_1.* Because the value ν_1 = 1880 cm^{-1}, found by Murphy and Schoen [3008], and the value 1782 cm^{-1}, found in the work [2128], are only approximate, the mean value ν_1 = 1830 cm^{-1} has been adopted in the present Handbook for the basic vibration frequency of the C = O bond in the molecule HCO. The second frequency found in the work [2128] (about 2851 cm^{-1}) lies in the frequency region of the valency vibrations of the C – H bond and was assigned by the authors of [2128] to the vibration ν_3. An estimate of this frequency in analogy with the corresponding frequencies in the molecule H_2CO (ν_1 = 2780 and ν_4 = = 2847 cm^{-1}) and also on the basis of a comparison of the frequencies of the valency vibrations of C – H in molecules of different types leads to a value of ν_3 = 2850 cm^{-1}, which agrees with the value found in the work [2128].

The authors of the Handbook calculated the values of the basic frequencies of HCO by means of the equations of the field of the valency forces (P4.25). The calculation was carried out on the assumption that the force constants of the C – H and C = O bonds and the deformation constant of the radical HCO are equal to the corresponding force constants of the formaldehyde molecule (respectively $4.43 \cdot 10^5$, $12.5 \cdot 10^5$ and $1.2 \cdot 10^{-11}$ dyne$\cdot cm^{-1}$). The calculated values of the frequencies ν_1 = 1820 and ν_3 = 2840 cm^{-1} practically coincide with the frequencies found experimentally and the value of the frequency of the deformation vibration ν_2 = 1410 cm^{-1}, although it is much smaller than that found experimentally [3008] (ν_2 = 1538 cm^{-1}), agrees with it within the limits of the accuracy of the calculation (about 10%).

The values of the basic frequencies of the molecule HCO adopted in the Handbook are given in Table 134. The possible error in the values of the frequencies ν_1 and ν_3 do not exceed 5%, while the uncertainty in the value of ν_2 may be considerably greater.*

An analysis of the structure of the bands, observed in the visible region and correlation of the electronic states of the molecule HCO with the electronic states of the hydrogen atom and the molecule CO enabled Herzberg and Ramsay [2042] to identify the investigated bands in the absorption spectrum of HCO as being connected with the transition $^2\Sigma^+ \leftarrow {}^2A''$. As Walsh [4142] showed, such a transition should correspond to an increase in $\angle$HCO to 180° in the upper state and to a partial increase in the distance $r_{C=O}$. Hence, such a transition should include a deformation vibration and a valency C = O vibration which is actually observed [3008, 2042].

The authors of the work [2042] pointed out that although it is natural to take the lower $^2A''$ state for the ground state, one cannot exclude the possibility that the $^2A''$ state is a lower metastable state. An analysis of the bands, carried out by Herzberg and Ramsay [2042] showed that the excitation energy of the $^2\Sigma^+$ state is 8468.13 ± 1.0 cm^{-1}. At the same time, several constants of HCO in this state were found in the work [2042]: $\omega_2^\circ = 811.0$, $\omega_2^\circ + x_{33}^\circ = 3337.5$ cm^{-1} and the value $B'_{000} = 1.3419$ cm^{-1}. To this rotational constant correspond the interatomic distances r_0C – H) = 1.07 ± 0.01 A (taken by analogy to the hydrocyanic acid molecule), r_0(C – O) = 1.183 ± 0.0025 A.

Herzberg remarked in the work [2026] that the HCO bands observed in the emission spectra of various hydrocarbon flames, are connected with a transition between the lower state, identical with the lower state of the absorption bands studied in the work [3357, 2042] which is the ground state of the molecule HCO, and the upper state, whose excitation energy considerably exceed the energy of the state $^2A''$. Herzberg also suggested that the complexity of the structure of the hydrocarbon bands can evidently be explained by the fact that in the upper state, with which these bands are connected, the molecule HCO is nonlinear, the same as in the ground state.

FCO and ClCO. The spectrum and the structure of the molecules FCO and ClCO have not been studied experimentally. In the present Handbook it is being assumed that the structure of the molecules FCO and ClCO is analogous to the structure of the molecule HCO, i.e., it is assumed that FCO and ClCO are nonlinear and asymmetrical molecules, whose geometrical structure is determined by the valency angle XCO and the lengths of the C – X and C = O bonds, where X = F and Cl, respectively. Because the interatomic distances $r_{C=O}$ and r_{C-H} and the angle between the HCO bonds in the molecule of formyl and the molecule of formaldehyde are practically identical, it is being assumed in the Handbook, that the structural parameters of FCO and ClCO are similar to the corresponding parameters of F_2CO and Cl_2CO and are equal to $r_{C=O} = 1.17$, $r_{C-F} = 1.31$ A and $\angle FCO = 120°$ for FCO and $r_{C=O} = 1.17$, $r_{C-Cl} = 1.74$ A and $\angle ClCO = 120°$ for ClCO, respectively.

The probable error in the values $r_{C=O}$ is ± 0.02 A, in r_{C-X} ± 0.05 A and in the values of $\angle XCO \pm 5°$. The values of the products of the inertial moments of FCO and ClCO, calculated on the basis of these magnitudes, are given in Table 135.

The nonlinear molecule XCO should have three fundamental frequencies: the frequencies ν_1 and ν_3, connected with the valency vibrations of the bonds C – X and C = O, respectively, and the frequency of the deformation vibration ν_2. The values of these frequencies can be estimated approximately by comparing the corresponding frequencies of HCO, H_2CO, F_2CO and Cl_2CO or as a result of calculation on the basis of Eqs. (P4.25) on the assumption that the force constants for FCO and ClCO are equal to the corresponding force constants of F_2CO and Cl_2CO [2749]. The values of the fundamental frequencies thus calculated are for FCO (in cm^{-1}):

$\nu_1 = 2020$, $\nu_2 = 640$, $\nu_3 = 1250$
$\nu_1 = 1940$, $\nu_2 = 590$, $\nu_3 = 1200$

and for ClCO (in cm^{-1}):

$\nu_1 = 1920$, $\nu_2 = 300$, $\nu_3 = 850$
$\nu_1 = 1830$, $\nu_2 = 400$, $\nu_3 = 840$

The values of the frequencies of FCO and ClCO, which are close to the averages of the values, obtained as the results of two different estimates, and which are presented in Table 135, have been adopted in the present Handbook. The possible error in the adopted values of the frequencies is 10%.*

Because there is a single free electron in the radicals FCO and ClCO, their electronic ground state should be a doublet. In analogy with HCO it is being assumed that this state is a state of the type $^2A_1$. In analogy with HCO one can also assume that excited electronic states with an energy of less than 10,000 cm^{-1} exist in FCO and ClCO.

$\underline{H_2CO}$. It has been shown unequivocally by electron diffraction and spectroscopic measurements that the formaldehyde molecule is flat and symmetrical, with a symmetry axis along the C = O bond (point group symmetry C_{2v}). H_2CO has six nondegenerate vibration frequencies which are active in the infrared spectrum and in the Raman spectrum.

The infrared absorption spectrum of gaseous formaldehyde has been studied by many researchers [3080, 1444, 1445, 841, 3743, 2501, 1272, 3085, 2085, 840].

TABLE 135

Adopted Values of the Molecular Constants of FCO, ClCO, F_2CO, HFCO, FClCO

Молекула A	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	$I_A I_B I_C$	σ
	$см^{-1}$						10^{-117} $(г \cdot см^2)^3$	
FCO	2000	600	1200	—	—	—	27,33	1
ClCO	1900	350	850	—	—	—	125,2	1
F_2CO	965	1928	626	1249	584	774	710,89	2
HFCO	2976	1834	1064	661	1344	1025	55,5	1
FClCO	776	1868	501	1095	415	667	2630	1

A) molecule.

On the basis of an analysis of the works carried out up to 1945, Herzberg [152] recommended the fundamental frequencies of H_2CO, proposed by Ebers and Nielsen [1444, 1445] ($\nu_1 = 2780$, $\nu_2 = 1743.6$, $\nu_3 = 1503$, $\nu_4 = 2874$, $\nu_5 = 1280$, $\nu_6 = 1167$ cm^{-1}). He pointed out that the investigations of the electronic spectrum of formaldehyde [2072, 1837, 3827] give slightly different values for the frequencies of the deformation vibrations ν_5 and ν_6. However, in the work of Brand [899] dealing with the study of the fluorescence spectrum of formaldehyde and in the work of Walsh [4138], in which the ultraviolet spectra of H_2CO and D_2CO have been analyzed, the frequency values $\nu_5 = 1280$ cm^{-1} and $\nu_6 = 1165.9$ cm^{-1} were found, which practically coincide with the frequencies, obtained as a result of the analysis of the infrared spectrum of H_2CO [1444, 1445]. Because the investigations of the infrared spectrum and the Raman spectrum of gaseous formaldehyde, carried out by Kuratani [2501] and Davidson, Stoicheff and Bernstein [1272] also confirmed the recommendation of Herzberg [152], the values of the basic frequencies, found by Ebers and Nielson [1444, 1445], were adopted in the first edition of the present Handbook.

The work of Blau and Nielson [841]* dealing with a study of the infrared absorption spectrum of formaldehyde vapor, carried out on high-dispersion apparatus, was published in 1957. The region 3-4 microns (3300-2500 cm^{-1}) was investigated on a modified Pfund spectrometer with an echelle-type grating. In the region 5.7, 6.7 and 7.5-10 microns, the work was carried out on a vacuum spectrometer with grating. The use of the vacuum device made it possible to avoid the appearance of atmospheric absorption bands which would be superposed on the investigated formaldehyde bands in the spectrum. Blau and Nielsen measured the fine structure of seven bands in the spectrum of H_2CO with great accuracy (six bands are connected with the fundamental frequencies and one with a Raman frequency). The coriolis interaction between the levels ν_5 and ν_6* was taken into account in the analysis. The frequencies of the band heads connected with the fundamental frequencies of H_2CO, which had been found in the work [841] are given in Table 134 and were adopted in the present Handbook. It should be pointed out that the values of ν_4, ν_5 and ν_6 correspond to perturbed energy levels.

As comparison with the frequencies, recommended by Herzberg [152] on the basis of earlier studies [1444, 1445] shows, considerable differences (approximately 30 cm^{-1}) exist only for the frequencies ν_4 and ν_5. In the case of ν_4 this difference is connected with the presence of a strong Fermi resonance between the levels $\nu_2 + \nu_5$ and ν_4 and, for ν_5, it may obviously be explained by a coriolis interaction with the state ν_6.

Investigating the microwave spectrum of formaldehyde and taking into account the centrifugal stretching into an asymmetrical rotator, Lawrence and Strandberg [2572] found rotational constants in the form (A – C) and (B – C). Using the measurement results of the band structure 101 ← 000, giving a value (B + C) [2571], the authors of the work [2572] determined the rotational constants A, B and C; their data are presented in Table 134 and were adopted in the Handbook. These values are in excellent agreement with the magnitudes found by Dieke and Kistiakowski [1343] as a result of an analysis of the ultraviolet spectrum. The results of the work [2572] are also confirmed by the data of Erlandsson [1493], the works of Bragg and Sharbraugh [894], Dam [1256], Dam and Bell [1257] and a series of works dealing with the investigation of the microwave spectrum of formaldehyde, carried out in Japan [3122, 3123, 2078, 2077]. On the basis of the results of research on the microwave spectra of $H_2C^{12}O$ and $H_2C^{13}O$, Lawrence and Strandberg [2572] estimated the equilibrium structural parameters of the formaldehyde molecule and found $r_{C-H} = 1.21 \pm 0.01$ A, $r_{C=O} = 1.21 \pm 0.01$ A, $\angle HCH = 118 \pm 2°$.*

The investigations of the ultraviolet absorption spectrum of the molecule H_2CO and the fluorescence spectrum of formaldehyde [4138, 1343, 895, 3655, 1434, 897, 1144, 896, 561, 2091, 3718, 3457, 1755] showed that the first excited electronic state $^3A_2$ is situated 24,279 cm^{-1} higher than the ground $^1A_1$ state of H_2CO. In agreement with theoretical concepts [2991, 2724, 4144] it was found that in this state the molecule H_2CO has the structure of a pyramid (with the C atom at the apex) slightly reminiscent of the shape of the molecule of halogensubstituted ammonia. On the basis of an analysis of the fine structure of the bands in the electronic spectrum, Brand [896] obtained for the molecule H_2CO in the excited $^3A_2$ state the following structural parameters: $r_{C-H} = 1.09$, $r_{C=O} = 1.32$ A, $\angle HCH = 120°$ and $\angle HCO = 116°$.

An analysis of the vibrational structure enabled him to calculate the four fundamental frequencies in this state: 2861, 1322, 1182 and 690 cm^{-1}.

It should also be pointed out that the next electronic state of

H_2CO is the state of type $^1A_2$ and has an excitation energy of about 28,000 cm^{-1} [561].

F_2CO . The molecule of carbon oxydifluoride, like the formaldehyde molecule, has a flat symmetrical structure and belongs to the point group C_{2v}. In analogy to the formaldehyde molecule, the intramolecular vibrations of the molecule F_2CO are characterized by six nondegenerate vibrations.

The spectrum of carbon oxydifluoride was studied by Nielsen [3069], Woltz, Jones and Nielsen [4312], Woltz and Jones [4311], Jones and Burke [2291]. In a joint work by these authors, published in 1952 [3072] the Raman spectrum of liquid F_2CO and the infrared spectrum of gaseous F_2CO in the range from 2 to 28 microns (5000-360 cm^{-1})' were again investigated. The values of the fundamental frequencies of F_2CO recommended in this work, were found by the authors as a result of the measurement and analysis of 22 bands in the infrared absorption spectrum of gaseous F_2CO. These values are given in Table 135 and have been adopted in the present Handbook.

The product of the principal moments of inertia of F_2CO, also given in Table 135, has been calculated by Nielsen [3069] on the basis of the results of an investigation of the microwave spectrum of the molecule F_2CO, carried out by Smith, Tidwell, Williams and Senatore [3778]. The values found by Nielsen [3069] for the moments of inertia $I_A = 6.988 \cdot 10^{-39}$, $I_B = 7.170 \cdot 10^{-39}$ and $I_C = 14.168 \cdot 10^{-39}$ $g \cdot cm^2$ and the results of an electron diffraction study of the structure of the F_2CO molecule [981] lead to the following values for the structural parameters: $r_{C-F} = 1.31 \pm 0.02$, $r_{C=0} = 1.17 \pm 0.02$ A and $\angle FCF = 112.5 \pm 6°$.

HFCO. The molecule HFCO is flat, and belongs to the point group symmetry C_s. The spectrum of HFCO and DFCO was first obtained by

Morgan, Staats and Goldstein [2950]. The authors of [2950] investigated the infrared spectrum of HFCO and DFCO, in the gas phase and in the form of a solid solution and the Raman spectrum of liquid formyl fluoride. The infrared spectrum was studied in the region from 400 to 5000 cm^{-1}. The Raman spectrum of liquid HFCO and DFCO was investigated at temperatures of –(34-40)°C. The values of the frequencies of the observed bands were determined with an accuracy of ±1 cm^{-1} in the region 800 cm^{-1} ± 2 cm^{-1} in the region 1600 cm^{-1} and ±4 cm^{-1} in the region 2500 cm^{-1}. An analysis of the shape, intensity and isotope shifting of the bands enabled the authors of the work [2950] to find the values of five fundamental frequencies of the molecule HFCO. The determination of the frequency of the nonplanar vibration ν_6 involved considerable difficulties. One would have expected that such a vibration would give a weak band of the perpendicular type near 1000 cm^{-1}. However, it was not possible to detect in the infrared spectrum of HFCO any other bands in this region except the P-branches of the band which is connected with the valency vibration C – F. On the basis of the Teller-Redlich product rule, on the assumption that the fundamental frequency ν_6 of the molecule HFCO is situated in the region 1000-1050 cm^{-1}, the authors of this work calculated that the band of the corresponding vibration of the molecule DFCO should be in the region 850-900 cm^{-1}. A band of the perpendicular type with a maximum at 858 cm^{-1} was actually found in the spectrum of DFCO. This confirms the hypothesis that the band corresponding to the frequency ν_6 of HFCO should lie in the region 1000-1050 cm^{-1}. This hypothesis is confirmed by a comparison of the values of the fundamental frequencies of the molecule HFCO with those of the structurally similar isoelectronic molecules HCOOH [363] and $HCONH_2$ [1508].

The correctness of the interpretation of the HFCO spectrum was confirmed by a theoretical calculation of the vibration frequencies for a model of the field of valency forces, carried out in the work [2950].

The values of the fundamental frequencies of the molecule HFCO adopted in the present Handbook on the basis of the work [2950] are given in Table 135.* This Table also gives the value of the product of the moments of inertia, calculated on the basis of the following structural parameters of HFCO which were found as a result of lectron diffraction measurements [2304]: $r_{C-H} = 1.09$ A (adopted), $r_{C-F} = 1.351 \pm 0.013$, $r_{C=O} = 1.192 \pm 0.011$, $r_{O...F} = 2.225 \pm 0.019$ A, $\angle FCO = 121.9 \pm 0.9°$. The angle HCF which is necessary for the calculation was estimated as 118° on the basis of a comparison of the results of the electron diffraction and microwave measurements on analogous molecules.**

The ultraviolet spectrum of gaseous formyl fluoride was investigated in the works of Giddings and Innes [1726a, b] and Foffani and coauthors [1570a]. A large number of sharp bands with well developed fine structure was observed in both works in the region 2200-2700 A. The bands are connected with a singlet-singlet electronic transition between the excited and ground state of HFCO. The frequency of the transition 0-0 is 37,500 cm^{-1}. The spectrum consists of progressions which correspond to the valency vibration of the carbonyl group (about 1100 cm^{-1}) and deformation vibration of the FCO group (about 640 cm^{-1}).

The rotational constants in the excited states $A-\bar{B} = 1.743$ and $\bar{B} = 0.360$ cm^{-1}, found in the work [1726a] show that in this state the molecule HFCO is not flat.

$\underline{Cl_2CO}$. Like the molecules H_2CO and F_2CO, the molecule of phosgene, Cl_2CO, has a flat symmetrical shape and belongs to the point group symmetry C_{2v}. The molecule Cl_2CO has six normal nondegenerate vibrations, which are active in the infrared spectrum as well as in the Raman spectrum.

The Raman spectrum of Cl_2CO was first obtained by Ananthakrishnan [545], who observed five lines, connected with basic vibrations. The infrared spectrum of phosgene in the region from 2 to 19 microns (from 500 to 5000 cm^{-1}) was investigated by Bailey and Hale [617]. These authors found only three fundamental frequencies in the above-indicated region.

The spectrum of Cl_2CO was very carefully studied by Nielsen, Burke, Woltz and Jones [3072]. As a result of the investigation of the Raman spectrum of liquid phosgene and the infrared absorption spectrum of gaseous Cl_2CO (the region from 2 to 38 microns (from 260 to 5000 cm^{-1} was investigated)), the authors of the work [3072] recommended the following values for the fundamental frequencies of the molecule Cl_2CO: $\nu_1 = 575$, $\nu_2 = 1827$, $\nu_3 = 297$, $\nu_4 = 849$, $\nu_5 = 240$,* and $\nu_6 = 440$ cm^{-1}, which were adopted in the first edition of the present Handbook.

It was shown, however, in the work of Catalano and Pitzer [1072] that the entropy of Cl_2CO, calculated on the basis of the frequencies, recommended by Nielsen et al. [3072] differs from the value $S_{280.66°K}$ found as a result of calorimetric measurements [1715], by 1.6 cal/ /mole·degree. For this reason, Catalano and Pitzer [1072] again investigated the infrared absorption spectrum of Cl_2CO. The spectrum was recorded in the near infrared on a Perkin-Elmer apparatus, model 21 and 12C and in the far infrared, on a specially designed apparatus with diffraction grating [859]. The frequencies, obtained in the absorption spectrum of gaseous Cl_2CO agreed in the main with the frequencies found by Nielsen et al [3072]. The band with the lowest frequency was found in the region 285 cm^{-1} which corresponds to the band $\nu_3 = 297$ cm^{-1}, obtained in the work [3072]. The value of ν_3 found by Catalano and Pitzer [1072] is obviously more reliable, because the measurements in the far infrared region were carried out in the work [1072] on an apparatus with a diffraction grating. In the region of 240 cm^{-1}, absorption bands were not observed.

In addition to the infrared spectrum of gaseous Cl_2CO, the absorption spectrum of Cl_2CO was also studied in the work [1072] by the method of matrix isolation, which makes it possible to obtain very narrow absorption bands of pure substances.* Examination of the absorption curves, obtained by this method, showed, that the band 575 cm^{-1} consists of two bands with different symmetry with centers at 568 and 582 cm^{-1}.

Using the results of the measurements of the intensity and polarization of the lines in the Raman spectrum [545, 3072] and also the product rule for the frequencies of the substituted compounds, the authors of the work [1072] determined the symmetry of the bands of different vibrations and gave a new assignment of the frequencies of Cl_2CO.

Because the differences between the entropy value $S_{280.66°K}$, calculated on the basis of the frequencies, recommended in the work [1072], and the values $S_{280.66°K}$, obtained as a result of calorimetric measurements [1715]** (0.36 cal/mole·degree) are much less than when calculated on the basis of the frequencies, found in the work of Nielsen et al [3072], the values of the basic frequencies of the molecule Cl_2CO recommended in the work [1072]*** were adopted in the present Handbook. These frequencies are given in Table 134.

The same Table gives the values of the rotational constants of Cl_2CO found by Robinson [3456] on the basis of an analysis of the structure of the microwave spectrum of Cl_2CO. To these values correspond the following structural parameters of the phosgene molecule: $r_{C=O} = 1.166 \pm 0.002$, $r_{Cl-Cl} = 2.884 \pm 0.001$, $r_{Cl-O} = 2.589 \pm 0.001$,

$r_{C-Cl} = 1.746 \pm 0.004$ A and $\angle ClCCl = (111.3 \pm 0.1)°$, which agree well with the results of the electron diffraction measurements [959].

FClCO. FClCO is a flat molecule and belongs to the point group symmetry C_S. Like the molecules F_2CO and Cl_2CO, the molecule FClCO has six nondegenerate vibrations which are active in the infrared spectrum and in the Raman spectrum.

The infrared spectrum and the Raman spectrum of FClCO were first obtained by Jones and Burke [2292]. This work was later continued by Nielsen, Burke, Woltz and Jones [3072] during a detailed study of the spectra of F_2CO, Cl_2CO and FClCO. In the Raman spectrum of liquid FClCO the authors of the works [2292, 3072] observed seven lines (six of which are connected with fundamental vibrations and one which is due to the frequencies $\nu_1 + \nu_4$).

The infrared absorption spectrum of gaseous FClCO was studied in the region from 250 to 4200 cm^{-1}. A cell with a length of 1 m was used in order to obtain the maximum possible number of Raman bands and harmonics. Gratings with 144 and 288 lines per mm were used for the recording of several bands with very complex structure as dispersing systems.

Nielsen, Burke et al [3072] detected six bands in the infrared spectrum which are connected with basic vibrations and 24 absorption regions due to Raman bands and harmonics. An investigation of the form of the contours and structure of the observed bands led the authors of the work [3072] to the conclusion that the molecule FClCO is an asymmetrical rotator. The assignment of the bands proposed in this work does not arouse any doubts because the calculated values of the frequencies of the Raman bands and harmonics agree well with those observed experimentally. The values of the basic frequencies of the molecule FClCO recommended in the works [3072, 2292] were adopted in the present Handbook and are given in Table 135. It should be pointed out that because of the Fermi resonance between the levels ν_2 and $\nu_1 + \nu_4$ the corresponding bands are slightly displaced in the spectrum. Table 135 gives the undisplaced value of ν_2.

Experimental data on the structure of the molecule FClCO are lacking. In the works [3072, 2662, 2749], the interatomic distances r_{C-F} and r_{C-Cl} in the molecule FClCO were taken to be equal to the corresponding parameters of the symmetrical molecules F_2CO and Cl_2CO and the angle FCCl and the interatomic distance $r_{C=O}$ were taken as equal to the mean values for F_2CO and Cl_2CO.*

In agreement with this, the following values are adopted in the present Handbook for the structural parameters of FClCO: $r_{C=O} = 1.17 \pm 0.02$, $r_{C-F} = 1.31 \pm 0.02$, $r_{C-Cl} = 1.74 \pm 0.02$ A, $\angle FCCl = 112 \pm 5°$ and $\angle FCO = \angle ClCO = 124 \pm 5°$, on the basis of which the product of the moments of inertia, given in Table 135, was calculated.

§58. THERMODYNAMIC FUNCTIONS OF THE GASES

The thermodynamic functions of the substances, examined in the present chapter, in the ideal gas state, were calculated on the basis of the molecular constants, adopted in the preceding paragraph and given in Tables 130-137, 142, 143, 148, 149, 156, 161, 162, 169 of Volume II of the present Handbook. For four gases (C, C^+, CO, CO^+), the calculations were carried out up to 20,000°K, for the others, to 6000°K. The differences between the constants of individual isotope modifications of the compounds, which are considered in the present chapter, were not taken into account in these calculations.

Appendix 5 gives data which enable the influence of the molecular interactions on the thermodynamic functions of CO, CO_2 and Cl_2CO to be taken into account. For the other gases the data, necessary for taking into account such molecular interactions, are lacking.

TABLE 136

Values of the Constants for the Calculation of the Thermodynamic Functions of C, C^+, CO, CO^+ and C_2

Вещество A	A_Φ	A_S
	кал/моль·град B	
C,C^+	0,1264	5,0946
CO,CO^+	2,6505	7,6187
C_2	0,8152	5,7834

A) Substance; B) cal/mole•degree.

C. The thermodynamic functions of monatomic carbon, given in Table 130 (2), were calculated for the temperatures from 293.15 to 20,000°K by means of Eqs. (II.22)-(II.23). The translational components were calculated by means of the relations (II.8) and (II.9) using the values of A_Φ and A_S given in Table 136; the electronic components, by means of the Eqs. (II.20) and (II.21). The partition function of the electronic states and its derivative with respect to temperature were calculated by direct summation over the energy levels given in Table 124 on a fast electronic computer. The calculation was carried out, taking into account the finite number of the states of the carbon atom in correspondence with the method, described in §6 (see page 133, Eq. (II.18)). In order to simplify the calculation at temperatures under 8000°K, all energy levels with values of the principal quantum numbers $n \leq 11$ were taken into account. Owing to the high excitation energies of the levels of the carbon atom with $n > 7$, the error due to taking into account the excess levels is negligibly small and does not exceed 0.0005 cal/g-atom•degree. At temperatures above 8000°K all energy levels with values of $n \leq n_{max}$ were taken into account, the magnitude of n_{max} increasing monotonously with increase in the temperature from 8000 to 20,000°K (see page 135).

The error in the values of the thermodynamic functions of monatomic carbun thus calculated at temperatures under 10,000°K was due mainly to the inaccuracy of the universal constants and does not exceed 0.002-0.003 cal/g-atom•degree in the values of Φ^*_T. At higher temperatures, the errors connected with the use of an approximate method of determining the maximum value of the main quantum number becomes important. An error in this value of ± 1 (at $n_{max} = 13$) leads to errors in the values of Φ_T^*, of 0.06 and 0.3 cal/g-atom·degree at 15,000° and 20,000°K, respectively.

It should be pointed out that the errors in the values of the thermodynamic functions due to the inaccurate estimation of the energies of individual levels in the cases, when experimental data for them are lacking, are smaller than these values by an order of magnitude.

The thermodynamic functions of monatomic carbon have been calculated earlier by several authors.* Among the calculations, carried out in the last years, in addition to the first edition of the present Handbook we must mention the works of Kolsky and coauthors [2462] ($T \leq 8000$°K) Kroeplelin, Neumann and Winter [2489] (Φ_T^* for $T \leq 7000$°K) and also the Tables of functions, given in the Handbook of Huff, Gordon and Morrell [2142] ($T \leq 6000$°K) and the U.S. Bureau of Standards [3680] ($T \leq 5000$°K). The results of most of these calculations agree with each other and with the data given in volume II of the present Handbook with an accuracy which is determined by the differences in the values of the universal constants.

$\underline{C^+}$. The thermodynamic functions of the positive ion of monatomic carbon, calculated by means of Eqs. (II.22), (II.23) for temperatures from 293.15 to 20,000°K, are given in Table 131 (2). The translational components in the values of the thermodynamic functions of C^+ were calculated by using the same values for A_Φ and A_S as for monatomic carbon (see Table 136) and the electronic components, by means of Eqs.(II.20) and (II.21) on the basis of the energy levels, given in Table 125.

At temperatures under 10,000°K, the uncertainties in the calculated values of the thermodynamic functions are due to the inaccuracy of the adopted values of the universal constants and do not exceed 0.003-0.005 cal/g-atom•degree. At higher temperatures, the errors due to neglecting the contributions of the levels which are not given in Table 125, become important. However, because of the large excitation energies of these levels and the large ionization energy of the ion C^+ (see page 950), the corresponding errors, amount to several hundred cal/g-atom•degree in the values of $\Phi^*_{20,000}$.

The thermodynamic functions of C^+ were calculated in work of Green, Poland and Margrave [1851a] for temperatures from 298.15 to 50,000°K. The results of this calculation are practically identical with those given in Table 131 (2).

$\underline{C_2}$. The thermodynamic functions of diatomic carbon for temperatures from 293.15 to 6000°K, given in Table 132 (2), were calculated by means of Eqs. (II.34) and (II.35). The translational components were calculated by means of Eqs. (II.8) and (II.9), using the values of A_Φ and A_S, given in Table 136, and the intramolecular components, by means of Eqs. (II.131) and (II.132) on the basis of the molecular constants, given in Table 126. The partition functions of the vibrational and rotational levels of the states $X^1\Sigma^+_g$, $a^3\Pi_u$, $b^3\Sigma^+_g$, $A^1\Pi$ and their derivatives with respect to temperature were calculated by direct summation over the energy levels of these states by means of an electronic computer. The values of the energies of the vibrational and rotational levels required for the calculation were given by the equations as functions of the vibrational and rotational quantum numbers and the corresponding molecular constants, given in Table 126. The components of the three substates of the state $a^3\Pi_u$ were calculated as the components of three individual states; the energies of the rotational levels of this state were calculated by the Budo Eqs. (1.26);

the multiplet nature of the electronic states $b^3\Sigma$ and $A^1\Pi$ was taken into account by means of statistical weighting.

The components of the states $B^1\Delta$, $C^1\Sigma$, $c^3\Sigma$ and $d^3\Pi$ were calculated by the Eqs. (II.117) and (II.118). The values of M_i and N_i in these equations were calculated by the method of Gordon and Barnes (relations (II.137) and (II.138) without limitation of the number of rotational levels of each state. The components of the four electronic states with excitation energies of 34,261 to 43,240 cm^{-1} (see Table 126) were calculated by means of Eqs. (II.120) and (II.121).

The basic errors in the calculated values of the thermodynamic functions C_2 are due to: a) the absence of experimental data on the energies of the high vibrational and rotational levels of the states $X^1\Sigma$, $a^3\Pi_u$, $b^3\Sigma^+$, $A^1\Pi$; b) the absence of experimental data on the excitation energies of the states $B^1\Delta$, $C^1\Sigma$ and $c^3\Sigma$ and the constants C_2 in these states; c) the use of an approximate method of calculating the components of the electronic states with excitation energies over 9000 cm^{-1}. The total error in the values $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000}, given in Table 132 (2), is estimated as 0.01; 0.03 and 0.1 cal/mole•degree, respectively.

The thermodynamic functions of diatomic carbon over a wide temperature range were calculated in the works of Overstreet [3158] (Φ^*_T to 5000°K), Gordon [1808] (Φ^*_T from 2000 to 6000°K), A. Gurvich and Frost [168] (Φ^*_T to 5000°K), Fickett and Cowan [1556] (S°_T from 3000 to 12,000°K), Kroepelin and Neumann [2489] (Φ^*_T from 2000 to 7000°K), Pitzer and Clementi [3256] (from 2000 to 4000°K), Altmann [527] (to 5000°K) and Clementi [1128b] (from 2000 to 6000°K). In all these works, with the exception the last two, the calculations were carried out on the assumption that the electronic ground state of the molecule C_2 is the state $^3\Pi_u$. Because the state $^1\Sigma^+_g$ (see page 863) has been taken in the present Handbook as the electronic ground state of C_2 and, moreover, a large number of other electronic states with low excitation energies has been taken into account, the values of the thermodynamic functions of C_2, given in these works, differ considerably from the data in Table 132 (2).

The book of Zeise [4384] gives the results of the calculation of Gordon [1808] for C_2. The values of Φ^*_T tabulated in the Handbook of Kelley [2363] ($T \leq 5000°K$) and also the values of Φ^*_T and S°_T, tabulated by Stull and Sinke [3894] ($T \leq 3000°K$) are smaller than the data of other authors by the amount R ln 3; the causes of this difference have not been ascertained by the discrepancies between the tabulated values and those given in Table 132 (2) attain 1-2 cal/mole•degree.

The calculations in the works of Altmann [527] and Clementi [1128b] for the thermodynamic functions of C_2 were carried out on the assumption that the molecules of this gas have the ground state $^1\Sigma^+_g$ as adopted in the present Handbook. In the work of Alatmann, the calculation was carried out by the method of Pennington and Kobe, in the work of Clementi, by means of a method, based on the calculation of the partition functions and their derivatives by direct summation over the vibrational energy levels. The excited electronic states of C_2 were taken into account in both calculations, the states $B^1\Delta$, $C^1\Sigma$, $c^3\Sigma$ which are not observed experimentally in the spectra, being taken into account in the work of Clementi. The difference between the results of these calculations and the values given in Table 132 (2) amount to 0.2-0.5 cal/mole•degree for the work of Altmann and 0.02--0.15 cal/mole•degree for the work of Clementi. They are due to the fact that less accurate methods of computation have been used in these works.

In the first edition of the Handbook, the thermodynamic functions of C_2 were calculated by the method of Gordon and Barnes, on the assumption that the molecule C_2 has the electronic ground state $^3\Pi_u$. The differences between the values of the thermodynamic functions, given in the first and present editions of the Handbook, attain 3 cal//mole•degree in the values of Φ_T^* (they are a maximum at 293.15°K, decrease with increase in temperature, change sign at 3000°K and again increase towards 6000°K) and 1 cal/mole•degree in the values of S_T°.

CO. The thermodynamic functions of carbon monoxide, calculated by means of Eqs. (II.34) and (II.35) for temperatures from 293.15 to 20,000°K, are given in Table 134 (2). The translational components were found by means of the relations (II.8) and (II.9), using the values of A_Φ and A_S, given in Table 136; the intramolecular components by means of Eqs. (II.131) and (II.132). The partition functions of the vibrational and rotational states of the electronic states $X^1\Sigma^+$, $a^3\Pi$ and $a'^3\Sigma^+$ of the molecule CO and their drivatives with respect to temperature in the Eqs. (II.131)-(II.132) were calculated by means of an equation of the type (II.131) by direct summation on an electronic computer. The values of the energies of the vibrational and rotational levels of these states needed for the calculation were given by the equation as functions of the vibrational and rotational quantum numbers and the corresponding molecular constants, given in Table 128. The dependence of the values of J_{max}, calculated by means of the method, described in §3 (see page 73) on the values v for $X^1\Sigma^+$-, $a^3\Pi$- and $a'^3\Sigma$- states of CO is shown in Fig.17.

In the calculation of the partition functions of the states and their derivatives for the $a^3\Pi$ and $a'^3\Sigma$- electronic states, the multiplet nature of the rotational levels of both states were taken into account by means of the statistical weights 6 and 3, respectively. This simplification does not affect the calculation accuracy because the splitting of the levels of the states $a^3\Pi$ and $a'^3\Sigma$ is negligibly small as compared with the energy of the corresponding rotational levels relative to the level $J = 0$, $v = 0$ of the state $X^1\Sigma^+$.

In addition to the three above-examined electronic states, the molecule CO has several other states with excitation energies over 60,000 cm^{-1} (see Table 128). The components of the states $d^3\Pi$, $A^1\Pi$ and $e^3\Sigma$, whose excitation energies do not exceed 70,000 cm^{-1}, were calculated by means of Eqs. (II.126), (II.127), and the components of the eight higher states, given in Table 128, on the basis of Eqs. (II.120) and (II.121), i.e., without taking into account the differences in the constants of the molecule CO in these and the $X^1\Sigma^+$ ground state.

The molecular constants of CO in the ground state are known with great accuracy and the dissociation energy of the carbon monoxide molecule is very large. Because of this, the use of the method of direct summation made it possible to obtain highly accurate values of the thermodynamic functions of carbon monoxide, the errors of which at temperatures to 10,000-12,000°K are due mainly to the inaccuracy of the adopted values of the physical constants and do not exceed 0.005 cal/mole•degree. At higher temperatures, the error in the calculated values of the functions increase owing to the absence of experimental data on the energies of the high vibrational and rotational levels of the ground state and also the molecular constants of CO in the excited states. Nonetheless, it can be assumed that even at 20,000°K, the error in the calculated values of the functions of CO do not exceed some tens cal/mole•degree.

It should be pointed out that the thermodynamic functions of carbon monoxide, calculated for $T \leq 6000°K$ in the first edition of the Handbook by the method of Gordon and Barnes, practically coincide with those found by direct summation. This is explained by the high dissociation energy of the molecule CO and the fact that it agrees well with the value found by linear extrapolation.

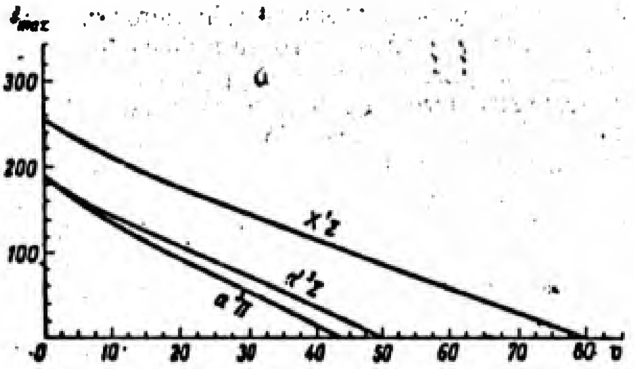

Fig.17. J_{max} as a function of v for the electronic states $X^1\Sigma^+$, $a^3\Pi$ and $a'^3\Sigma^+$ of the molecule CO.

The thermodynamic functions of CO have been calculated previously by many authors. In several Handbook editions ([4384, 2142, 3680, 3507, 137] and others) Tables of the thermodynamic properties of carbon monoxide are presented, based on the calculations of Clayton and Giauque [1126, 1127] (Φ_T^* for $T \leq 5000°K$) and Johnston and Davis [2274] (S_T° for $T \leq 5000°K$) carried out in the years 1932-1933 and recalculated to the modern values of the universal constants by Warman and others [4122]. The differences between these data and the data given in Table 134 (2) are of the order of 0.085 cal/mole•degree in the values of Φ_T^* and S_T° over the entire temperature range and are due to the fact that the calculations in the works [1126, 1127, 2274] were carried out on the basis of the erroneous value $B_e = 1.853\ cm^{-1}$, found by Birch on the basis of the measurements of Snow and Rideal [3808].

Of the calculations of the thermodynamic functions of carbon monoxide, carried out in later years, we must mention the work of Goff and Gratch [1786] (Φ_T^* and S_T° for $T \leq 2777°K$ by the method of Kassel) and also the work of Belzer and Savedov (Φ_T^* and S_T° for $T \leq 5000°K$)

whose results are given in the Handbook [2076]. The values of the thermodynamic functions of CO, calculated in these works, agree with those given in Table 134 (2) with an accuracy of a few thousandths cal/mole•degree.

Fickett and Cowan [1555, 1556] extrapolated the thermodynamic functions of CO, recommended in the work [3680], to a temperature of 12,000°K as they had done for several other gases (see, for example, page 320). At temperatures up to 10,000°K, the differences between the data of Fickett and Cowan and the values given in the present Handbook, as in the case of the other Tables, are based on the calculations of Clayton, Giauque, Johnston and Davis, are approximately 0.086 cal/ /mole•degreee. At higher temperatures, the errors due to the use of the approximate method of calculation by Fickett and Cowan, which partially compensate the errors, due to the incorrect value of B_e, begin to exert an effect.

Calorimetric measurements of the specific heat and the heats of the phase transformations of CO were carried out in several works (see [2364]. Kelley [2364], based on the data obtained by Clayton and Giauque [1126], recommends the value $S^\circ_{298} = 46.22$ cal/mole•degree which is considerably less than the value given in Table 134 (2) and amounts to 47.2167 ± 0.0050 cal/mole•degree. The difference of about 1 cal/mole•degree between the values of the standard entropy of CO, calculated by statistical methods and obtained as a result of the calorimetric measurements, Clayton and Giauque explained by the presence of the residual entropy in crystalline carbon monoxide at 0°K.

$\underline{CO^+}$. The thermodynamic functions of ionized carbon monoxide were calculated by means of Eqs. (II.34) and (II.35) for the temperatures from 293.15 to 20,000°K and are given in Table 135 (2). In the calculation of the translational components Φ^*_T and S°_T, the same values of

A_Φ and A_S were used as for carbon monoxide (see Table 136). The intramolecular components were calculated by means of Eqs. (II.131) and (II.132). The partition functions of the vibrational and rotational levels $X^2\Sigma$ and $A^2\Pi$ of the electronic states of CO^+ and their derivatives with respect to temperature in the Eqs. (II.131) and (II.132) were calculated by direct summation on a fast electronic computer. The energy values of the individual levels required for the calculation were given by the equations as functions of the molecular constants, given in Table 130 and the corresponding quantum numbers. Allowance was made for the multiplet nature of the rotational levels of the $X^2\Sigma$- state by introducing the statistical weight 2, and the components $A^2\Pi_{1/2}$- and $A^2\Pi_{3/2}$- substates were calculated as components of individual states. Figure 18 shows the curves which determine the maximum values of the quantum numbers v and J for the $X^2\Sigma$- and $A^2\Pi$- states, calculated according to the methods described in §3.

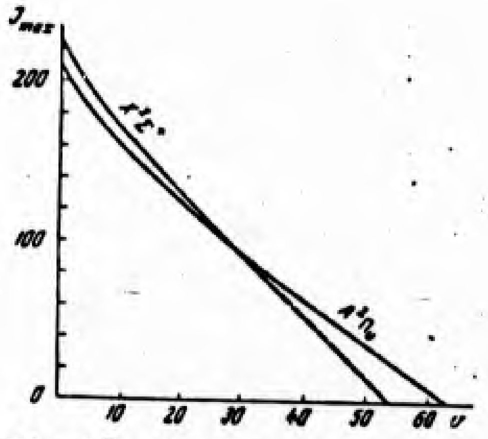

Fig.18. Dependence of J_{max} on v for the electronic states $X^2\Sigma^+$ and $A^2\Pi$ of the molecule CO^+.

The components of the state $B^2\Sigma$ in the values of Φ_T^* and S_T° were calculated by means of the relations (II.126) and (II.127), i.e., by making allowance for the difference in the constants of the $B^2\Sigma$- and $X^2\Sigma$- states.

Because of the large value of the dissociation energy and the vibration frequency of CO^+ (see §57 and 60), and also the existence of reliable data on the molecular constants of CO^+ in the ground state, the use of the method of direct summation of energy levels enabled the thermodynamic functions of ionized carbon monoxide to be calculated with great accuracy. At temperatures to 8000-10,000°K, the uncertainty in the calculated values of Φ_T^* and S_T° is determined only by the inaccuracy of the values of the physical constants used in the calculations; the absence of experimental data on the energies of the higher electronic, vibrational and rotational levels leads to considerable errors only at higher temperatures.

The thermodynamic functions of CO^+ are published here for the first time.

$\underline{CO_2}$. The thermodynamic functions of carbon dioxide, calculated on the basis of Eqs. (II.241) and (II.242) for the temperatures 293.15-6000°K, are given in Table 136 (2). The calculation of the values $\ln\Sigma$ and $\ln\Sigma + T\, \partial/\partial T \ln\Sigma$ was carried out by the method of Kassel on the basis of the vibrational constants of CO_2, adopted by Wooley [4325] on the basis of the data of Taylor, Benedict and Strong [3951] and unpublished work of Benedict, and the rotational constants of CO_2, found by G. Herzberg and L. Herzberg [2030] (see Table 132). Table 138 gives the values of C_Φ and C_S, by means of which the components of the translational motion and the rigid rotator in the thermodynamic functions of carbon dioxide gas and also the values of θ_n for the calculation of the harmonic oscillator components were calculated.

The corrections for the anharmonicity of the vibrations of the molecule CO_2, its centrifugal stretching and the rotation and vibration interactions in the values of Φ_T^* (values $R \ln\Sigma$) were calculated by the method of Kassel [$R \ln \alpha$ in Eq. (II.210)] for the temperatures 298.15; 500; 700; 1000; 1500; 2000; 3000; 4000; 5000 and 6000°K. For the first three temperatures terms with $i + j + k \leq 2$ were included in the sums $\Sigma\, \Pi_{ijk} Y_{ijk}$; for the five following temperatures with $i + j + k \leq$ ≤ 4, and at 5000 and 6000°K, $ci + j + k \leq 6$. For the other temperatures the values $R\ln\alpha$ were found by quadratic interpolation.

As pointed out earlier (see page 888), there is a sharp resonance of the vibrational states v_1, v_2, v_3 and $v_1 - 1$, $v_2 + 2$, v_3 in the CO_2 molecule. To make allowance for the influence of this resonance on the magnitude of Φ^*_T, the approximate relation, proposed by Wooley [4323] was used, according to which*

$$\frac{\Delta Q}{Q} = \frac{1}{2}\left(\frac{hc}{kT} W_0\right)^2 e^{-2\theta_2/T} \cdot (1 - e^{-2\theta_2/T})^{-1} \cdot (1 - e^{-\theta_2/T})^{-2},$$

where Q is the sum over the intramolecular states, calculated without taking the resonance into consideration, and ΔQ is the correction for the resonance applied to the value of Q.

On the basis of the values Rlnα and ΔQ/Q thus found, the corrections for the values of Φ^*_T of carbon dioxide were calculated and the rigid rotator-harmonic oscillator calculated in approximation

$$R \ln \alpha' = R \ln \alpha + R \frac{\Delta Q}{Q}.$$

The corresponding corrections for the values of S°_T were obtained by numerical differentiation of the values Rlnα' on the basis of the usual Equations (see [265]).

The errors in the values of the thermodynamic functions of CO_2 calculated in this manner at low temperatures are mainly due to the inaccuracy of the molecular constants of CO_2 used in the calculations. At higher temperatures the deficiencies of the adopted method of calculation begin to have an effect, in particular, the calculation of the sum of the vibrational and rotational quantum numbers on the assumption that the upper limits are equal to infinity. Another source of error may be the calculation of the Fermi resonance by an approximate method.

In order to evaluate the accuracy of the calculated values of the thermodynamic functions of CO_2, they were calculated by the method proposed by Gordon, using the same constants as in the basic calculation (1) and also by means of the more accurate constants of CO_2, found by Courtoy (2) (see page 890). The results of the two calculations are given in Table 137, where they are compared with the values, given in Table 136 (2).

TABLE 137

Comparison of the Thermodynamic Functions of CO_2, Calculated by the Method of Gordon and Kassel and Different Sets of Molecular Constants

T, °K	$\overset{*}{\Phi}_T$, кал/моль·град A			$\overset{\circ}{S}_T$, кал/моль·град A		
	Метод B					
	Касселя C	Гордона (I) D	Гордона (II) D	Касселя C	Гордона (I) D	Гордона (II) D
298,15	43,562	43,562	43,562	51,071	51,067	51,066
1000	54,113	54,110	54,110	64,333	64,326	64,325
2000	61,845	61,838	61,838	73,892	73,872	73,874
3000	66,911	66,890	66,900	79,838	79,802	79,807
4000	70,705	70,686	70,690	84,151	84,098	84,107
5000	73,744	73,716	73,719	87,545	87,467	87,475
6000	76,283	76,250	76,258	90,355	90,253	90,270

A) cal/mole•degree; B) method; C) Kassel; D) Gordon.

It can be seen from Table 137 that the inaccuracy of the molecular constants of CO_2 result s in errors of not more than 0.01-0.02 cal/mole•degree in the values of $\overset{*}{\Phi}_T$ and $\overset{\circ}{S}_T$. A comparison of the values obtained in the calculations by different methods, shows that at $T \leq$ ≤ 3000°K, the error in the value of $\overset{*}{\Phi}_T$ does not exceed 0.01-0.02 cal/ /mole•degree. At higher temperatures, the errors increase but because of the great stability of the molecule CO_2 and its high vibrational frequency, they apparently do not exceed 0.15-0.20 cal/mole•degree in the value of $\overset{*}{\Phi}_{6000}$. The uncertainty in the values of $\overset{*}{\Phi}_{298.15}$ and $\overset{*}{\Phi}_{3000}$ is 0.005 and 0.03 cal/mole•degree, respectively.

The thermodynamic functions of carbon dioxide gas have been calculated by many authors. References to the calculations, carried out before 1940, can be found in the paper by Wilson [4291]. Of these works, we need mention only the calculation of Kassel [2332], carried out on the basis of the constants found by Adel and Dennison [490]. At temperatures under 1500°K, the calculation was carried out by the method worked out by Kassel, but without allowing for the rotation-vibration interaction in the molecule CO_2, owing to the absence of the respective constants. At higher temperatures ($1500 \leq T \leq 3500$°K), certain simplications were used in the calculations, whose nature has not been indicated in the work [2332]. The data of Kassel were recalculated for the modern values of the universal constants in the work of Wagman et al. [4122] and were incorporated in several Handbook editions [4384, 3507, 2142, 3680].

Of the calculations, carried out in the Forties and Fifties, the works of Wooley [4325] ($T \leq 5000$°K, Kassel method) and Gratch [1843] ($T \leq 2777$°K, Kassel method) must be mentioned. The data obtained by Wooley, were calculated on the basis of constants similar to those adopted in the present Handbook; they agree well with those given in Table 136 (2) (the differences over the entire temperature range do not exceed 0.01 cal/mole•degree) and are presented in the Handbook [2076]. At the same time, the functions of CO_2, calculated in the work of Gratch, differ from the data of Wooley and from the values presented in Table 136 (2), by 0.04-0.08 cal/mole•degree, in spite of the fact that the calculations were carried out by identical methods practically with the same values of the molecular constants. This entitles us to assume that certain systematic errors must have been committed in the work [1843].

An analysis of the data of Gratch, carried out by the authors of the Handbook during the preparation of the first edition, showed that the vibrational components in the work [1843] were evidently calculated on the basis of the constants ω_n instead of the constants ω_n°.

As pointed out earlier, the thermodynamic functions of carbon dioxide, given in several Handbook editions [3507, 2142, 3680] at $T \leq 2000°K$, are based on the calculations of Kassel [3808] and Wagman et al. [4122]. At higher temperatures ($2000 < T \leq 5000°K$) [3507, 3680] and ($2000 < T \leq 6000°K$) [2142] these Handbooks give practically the same values which differ greatly (by 0.1-0.2 cal/mole•degree) from those calculated in the present Handbook and in the work [4325]. These values were obviously obtained by the U.S. Bureau of Standards as a result of an approximate calculation and were used by Fickett and Cowan [1555, 1556] for the extrapolation of the functions of CO_2 to 12,000°K.

The entropy of carbon dioxide at 298°K was determined on the basis of calorimetric measurements by several authors. Kelley [2364] recommended the value $S_{298} = 51.11 \pm 0.10$ cal/mole•degree, found by Giauque and Egan [1713a]. This value agrees well with that calculated in the present Handbook: $S^\circ_{298.15} = 51.071$ cal/mole•degree [see Table 136 (2)].

$\underline{C_3}$. The thermodynamic functions of triatomic carbon, calculated by means of Eqs. (II.241) and (II.242), using the approximate model of the rigid rotator-harmonic oscillator for temperatures of 293.15-6000°K are given in Table 133 (2). The calculations were carried out by means of the constants, given in Table 131. Table 138 presents the values of C_Φ, C_S and θ_n, used in these calculations.

The basic error in the calculated values of the functions of C_3 is due to the absence of reliable data on the type of electronic ground state of this molecule. If we assume that the ground state of C_3 is a quintet, which is not very probable, the errors in the values of Φ^*_T and S°_T amount to approximately 3.13 cal/mole•degree. However, if it is assumed that the ground state of C_3 is the state $^1\Sigma$ (see page 888), the errors in the values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} due to the inaccuracy of the chosen values of the molecular constants and the approximate method of calculation amount to about 0.3, 1.5 and 3 cal/mole••degree, respectively.

The thermodynamic functions of C_3 were calculated previously in the work of Glockler [1765] on the basis of the constants, obtained as a result of approximate estimates (see page 886) and with the statistical weight of the ground state of this molecule, taken as 5. The differences between the results of Glocker's calculation and the data, given in the Handbook, should be quite considerable, but because Glockler does not give the values calculated by him, a comparison is not possible.

Stull and Sinke [3894] gives the values for the thermodynamic functions of C_3 for $T \leq 3000°K$, calculated by means of the constants proposed by Glockler. The values recommended by them differ from those given in Table 133 (2) by 3.7-4.8 cal/mole•degree.

TABLE 138

Values of the Constants for the Calculation of the Thermodynamic Functions of C_3, CO_2, HCO, FCO and ClCO

Вещество A	θ_1	θ_2	θ_3	C'_Φ	C'_S
	град B			C кал/моль·град	
C_3	1726,6	719,40 (2)	2834,4	2,9871[a]	9,9426[a]
CO_2	1934,9	959,51 (2)	3397,2	3,7680[a]	10,7235[a]
HCO	2633,0	2212,9	4100,6	0,3646	8,3137
FCO	2877,6	863,27	1726,5	5,8434	13,7925
ClCO	2733,7	503,58	1223,0	8,2504	16,1995

A) Substance; B) degree; C) cal/mole•degree
a) the values of C_Φ and C_S are given.

The thermodynamic functions of C_3 for various temperatures in the range from 2000 to 4000°K were also calculated in the work of Pitzer and Clementi [3256] on the basis of estimated values of the molecular constants (see remark on page 887). The authors of this work assumed that the molecule C_3 has an electronic ground state of the type $^1\Sigma$. The results of the calculations by Pitzer and Clementi agree with the data of Table 133 (2) to within 0.4-0.7 cal/mole•degree.

$\underline{C_3O_2}$. The thermodynamic functions of carbon suboxide for temperatures of 293.15-6000°K, given in Table 137 (2), were calculated by means of Eqs. (II.241) and (II.242) using the approximate model of the rigid rotator-harmonic oscillator on the basis of the molecular constants, adopted in the Table 133. Table 139 gives the values of C_Φ and C_S, which enter into the equations for calculating the rotational-translational components in the values of Φ_T^* and S_T° and also the value of θ_n, by means of which the vibrational constants were calculated.

TABLE 139

Values of the Constants in the Calculations of the Thermodynamic Functions of C_3O_2, H_2CO, F_2CO, HFCO, Cl_2CO and FClCO

Вещество A	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7	C'_Φ	C'_S
	град B							C кал/моль·град	
C_3O_2	3165	1197	3249	2266	832 (2)	790 (2)	285 (2)	8,4254[a]	15,3809[a]
H_2CO	3980,3	2512,2	2159,1	4091,1	1794,8	1682,7	—	—1,0766	6,8725
F_2CO	1388,4	2774,0	900,7	1797,0	840,25	1113,6	—	7,3395	15,2882
HFCO	4282	2639	1531	951	1934	1475	—	5,2330	13,1821
Cl_2CO	820,11	2628,7	410,055	1221,5	663,07	841,69	—	11,0552	19,0043
FClCO	1116,5	2687,7	720,83	1575,5	597,10	959,67	—	10,6789	18,6280

A) Substance; B) degree; C) cal/mole•degree; a) the values of C_Φ and C_S are given

The errors in the calculated values of the thermodynamic functions of carbon suboxide are mainly due to the impossibility of allowing for the anharmonic vibrations of the molecule C_3O_2 and also to the absence of data for limiting the number of vibrational and rotational levels. The latter should be considerable because of the slight stability of C_3O_2. The errors in the values of $\Phi^*_{298.15}$ and Φ^*_{3000} are of the order of 0.15 and 3 cal/mole•degree.

The thermodynamic functions of carbon suboxide were calculated previously by Thompson [3969] for temperatures up to 1000°K. The differences between the calculation results are 0.05-0.07 cal/mole•degree but at 600°K, probably because of an accidental mistake, it attains 0.26 cal/mole•degree. The results of Thompson's calculations are given in the book of Zeise [4384]. In the work of Kobe et al [2449a], values of C°_p and $H^\circ_T - H^\circ_{298}$ for temperatures to 1500°K were given, calculated on the basis of the same values of the molecular constants, as those used by Thompson.

HCO, FCO and ClCO. The thermodynamic functions of formyl, and carbon oxyfluoride and oxychloride, calculated by means of Eqs. (II.243) and (II.244) for the temperatures 293.15-6000°K, are given in Tables 142, 148 and 161, respectively, of volume II of the present Handbook. The calculation was carried out using the approximate model of the rigid rotator-harmonic oscillator on the basis of the constants, used in the preceding paragraph (Tables 134 and 135). Table 138 presents the values of C'_Φ and C'_S in the equations for calculating the rotational-translational components of Φ^*_T and S°_T and also the values of θ_n by means of which the vibrational components were calculated. Because it has been assumed earlier, that the ground states of the molecules of the gases under consideration are doublet states, the components R ln 2 are included in the values of C'_Φ and C'_S.

The molecule HCO has an excited electronic ground state with a low excitation energy; the components of this state in the values of Φ^*_T and S°_T were calculated by means of the relations (II.120) and (II.121), i.e., without allowing for the differences in the constants and the structure of HCO in the excited and ground states.

The main errors in the calculated values of the thermodynamic functions of formyl are due to the isufficient accuracy of the adopted values of the basic frequencies of HCO and the fact that the calculation was carried out on the basis of the approximate model of the rigid rotator-harmonic oscillator (about 0.2 and 0.3 cal/mole•degree, respectively, in the values of Φ^*_{3000}). At temperatures above 3000--4000°K, the errors due to the approximate method of calculation of the excited state $^2A_1$ are added to these errors. The errors in the values of $\Phi^*_{298.15}$; Φ^*_{3000} and Φ^*_{6000} are of the order of 0.03, 0.6 and 1.5 cal//mole•degree, respectively.*

The errors in the calculated values of the thermodynamic functions of FCO and ClCO at low temperatures are due to the absence of reliable data on the structure and rotational constants of these molecules. The corresponding values are 0.06-0.09 cal/mole•degree. At higher temperatures the errors due to the absence of experimental data on the basic frequencies of the two molecules and also the approximate nature of the calculation and the failure to allow for the excited electronic states begin to become important. The probable errors in the values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} are 0.25; 1.2 and 2.5 cal/mole••degree.

The thermodynamic functions of HCO were calculated previously by Ribeaud [3426] for temperatures under 3500°K and by Ewing, Thompson and Pimentel [1517a] for the temperatures to 5000°K. The differences between the calculation results of Ribeaud and the data of the Handbook vary from 0.25 to 0.83 cal/mole•degree over the range from 298.15 to 3500°K, but because of the absence of any indication concerning the values of the constants of HCO, used in the work [3426], the cause of the differences remains unknown. The thermodynamic functions of formyl, calculated in the work [1517a], differ from those given in Table 142(II) by 0.8-1.3 cal/mole·degree. These differences are a maximum at T = = 298.15°K because of the fact that the multiplet nature of the rotational levels of the ground state of HCO was not allowed for in the work [1517a]. With increasing temperature, the differences decrease because of the partial compensation of this error by difference in the basic frequencies and then increase again because the excited state of HCO was not allowed for in the work [1517a].

The differences between the values of the thermodynamic functions of formyl, and carbon oxyfluoride and oxychloride, given in the first and present editions of the Handbook, are due to certain improvements in the values of the constants of HCO, FCO and ClCO and also the fact that the excited state $^2A_1$ of HCO had been taken into account. Other calculations of the thermodynamic functions of FCO and ClCO are not known in the literature.

$\underline{H_2CO}$. The thermodynamic functions of formaldehyde, presented in Table 143(II) were calculated by means of Eqs. (II.243) and (II.244), using the approximate rigid rotator-harmonic oscillator model on the basis of the constants, used in the preceding paragraph (see Table 134). Table 139 gives the values of the constants C'_Φ and C'_S in the Eqs. (II.243) and (II.244) and also the values of θ_n, by means of which the vibrational constants were calculated.

The errors in the calculated values of the thermodynamic functions of formaldehyde are predominantly due to the approximate method of calculation, chosen because of the absence of data on the constants of the anharmonic vibrations and the rotational-vibrational interactions The total error in the calculated values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} is 0.02; 0.8 and 1.5 cal/mole·degree, respectively.

The thermodynamic functions of formaldehyde have been calculated in works of Thompson [3970], Beach and Stevenson [698] and Dworjanyn

[1430b]. The calculations of Thompson [3970] and Dworjanyn [1430b] were carried out on the basis of constants of H_2CO, close to those adopted in the Handbook, for temperatures up to 1500 and 1200°K, respectively. The results of these calculations agree within the limits 0.1 cal/mole•degree with the values, given in Table 143(II). The book of Zeise [4384] gives the values of the thermodynamic functions of H_2CO, calculated by Thompson. The work of Kobe and Pennington [2452a] gives the values C_p° and $H_T^\circ - H_{293}^\circ$, based on the results of the calculation of Matsen and Hamper which remained unknown to the authors of the Handbook.

The Tables of the thermodynamic functions of formaldehyde, given in the first and present edition of the Handbook, differ by 0.03 to 0.25 cal/mole•degree on account of a slight change in the physical constants and the molecular constants of H_2CO, used in the calculations.

F_2CO, HFCO, Cl_2CO and FClCO. The thermodynamic functions of these gases, given in Tables 149, 156, 162 and 169 of Volume II of the Handbook, were calculated by means of Eqs. (II.243) and (II.244) from 293.15 to 6000°K using the approximate model of the rigid rotator-harmonic oscillator. The calculation was carried out on the basis of the constants, adopted in Tables 134 and 135. Table 139 gives the values of the constants C_Φ' and C_S' in the Eqs. (II.243) and (II.244) and also the values of θ_n, used for calculating the vibrational components.

The basic uncertainties in the values of the thermodynamic functions of F_2CO, HFCO, Cl_2CO and ClFCO are due to the approximate nature of the calculation. The errors in the value of Φ_{3000}^* due to the failure to allow for the anharmonicity of the vibrations of F_2CO, HFCO, Cl_2CO and ClFCO are of the order 1.2; 1.0; 2.0 and 1.4 cal/mole•degree respectively. Owing to the slight stability of the molecules of these gases, the error caused by neglecting in the calculations the necessity for limiting the number of rotational and vibrational levels of the molecules may be of the same order. Hence the probable errors in the values of Φ^*_{3000} for F_2CO, HFCO, Cl_2CO and ClFCO are 1.5-2 cal/ /mole·degree. At room temperature, the errors in the values of the thermodynamic functions are determined only by the inaccuracy of the molecular constants used in the calculation and are of the order of 0.05-0.1 cal/mole·degree.

In 1960, Giauque and Ott [1717a] carried out careful measurements of the specific heat of three forms of crystalline Cl_2CO and, using the data on the specific heat of liquid Cl_2CO and the heat of evaporation, obtained earlier in the work of Giauque and Jones [1715], found $S_{298} = 67.81 \pm 0.05$ cal/mole·degree. This figure agrees well with that given in Table 162 (II) at 67.780 cal/mole·deg. Kelley [2364] recommends the value $S^\circ_{298.15} = 67.50$ cal/mole·degree, found by Giauque and Jones on the basis of specific heat measurements on another crystalline form of Cl_2CO, in which a disorderly orientation of the molecules is retained at low temperatures.

The thermodynamic functions of F_2CO were calculated earlier by Krishnamachari [2487] up to 1000°K and by Lovell et al [2662 to 1500°K. Both calculations were carried out on the basis of constants identical with those adopted in the Handbook. The differences between the values given in Table 149 (2) and the data of [2487] do not exceed 0.01 cal/mole·degree, while the differences with regard to the data of [2662] attain 0.04 cal/mole·degree at certain temperatures, evidently because of accidental errors committed in this work. The thermodynamic functions of Cl_2CO were calculated in the works of Beach and Stevenson [698], Pertierra [3224] and also Thompson [3970] to 1500°K, Gordon and Goland [1818] to 4000°K and Giauque and Ott [1717a] to 500°K. All calculations, with the exception of those effected in the work [1717a], were carried out by means on incorrect values of the vibrational states, in consequence of which their data differ from those given in the present Handbook by 0.7-1.6 cal/mole•degree. The data of [1717a] agree with those presented in Table 162(II) to within 0.04 cal/mole•degree. This difference is due to the fact that the rotational constants of the molecule $Cl_2^{35}CO$ were used for the calculations in the present Handbook, while the calculation in the work [1717a] was carried out on the basis of moments of inertia, averaged for the natural isotope mixture of Cl_2CO.

The thermodynamic functions of FClCO had been calculated earlier in the work of Lovell, Stevenson and Jones [2662] by means of practically the same constants as those used in the present Handbook, for temperatures of 298.15-1500°K. The results of these two calculations agree within 0.08 cal/mole•degree.

The thermodynamic functions of F_2CO in the first and present editions are identical and differ from Cl_2CO by 0.7-1.6 cal/mole•degree because of the change in the vibrational constants. The thermodynamic functions of HFCO are published for the first time in the literature.

§59. THERMODYNAMIC PROPERTIES OF CARBON IN THE SOLID AND LIQUID STATE

As indicated in the introduction to the present chapter (see page 856), the present Handbook gives Tables of the thermodynamic functions of graphite (293.15-5000°K) and liquid carbon (5000-6000°K) and also of diamond within the range of 293.15-1200°K. Diamond is a metastable crystalline modification of carbon within this temperature range; its thermodynamic functions are given in Table 142.

Table 140 gives thermodynamic values, including the equations for the specific heats, used in the Handbook for calculating the thermodynamic functions of graphite, liquid carbon and diamond.

C (graphite). A resume of the literature data on the specific heat of graphite at low temperatures is given in Table 141.

TABLE 140

Adopted Thermodynamic Values for Graphite, Diamond and Liquid Carbon

Вещество A	$H^{\circ}_{298,15}-H^{\circ}_{0}$	$S^{\circ}_{298,15}$	$C^{\circ}_{p298,15}$	D Коэффициенты в уравнении для $C^{\circ a}_{p}$			E Интервал температуры	Tm	ΔHm
	B кал/г-атом	C кал/г-атом·град		a	$b\cdot10^{3}$	$c\cdot10^{-5}$	°K	°K	B кал/г-атом
3 Графит	234	1,29	1,874	2,074	3,79	1,182	298,15—500	—	—
»	—	—	—	4,785	0,774	4,189	500—1500	—	—
»	—	—	—	5,758	0,25	8,403	1500—3000	—	—
»	—	—	—	5,52	0,30	—	3000—5000	5000	35000
2 Жидкий углерод	—	—	—	7,0	—	—	5000—6000	—	—
1 Алмаз	124	0,566	1,41	b ^{b}—			298,15—1200	—	—

A) Substance; B) cal/g-atom; C) cal/g-atom·degree; D) coefficients in the equation for C_p° ^{a}; E) temperature range; a) $C_p^{\circ} = a + bT - cT^{-2}$ (cal/g-atom·degree); b) Table data [3680]. 1) Diamond. 2) liquid carbon; 3) graphite.

As De Sorbo and Tyler showed [1320, 1324], the specific heat of graphite depends on the structure and condition of the specimen. Thus, the specific heat of natural Ceylon graphite [1320] differs from the specific heat of synthetic Acheson graphite [1323] by 9% (at 250°K) and the values $S^{\circ}_{298.15}$ differ by 6.4% (1.29 ± 0.01 and 1.372 ± 0.005 cal/g-atom·degree). This difference cannot be accounted for by experimental error, which does not exceed 1%, or by the slight difference in the ash content (0.06 and 0.2%, respectively). In the opinion of De Sorbo [1320], the differences are due to the different mean dimensions, of the crystal particles of Ceylon and Acheson graphites (400 and 230A)* and also to the fact that the specimen of artificial Acheson graphite contained an admixture of amorphous carbon.** Because data obtained under conditions as near to equilibrium as possible, are required in the thermodynamic calculations, the data obtained by De Sorbo [1320] for natural Ceylon graphite have been adopted in the Handbook: $S^{\circ}_{298.15} = 1.29 \pm 0.01$ cal/g-atom·degree and $H^{\circ}_{298.15} - H^{\circ}_{0} =$

= 234 ± 4 cal/g-atom.*

TABLE 141

Summary of the Data on the Results of the Specific Heat Measurements on Different Graphite Specimens at Low Temperatures

Авторы A	Год B	Образец графита C	D Число измерений	Интервал температуры, °K E	$S^{\circ}_{298,15}$	$H^{\circ}_{298,15}-H^{\circ}_0$
					кал/г-атом·град F	кал/г-атом G
a Нернст [3042]	1911	Ачесоновский g	6	28—87,5	1,36±0,02	252±3
b Джейкобс, Паркс [2198]	1934	Ачесоновский	30	93—294		
c Де-Сорбо, Тайлер [1323]	1953	Ачесоновский*	73	13—300	1,372±0,005	251±2
d Бергенлид и др. [754] .	1954	—	78	1,5—90	—	—
e Кисом, Перлман [2343] .	1955	Искусственный h	68	1—20	—	—
f Де-Сорбо [1321]	1955	Ачесоновский g	61	1,5—20	—	—
Де-Сорбо [1320]	1955	Цейлонский** i	67	17—300	1,29±0,01	234±4
Де-Сорбо, Тайлер [1324]	1957	Ачесоновский, облученный k	72	13—304	1,492±0,009	268
Де-Сорбо, Николс [1322]	1958	Канадский, природный l	144	1,3—20	—	—
» » »	1958	Графит из кокса m	67	1,3—20	—	—
» » »	1958	Графит из ламповой сажи n	96	1,3—20	—	—

*) mean dimensions of the graphite crystals 230 A
**) mean dimensions of graphite crystals over 400 A
A) Authors;
B) year;
C) graphite specimen;
D) number of measurements;
E) temperature range, °K;
F) cal/g-atom•degree;
G) cal/g-atom.
a) Nernst;
b) Jabos, Parkes;
c) de Sorbo, Tyler;
d) Bergenlid et al.;
e) Keesom, Pearlman;
f) de Sorbo;
g) Acheson;
h) artificial.
i) Ceylon;
k) Acheson, irradiated
l) Canadian, natural;
m) graphite from coke;
n) graphite from carbon black.

In 1958, de Sorbo and Nichols [1322] carried out careful specific heat measurements on three graphite specimens over the range from 1.3-20°K. For the same of Canadian natural graphite, the authors of

[1322] obtained even lower values of the specific heat than those found in the work [1320] for Ceylon graphite and also the values found in the works [754, 2343]. Calculation of the entropy at 16°K on the basis of the date [1322] leads to a value of $S^\circ_{16} = 0.0040$ cal/g-atom·degree, while in the work [1320] the larger value $S^\circ_{16} = 0.0062$ cal/g-atom·degree was used in the determination of $S^\circ_{298.15}$. In view of the fact that the absolute entropy values of graphite at these temperatures are negligibly small as compared with the value $S^\circ_{298.15}$, a correction was not applied to the value found in the work [1320]. However, the error in the values of $S^\circ_{298.15}$ and $H^\circ_{298.15} - H^\circ_0$, used on the basis of the data [1320], must be assumed to be ± 0.05 cal/g-atom·degree and ±20 cal/g-atom, respectively.

Enthalpy measurements on graphite at temperatures above 298.15°K have been carried out by several researchers (see [2363]). Kelly [2363] proposed on the basis of these data, a single equation for the specific heat of graphite over a wide range of temperatures (298-2300°K). Extrapolation of the specific heats by means of this equation for higher temperatures leads to excessively large specific heats.

The values of the specific heat, given in the Handbook of Rossini et al [3507] were adopted in the present Handbook for the calculation of the thermodynamic functions of graphite. Up to 1500°K these values coincide with those obtained in the work [4122] as a result of an analysis of experimental data. For the purpose of establishing the equations for the specific heat of graphite, the temperature interval between 298.15 and 4000°K was divided into four parts (298.15-500; 500-1500; 1500-3000 and above 3000°K); the values of the specific heat recommended in the Handbook [3507] at 400, 500, 1000, 1500, 2000, 3000 and 4000°K were used as reference points and also the value $C^\circ_{p298.15} =$

= 1.874 cal/g-atom•degree, found by de Sorbo [1320]. Trinomial equations of the type of Maier-Kelley equations [2745] ($C_p^\circ = a + bT - cT^{-2}$) were derived for the three first temperature ranges on the basis of the above-indicated specific heats and for the fourth interval, a linear equation (see Table 140).*

The data existing in the literature on the melting point of graphite are contradictory. Some experimental studies, carried out in the middle Twenties,** involving the determination of the melting point of carbon in the crater of a Voltaic arc, lead to values of 3760 to 3900°K (3800 ± 100°K [1524, 3570]; 3900°K [1927]; 3760 ± 65°K [525]; 3845°K [3571]). Basset [674] found that the ternary point of graphite is approximately at 4000°K and a pressure of 100 atmospheres. However, Steinle [3844] showed that the melting point of graphite had not been attained in any of these investigations. As Brewer [915] pointed out, the temperature measurement on graphite by means of the optical pyrometer is difficult because of the condensation of carbon vapor whose pressure at temperatures of 4000°K and over attains a considerable magnitude. Taking into account that in accordance with the data of Basset [674] and Steinle [3844], the ternary point of graphite is at a pressure of over 100 atmospheres, Brewer, on the basis of measurements of the pressure of saturated graphite vapor [921], arrived at the conclusion, that the melting point of graphite is over 5000°K.***

Thus, the above-listed data**** are not quite reliable and do not allow a selection of a reliable value for the melting point of graphite. The value recommended in the Handbook of Bichowski and Rossini [813] of 3873°K is certainly much too low. The value 4700°C, adopted by Kubashevskiy and Evans [267] is evidently based on the recommendations of Brewer [915]. In agreement with the recommendations of [267, 915], a melting point of 5000°K*****has been used in the present

Handbook for the calculation of the thermodynamic functions of graphite at high temperatures. The error in this value is several hundred degrees. The value of 5000°K for the ternary point of graphite was used by Udy and Boulger [4031] for the construction of the phase diagram of graphite (see [479a], page 110).*

Experimental data of any kind on the heat of melting of graphite are lacking. The values of 11 and 10 kcal/g-atom for the heat of melting, calculated by Ryschkewitsch [3570, 3571] and Fajans [1522], respectively, on the basis of the difference in the slope of the vapor pressure curves for solid and liquid carbon, are not reliable. An estimate of the entropy and heat of melting of carbon can be obtained on the basis of the entropies of melting of the elements of the IVth (main) group of the Periodic System. Scheil [3616] estimated the entropy of melting of carbon in this manner as 6.7 cal/g-atom•degree. Taking into consideration the more reliable values for the entropy of melting of silicon and germanium, found in recent times, the value $\Delta Sm = 7 \pm 1$ cal/g-atom•degree to which corresponds a heat of melting of graphite of $\Delta Hm_{5000} = 35 \pm 10$ kcal/g-atom•degree** has been adopted in the present Handbook. The specific heat of molten carbon above 5000°K has been estimated to be 7.0 cal/g-atom•degree.

C (Diamond). Kelley [2364] based on specific heat measurements on diamond over the temperature range 70-288°K, carried out by Pitzer [3253a], recommended a value of $S^\circ_{298.15} = 0.585 \pm 0.005$ cal/g-atom•degree. Extrapolation of the specific heat below 70°K leads to a value of $S^\circ_{70} = 0.008$ kcal/g-atom•degree.

Measurements of the entropy changes of diamond $H^\circ_{90} - H^\circ_4$ and $H^\circ_{291} - H^\circ_{90}$ carried out by Berman and Poulter [758b] showed that the results, obtained by Pitzer for low temperatures, are too high. De Sorbo [1318c] carried out an investigation into the specific heat of diamond over the temperature range of 17.4-300°K and obtained the value $S^\circ_{298.15} = 0.568 \pm 0.005$ cal/g-atom·degree. Desnoyers and Morrison [1318b] and Burk and Friedberg [1024a] recently carried out careful measurements of the specific heat of diamond within the temperature range 12.8-277° and 11-200°K, respectively, and found a more accurate value for the entropy of diamond at 100°K ($S^\circ_{100} = 0.017$ instead of $S^\circ_{100} = 0.019$ cal/g-atom·degree according to the data of de Sorbo). The Handbook gives the values $S^\circ_{298.15} = 0.566 \pm 0.005$ cal/g-atom·degree and $H^\circ_{298.15} - H^\circ_0 = 124 \pm 1$ cal/g-atom, obtained on the basis of the data [758b, 1318b, 1318c, 1024a].

The most careful measurements of the enthalpy of diamond at high temperatures (272-1180°K) were carried out by Magnus and Hodler [2734a]. On the basis of these data, the U. S. Bureau of Standards calculated of Table of the thermodynamic functions of diamond to 1200°K, which has been adopted in the Handbook, allowing for the changes in the values $S^\circ_{298.15}$ and $H^\circ_{298.15} - H^\circ_0$.

The calculated thermodynamic functions of graphite and liquid carbon are given in Table 129 (II). The thermodynamic functions of diamond to 1200°K are given in Table 142.

Table 143 gives the results of the estimate concerning the errors in the values of Φ^*_T for diamond and graphite. The abovementioned dependence of the specific heat of graphite on its structure was taken into account in the estimate of the accuracy of the thermodynamic functions of graphite. The marked increase in the magnitude of the error above 4000°K is mainly due to the absence of reliable data on the melting point and heat of melting of graphite.

TABLE 142

Thermodynamic Functions of Diamond over the Temperature Range 293.15-1200°K

T	C_p°	Φ_T°	Δ	S_T°	Δ	$H_T^\circ - H_0^\circ$	Δ
°K	кал/г-атом·град A					кал/г-атом B	
293,15	1,41	0,139		0,542		118	
298,15	1,46	0,147		0,566		125	
400	2,38	0,320		1,123		321	
500	3,14	0,539	219	1,733	610	597	276
600	3,79	0,798	259	2,373	640	945	348
700	4,29	1,067	269	3,003	630	1355	410
800	4,66	1,347	280	3,603	600	1805	450
900	4,90	1,626	279	4,163	560	2283	478
1000	5,03	1,906	280	4,683	520	2777	494
1100	5,10	2,186	280	5,173	490	3286	509
1200	5,16	2,445	259	5,613	440	3801	515

A) cal/g-atom•degree; B) cal/g-atom.

TABLE 143

Errors in the Values of Φ_T^* of Graphite and Diamond (in cal/g-atom•degree)

T, °K	298	1000	1500	2000	3000	4000	5000
Графит a	±0,05	±0,07	±0,10	±0,15	±0,2	±0,3	±1,0
Алмаз b	±0,01	±0,05	—	—	—	—	—

a) graphite; b) diamond.

§60. THERMOCHEMICAL VALUES

The standard state of carbon is C (graphite).

C (Diamond). Prosen, Jessup and Rossini [3334], on the basis of the measurements of Jessup [2243] calculated the heat of combustion of diamond to carbon dioxide $\Delta H_{298.16}$ = —94505,1 ± 22.9 cal/g-atom. Recalculation of this value, allowing for the atomic weight of carbon used, leads to the value $\Delta H_{298.16}$ = —94507 ± 23 cal/g-atom. Using this value and the heat of combustion of graphite (see section on the heat of formation of CO_2), the heat of formation of diamond from graphite was calculated:

$$\Delta H^{\circ}f_{298.15}(\mathrm{C,\ diamond}) = 0{,}453 \pm 0{,}025 \text{ kcal/g-atom,}$$

which has been adopted in the present Handbook.

C (gas). The heat of sublimation of carbon (graphite) can be determined on the basis of the measurements of the vapor pressure of carbon or the energy of dissociation of carbon monoxide because these values are connected by the simple thermochemical equation

$$\Delta Hs_0(\mathrm{C,\ graphite}) = D_0(\mathrm{CO}) - 86205 \text{ kcal/g-atom.} \quad (\mathrm{XVI.1})$$

The results of numerous studies carried out by different methods, have long led to contradictory values for the heat of sublimation of carbon. These works were examined in detail and evaluated in the reviews of Gaydon [141, 1668], Springall [3829], Long [2642], Glockler [1763], Goldfinger and Waelbroeck [1793], Cottrel [255], Kern [2372], Brewer and Searcy [932], Sehon and Szwarc [3677], et al. Hence, only the most important studies and works of recent years which are not included in the above-listed reviews, will be examined in the following.

The dissociation energy of CO can be obtained on the basis of a study of predissociation in the spectrum of CO and also an investigation of the dissociation of CO under the influence of electronic impact. As pointed out previously (pages 879-881), a discontinuity in the rotational levels appears in the $B^1\Sigma^+$- and $b^3\Sigma$- states of the molecule CO at v = 0 and v = 1 in consequence of the predissociation. Douglas and Moller [1378], as a result of an investigation of the band system $B^1\Sigma^+ - A^1\Pi$ in the spectra of isotopic molecules $C^{12}O$ and $C^{13}O$, determined the exact position of the dissociation limit, with which the repulsive state causing these predissociations, is connected. They found that the dissociation limit is situated at 89,595 ± 30 cm^{-1} above the lower level (v = 0, J = 0) of the electronic ground state of CO.* Because extrapolation of the vibrational levels of the ground state leads to the conclusion that they should converge in the region 90,000 cm^{-1} or higher, it is natural to assume that the dissociation energy of the molecule CO is 89,595 ± 30 cm^{-1}. However, it has been assumed in several works [see [255, 151]) that the dissociation limit of CO in the region 89,600 cm^{-1} is correlated with the excited state of oxygen or carbon atoms [for example, $O(^3P) + C(^1D)$ or $O(^1D) + C(^3P)$] and, consequently, that the dissociation energy is much lower: 79,401 cm^{-1} (9.85 ev) or 73,727 cm^{-1} (9.14 ev), respectively. These hypotheses were supported by the data of Gero [1689] and Schmid and Gero [3638] on the predissociation at certain vibrational levels of the state $A^1\Pi$ in the region 9.1-9.7 ev. However, it has been shown unequivocally in the works of Douglas and Moller [1378] and Tanaka et al [3935] that there is no predissociation in the state $A^1\Pi$.

Thus, the analysis of the spectra of CO shows that experimental data of any kind which would allow the assumption of the existence of a dissociation limit of the molecule CO with an energy of less than 89,595 ± 30 cm^{-1} are lacking. Moreover, the results of studies of the band system $A^1\Pi - X^1\Sigma$ (see page 880) leads to the conclusion that the levels of the vibrational energies of the state $A^1\Pi$ converge in the region around 90,000 cm^{-1}. In this region, the levels of the states $a'^3\Sigma$ and $d^3\Pi$ and, possibly, also the state $e^3\Sigma^-$, should evidently also converge in this region. Because the ground states of the oxygen and carbon atoms should correlate with several electronic states of the molecule CO, including the states $^1\Pi$, $^3\Sigma^+$, $^3\Sigma^-$ and $^3\Pi$, it must be assumed that the states $A^1\Pi$, $a'^3\Sigma$ and $d^3\Pi$ have a common dissociation limit identical with that which is connected with the repulsive state which causes the predissociation in the states $B^1\Sigma^+$- and $b^3\Sigma$- and which is the dissociation limit of the state $X^1\Sigma^+$. At the same time, the hypothesis that the dissociation limit of these states with an energy of about 89,600 cm^{-1}, may correspond to one of the excited states of the atoms O or C, requires a violation of the rule nonintersection of the potential curves, because in this case the molecule CO should have several $^1\Pi$-, $^3\Sigma$- and $^3\Pi$- states with a dissociation limit in the region 73,000 or 79,000 cm^{-1}. A detailed study of the state $A^1\Pi$ [3935] shows that data of any kind which would permit the assumption of an intersection of the potential curves of this state with the curve of the other $^1\Pi$ state or perturbation of the vibrational levels of the $A^1\Pi$- state are lacking. Thus, extrapolation of the vibrational levels of several excited states also confirms the value $D_0(CO) = 89{,}595$ cm^{-1}.

A serious argument in favor of a dissociation energy of CO of less than 89,595 cm^{-1} (11.11 ev) were at one time the data obtained in investigations carried out by means of the method of electronic impact [1928, 1929, 1557, 2702, 903]. Values of about 9.85 ev were found in these works for the dissociation energy of CO, i.e., values which agree with the hypothesis that $C(^1D) + O(^3P)$ corresponds to a dissociation limit of 89,595 cm^{-1}. However, Hagstrum [1930] showed that if a more accurate value of the electron affinity of the oxygen atom (see page 331) is used, the data obtained by the method of electronic impact lead to a value of $D_0(CO) \approx 11.11$ ev. Subsequent investigations of the dissociation of CO by the method electronic impact [885, 2518, 2956] confirmed this value of $D_0(CO)$.

The vapor pressure of graphite was measured by the effusion method by Brewer, Gilles and Jenkins [921], Brewer and Mastick [924], Simpson, Thorn and Winslow [3985, 3742] and particularly carefully by Doehaerd, Goldfinger and Waelbroek [1356, 1357]. It was found that the vapor pressure in the effusion vessel depends on the ratio of the cross section of the aperture to the area of the internal surface of the vessel. At ratios of 1: 250 and 1: 600, as was the case in the work of Brewer et al.[921], the measured vapor pressures proved to be in good agreement with the heat of sublimation of carbon of about 170 kcal/g-atom, which corresponds to $D_0(CO) \approx 11.11$ ev. Doehaerd, Goldfinger and Waelbroek [1356, 1357] carried out an investigation over a wider range of ratios of aperture cross section to internal surface (from 1: 100 to 1: 23,400) and found that when the dimensions of the orifice were reduced, the vapor pressure in the effusion vessel increased. They explained the dependence of the vapor pressure on the aperture dimensions by the fact that the evaporation coefficient of carbon is low (of the order of 10^{-3}) and recommended for the heat of sublimation of monatomic carbon the value $\Delta H_0 = 141.7$ kcal/g-atom. ($D_0(CO) \approx 9.8$ ev), obtained with the smallest orifices. However, several authors [932, 916, 923] pointed out that this relationship mentioned in the works [1356, 1357] may be explained by the complex composition of carbon vapor, in particular, by the proposed (see [1113]) existence in the vapor of negative C^- ions and molecules C_5 with a low evaporation coefficient.* These evaporation products may be of great importance at high temperatures and small relative orifices of the effusion cell.

It should also be pointed out that the very low value of the evaporation coefficient of carbon, used by Doehaerd, Goldfinger and Waelbroek, gives rise to serious doubts [1112, 916, 923]. Hoch, Blackburn, Dingledy and Johnston [2088] found during their investigations of the surface evaporation of graphite and tungsten and tantalum carbides that the evaporation coefficient of carbon is within the range of 0.1-1.0 and Thorn and Winslow [3985], based on the results of a comparison of the rate of effusion and evaporation from the surface of carbon, found the value 0.15.

A very important problem, arising during investigation of the vapor pressure of carbon, is the composition of the vapors.

In the works of Honig [2117] and particularly, of Chupka, Inghram and coworkers [1109, 1110, 1111, 1112, 1113 and 1405] it was shown that carbon vapor contains the molecules C, C_2, C_3, C_4 and C_5.* The complex composition of carbon vapor makes the processing of the data obtained by the effusion method and the surface evaporation method very difficult. Of special value under these circumstances are the mass-spectrometric methods which enables the relative concentrations and heats of sublimation of each component contained in the vapor to be measured. By means of this method, Chupki and Ingram [1109, 1110] and Honig [2117] investigated the composition of the vapor and determined the heat of sublimation during the surface evaporation of graphite. By means of the dependence of the intensity of the current of C^+ ions on temperature, the activation energies of the evaporation of carbon were found, by means of which the limit of the possible values of the heats of sublimation of carbon can be established: $\Delta H_0 \leq 180$ kcal/g-atom. Of particularly great value are the mass-spectrometric studies of the vapor flowing out of the effusion cell, carried out by Chupki and Inghram [1111, 1112, 1113]. As a result of these researches, the heats of sublimation of monatomic carbon, of C_2 and C_3, equal to 170.4 kcal/g-atom, 197 ± 4 and 200 ± 10 kcal/mole, were found.

Thus, the investigations on the predissociation in the $B^1\Sigma^+$- and $b^3\Sigma^+$- states, the later data, obtained by the method of electronic impact, the measurements of the vapor pressure of carbon and also the results of the measurement of some other magnitudes, connected with the value $D_0(CO)$, for example, $D_0(CO^+)$ and $D_0(CN)$ (see [141, 1668]), do not leave any doubt that the dissociation products, corresponding to a dissociation limit at 89,595 ± 30 cm^{-1}, are $O(^3P) + C(^3P)$ and, consequently, that the dissociation energy of CO corresponds to the largest of the several proposed values.* The studies of shock waves in carbon monoxide [3997, 2447a] and detonations in mixtures of acetylene and oxygen [2422] lead to the same conclusion. Because it is known, to which components of the ^3P states of oxygen and carbon atoms ($^3P_0$, $^3P_1$ or $^3P_2$) corresponds the dissociation limit with an energy of 89,595 cm^{-1}, the dissociation energy of CO may have a value between 89,300 cm^{-1} (255.332 kcal/mole) and 89,620 cm^{-1} (256.247 kcal/mole). Although it is difficult to find convincing arguments in favor of the fact that the dissociation limit of CO may not be connected with the basic components of the ^3P terms $O(^3P_2) + C(^3P_0)$, the mean value

$$D_0(CO) = 89\,460 \pm 160 \text{ cm}^{-1} = 255{,}79 \pm 0{,}43 \text{ kcal/mole},$$

is adopted in the Handbook in correspondence with the recommendations of Brewer and Searcy [932] to which, according to (XVI.1), corresponds a heat of sublimation of graphite of

$$\Delta Hs_0(C, \text{graphite}) = \Delta H^\circ f_0(C, \text{gas}) = 169{,}585 \pm 0{,}430 \text{ kcal/g-atom}.$$

C^+ (gas). The ionization potential of the carbon atom, according to Moore [2941], is

$$I(C) = 90878{,}3 \text{ cm}^{-1} = 259{,}845 \text{ kcal/g-atom}.$$

The error in the value does not exceed 1 cal/g-atom. To the adopted value of the ionization potential corresponds

$$\Delta H^\circ f_0(C^+, \text{gas}) = 429{,}43 \pm 0{,}43 \text{ kcal/g-atom}.$$

C_2 (gas). An estimate of the dissociation energy of the molecule C_2 on the basis of an extrapolation of its vibrational levels leads to very contradictory and inaccurate values. To the linear exteapolation of the levels of the $X^1\Sigma^+$- state corresponds a velue of 7 ev or approximately 160 kcal/mole. Phillips [3234], as a result of graphic extrapolation of the levels of the $d^3\Pi_g$- state, obtained for the values of $D_0(C_2)$: 5.3 and 4.04 ev, depending on whether C_2 in the state $^3\Pi$ dissociates into $C(^3P) + C(^3P)$ or $C(^3P) + C(^1D)$ atoms.

Herzberg [151, 2020], on the basis of the anomalous intensity of the band group with v' = 6 of the system $^3\Pi_g - {}^3\Pi_u$, assumed that the dissociation energy of C_2 is close to the energy of the level v' = 6 of the state $^3\Pi_g$ (about 3.6 ev), but this value contradicts other experimental data.

Brewer, Gilles and Jenkins [921] investigated the intensity of the Swan bands in the spectrum of C_2 as a function of the temperature of the King furnace and found the value $\Delta H^\circ f_0$ (C_2, gas) = 233.1 ± 7.0 kcal/mole, to which corresponds $D_0(C_2) \approx 107$ kcal/mole (4.7 ev). This value is evidently erroneous, as one of the authors of this work pointed out (see [1110, 255].

Chupka, Inghram et al [1109, 1110, 1111, 1112, 1113], as result of a mass-spectrometric investigation of the composition of carbon vapor on the ionic current of C_2^+ as a function of temperature, found for the heat of formation of C_2 the value 197 ± 15 kcal/mole. Drowart, Burns, de Maria and Inghram in the work [1405] used an effusion chamber with a much smaller orifice than in the preceding works (10^{-5} instead of 10^{-3}). In this work on the dependence of the ion current of C_2^+ on temperature, the value $\Delta H^\circ f_0$ (C_2, gas) = 194.1 ± 1.7 kcal/mole* was found. Furthermore, using the measured ionic current of C^+ as a standard, the authors of the work [1405] calculated the partial pressure of C_2 in the effusion chamber and, by means of Eqs. (IV.15), found the value $\Delta H^\circ f_0$ (C_2, gas) = 197.4 ± 1.7 kcal/mole.

The Handbook adopted the value

$$\Delta H^\circ f_0 (C_2,\ \text{gas}) = 196 \pm 3 \ \text{kcal/mole},$$

which is the mean of two values, calculated on the basis of the results obtained by Drowart et al. [1405].

To the adopted value corresponds

$$D_0(C_2) = 143{,}17 \pm 3 \text{ kcal/mole.}$$

C_3 (gas). Chupka and Inghram [1109, 1110, 1111, 1112, 1113], on the basis of mass-spectrometric studies on carbon vapor, carried out by them, found the value $\Delta H°f_0$ (C_3, gas) = 200 ± 10 kcal/mole. Thorn and Winslow [3985] investigated the rate of evaporation of carbon from a free surface and the flow of carbon vapor through the orifice of the effusion chamber and found that at 2400°K the vapor pressure of C_3 is $1.05 \cdot 10^{-7}$ atm and the heat of formation $\Delta H°f_{2400}$ = 184.4 kcal/mole (to which corresponds a $\Delta H°f_0$ = 188 kcal/mole.). A recalculation of the data of Thorn and Winslow, using the values of the thermodynamic functions of C_3(gas) and C (graphite) adopted in the present Handbook, leads to the value $\Delta H°f_0$ = 194 kcal/mole.

The mass-spectrometric investigation of carbon vapor in the work of Dworart, Burns, de Maria and Inghram [1405] was carried out with small relative orifices of the effusion chamber (less than 10^{-5} instead of 10^{-3} [1113]). Under these conditions, the authors were able to measure the current of C_3^+ with an accuracy considerably greater than in earlier measurements. On the basis of the relation of the ion current of C_3^+ on temperature, the authors [1405] found $\Delta H°f_0$ (C_3, gas) = 186.7 ± 1.5 kcal/mole. In the calculations, the authors of [1405] used the values of $H_T^\circ - H_0^\circ$ for C_3, calculated by Pitzer (see page 930). A recalculation using the values of $H_T^\circ - H_0^\circ$, given and Clementi [3256] in the present Handbook, gives $\Delta H°f_0$ = 186.2 kcal/mole.

A calculation by means of Eq. (IV.15), based on the absolute values of the partial pressure of C_3 over graphite, carried out by the authors of [1405], leads to a value of $\Delta H°f_0$ = 188.1 ± 2.3 kcal/mole. A similar value (190 kcal/mole) was obtained on the basis of these data by the authors of the Handbook, using the thermodynamic functions of graphite and C_3, given in Tables 129 (II) and 133 (II). On the basis of these data, the value

$$\Delta H^\circ f_0(C_3,\ \text{gas}) = 188 \pm 5\ \text{kcal/mole}^{-1}.^*$$

has been adopted in the present Handbook. This value is the average of the values obtained by two methods: on the basis of the dependence of the ionic current of C_3^+ on temperature and by means of the Eq. (IV.15) on the basis of the measurements of Dworart et al [1405]. To this value corresponds

$$D_0(C_3) = 320{,}755 \pm 5{,}0\ \text{kcal/mole}.$$

CO (gas). The heat of combustion of carbon monoxide has been measured many times. Review of these investigations are given in the works [813, 98, 3492, 3514, 3499]. Rossini [3492, 3496, 3499, 4122] carried out a very accurare measurement of the heat of combustion of carbon monoxide and obtained, after applying the necessary corrections, $\Delta H_{298.16} = -67{,}636.1 \pm 28.7$ cal/mole. The results of the determinations, carried out by Roth and Banse [3517], Fenning and Cotton [1550] and Awbery and Griffiths [591] coincide, within the limits of the measurement accuracy, with the value, recommended by Rossini. Recalculation of the value for the heat of combustion obtained by Rossini, allowing for the variability of the atomic weight of carbon (12.011 instead of 12.010) leads to the value $\Delta H_{298.15} = -67.638 \pm 29$ kcal/mole. To this value corresponds the heat of formation of carbon monoxide, given in the Handbook:

$$\Delta H^\circ f_{298{,}15}(CO,\ \text{gas}) = -26{,}416 \pm 0{,}031\ \text{kcal/mole}.$$

The value $D_0(CO) = 255.790 \pm 0.43$ kcal/mole adopted in the Handbook is discussed in the section on the determination of the heat of sublimation of carbon (see page 945).

CO^+ (gas). The ionization potential of the carbon monoxide molecule was determined by Takamine, Tanaka and Iwata [3918] by means of the edge of the Rydberg series in the absorption spectrum of carbon monoxide. According to the data of this study, the edge of the Rydberg series for the transition between the levels v = 0 of the state $X^2\Sigma$ of the molecule CO^+ and the state $X^1\Sigma$ of the molecule CO corresponds to 888.73 A or 113,029 cm^{-1}. Watanabe [4175] found the limit of photoionization of the molecule CO at 885 A or 112,934 cm^{-1}, which is in good agreement with the results of measurement of the limit of the Rydberg series.

The Handbook adopted the value of the ionization potential of carbon monoxide of 113,029 cm^{-1} [3918] or

$$I(CO) = 323{,}179 \pm 0{,}010 \text{ kcal/mole.}$$

To this value of I(CO) corresponds the energy of dissociation of CO^+ into C^+ and O:

$$D_0(CO^+) = 192{,}456 \pm 0{,}430 \text{ kcal/mole}$$

and the heat of formation

$$\Delta H^\circ f_0(CO^+, \text{газ}) = 295{,}961 \pm 0{,}033 \text{ kcal/mole.}$$

<u>Co_2(gas)</u>. Summaries of the results of the numerous measurements of the heat of formation of carbon dioxide are given in the works [813, 98, 3504, 3334]. Deway and Harper [1326], Jessup [2243] and Prosen and Rossini [3339] measured the heats of combustion of different graphite samples. These works were carried out extremely carefully and served as the basis for the selection by Prosen, Jessup and Rossini [3334] of the best value of the heat of formation of carbon dioxide $\Delta H^\circ f_{298.15} = 94{,}051 \pm 10.8$ kcal/mole. The application of a corrections to allow for the atomic weight of carbon, used in the Handbook, leads to the value

$$\Delta H^\circ f_{298{,}15}(CO_2, \text{газ}) = -94{,}054 \pm 0{,}011 \text{ kcal/mole,}$$

to which corresponds

$$D_0(CO_2) = 381{,}543 \pm 0{,}43 \text{ kcal/mole.}$$

C_3O_2 (gas). Reliable data on the heat of formation of C_3O_2 are absent in the literature. Klemenc, Wechsberg, and Wagner [2436, 2437, 2435] studied the equilibrium

$$C_3O_2\,(\text{gas}) = CO_2\,(\text{gas}) + C_2\,(\text{gas})$$

and found that at 200°C the equilibrium constant is about 10^{-7} mm Hg. To this value corresponds a heat of reaction of about 40 kcal/mole and $\Delta H°f(C_3O_2) \sim 55$ kcal/mole. However, the value of the equilibrium constant found by Klemenc, Wechsberg and Wagner is very unreliable because side reacgions took place in the system and because it is not certain that the concentration of the decomposition products attained the equilibrium value. These authors [2436, 2437, 2435] did not use their own value of the equilibrium constant for the calculation of the heat of formation of C_3O_2 but obtained it on the basis of the estimated heat of combustion of C_3O_2 (300 kcal/mole) to which corresponds a heat of formation of 18 kcal/mole.

A more reliable estimate of the heat of formation of C_3O_2 can be made by using the dissociation energies of ethylene, allene [3507] and Ketene [3508] on the assumption that

$$D(H_2C = C = CH_2) - D(OC = C = CO) = 2\,[D(H_2C = CH_2) - D(H_2C = CO)].$$

The value

$$\Delta H°f_{298{,}15}(C_3O_2,\ \text{gas}) = -8 \pm 5 \text{ kcal/mole}$$

thus found is used in the Handbook. Another possible method of estimation, based on the dissociation energies of C_3 and CO_2, is less justifiable because the valency states of carbon in the molecules C_3 and C_3O_2 are not identical.

To the adopted value of the heat of formation corresponds

$$D_0(C_3O_2) = 635{,}234 \pm 5 \text{ kcal/mole.}$$

HCO (gas). The energy required for removing the first hydrogen atom from the formaldehyde molecule can be estimated on the basis of data on the photolysis of formaldehyde. This problem is discussed in detail in the work of Steacie [3841].

Two values are proposed in the literature for the activation energy of the breaking of the bond H-CHO, equal to approximately 90 and 78 kcal/mole, which corresponds to H-CO bond-rupture activation energies of about 15 and 27 cal/mole. These values can be equated with the dissociation energies of the respective bonds, if the activation energy of the reverse process of recombination of the radicals is zero. At the present time there are several indications in favor of this hypothesis [3841, 3677].

Calvert, Steacie et al [1052, 1051, 1050] proposed a mechanism for the photolysis of formaldehyde and expressed the opinion that the value $D(H-CHO) = 91$ kcal/mole agrees best with this mechanism. However, this mechanism has caused serious doubts among other authors [2431, 1365]. The arguments in favor a smaller value for $D(H-CHO)$ are more convincing. Thus, Gorin [1826] investigated the process of photodissociation of formaldehyde in presence of iodine vapor and showed that the dissociation energy of the bond H-CHO should be less than 78 kcal/mole. Klein and Schoen [2431] investigated the photolysis of a mixture of H_2CO and D_2CO under the influence of monochromatic light and found that dissociation begins at a wavelength of about 3650 A which corresponds to $D(H-CHO) < 78$ kcal/mole. Dorman and Buchanan [1364] based on the existing thermodynamic data and a theoretical investigation of the surface potential energy of the system CO + H arrived at the conclusion that $D(H-CO) = 23$ kcal/mole and $D(H-CHO) \approx$ ≈ 82 kcal/mole. Herzberg and Ramsey [2042] determined, on the basis of the predissociation in the band system $^2A_1 - {}^2B_1$, that the upper limit of the possible values of $D(H-CO) = 37.7$ kcal/mole.

A convincing argument in favor of a smaller value for $D(H-CHO)$

is the investigation by Reed [3411] of formaldehyde under the influence of electronic impact, in which the value D(H – CHO) = 3.23 ± 0.1 ev = 74.5 ± 2.3 kcal/mole was found. Brand and Reed [898] investigated the electronic spectrum of formaldehyde and found that its peculiarities can be explained if one adopts the value D(H – CHO), found by Reed [3411]. A further predissociation in the region of 3500 A detected in the electronic spectrum of H_2CO is also a confirmation of this value for D(H – CHO). Klein and Schoen [2432] examined the results of the determination of D(H – CO) carried out by different methods and showed that the value 27 kcal/mole is correct, thus confirming the smaller value of D(H – CHO).

The value D(H – CHO) = 74.5 kcal/mole, to which corresponds*

$$\Delta H^\circ f_{298,15}(\mathrm{HCO,\ gas}) = -5{,}3 \pm 3 \text{ kcal/mole.}$$

has been adopted in the Handbook. This value is based primarily on the measurement results of Reed [3411] and Brand and Reed [898]. To the adopted value of the heat of formation corresponds

$$D_0(\mathrm{HCO}) = 285{,}596 \pm 3 \text{ kcal/mole.}$$

H_2CO (gas). The heat of combustion of gaseous formaldyhyde has been measured by Wartenberg, Muchlinski and Riedler [4167] and by Wartenberg and Lerner-Steinberg [4165]. The greatest difficulty in this work was the preparation of the monomer of formaldehyde. Heats of combustion of -158.8 kcal/mole [4167] and -134.1 kcal/mole [4165] (at constant volume) were found in these investigations; the causes of this difference are not yet clear. Wartenberg and Lerner-Steinberg [4165] applied certain corrections more accurately and the value found by them is the most reliable. To this value corresponds $\Delta H^\circ f_{293.15}$ (H_2CO, gas) = -27.7 ± 1 kcal/mole.

Newton and Dodge [3065] investigated the equilibrium of the formation of formaldehyde from hydrogen and carbon monoxide. To the equilibrium constant found by them corresponds $\Delta H°f_{293.15}(H_2CO, \text{gas}) = -27.2$ kcal/mole, which confirms the results of the measurements [4165].

The heat of formation of H_2CO

$$\Delta H°f_{298.15}(H_2CO, \text{gas}) = -27{,}7 \pm 1 \text{ kcal/mole},$$

based on the measurements of Wartenberg and Lerner-Steinberg [4165] has been adopted in the Handbook. To this value corresponds

$$D_0(H_2CO) = 358{,}66 \pm 1{,}1 \text{ kcal/mole}.$$

FCO (gas). The heat of formation of FCO adopted in the Handbook

$$\Delta H°f_{298.15}(FCO, \text{gas}) = -45 \pm 20 \text{ kcal/mole}$$

adopted in the Handbook was estimated on the basis of the bond energies in the molecules F_2CO, Cl_2CO, and ClCO. To this value corresponds

$$D_0(FCO) = 292{,}21 \pm 20 \text{ kcal/mole}.$$

F_2CO (gas). Wartenberg [4156] measured the heat of hydrolysis of F_2CO in caustic potash solution and found for the heat of formation of F_2CO the value -142 kcal/mole. Later on, Wartenberg and Riteris [4168] measured the heat of hydrolysis of F_2CO in water more accurately and found the value -26.73 ± 0.2 kcal/mole. To the heat of hydrolysis found in the work [4168] corresponds the heat of formation $\Delta H°f_{298.15}(F_2CO) = -150.5$ kcal/mole.

Ruff and Shih-Chang Li [3565, 3708] investigated the equilibrium $2F_2CO \text{ (gas)} \rightleftarrows CO_2 \text{ (gas)} + CF_4 \text{ (gas)}$ in a furnace at a temperature of 650-1000°C in presence of platinum catalyst and on the basis of the equilibrium constant as a function of temperature they found the heat of this reaction $\Delta H = -26$ kcal/mole, to which corresponds $\Delta H°f_{298.15}(F_2CO) = -164$ kcal/mole. The calculation of the heat effect of this reaction on the basis of Eq.(IV.15), using the thermodynamic functions of the reaction components adopted in the present Handbook, leads to the value $\Delta H_0 = -12$ kcal/mole ($\Delta Hf_0 (F_2CO) = -149$ kcal/mole) which differs markedly from the value obtained by means of the logarithms of the equilibrium constants as a function of temperature. This attests to the unreliability of the data obtained in the works [3565, 3708]. The data of these works are also insufficiently reliable because of the small number of experiments, the marked divergence of individual points (these were not used in the calculations), the narrow temperature interval and the side reactions which took place [23].

Medvedev, Baybuz and Bergman [23] measured the heat of formation of F_2CO by the method of explosion in a spherical bomb. The maximum pressures during the explosion of mixtures containing CF_4, Co and O_2* were measured in the work [23]. The results of six tests (maximum explosion temperature 2364 to 2804°K) enabled the value $\Delta H^\circ f_{298.15}$ (F_2CO) = -148.5 ± 2 kcal/mole to be calculated.

The value

$$\Delta H^\circ f_{298,15}(F_2CO,\ \text{gas}) = -149,5 \pm 2\ \text{kcal/mole},$$

to which corresponds

$$D_0(F_2CO) = 414,348 \pm 2,3\ \text{kcal/mole}.$$

has been adopted in the Handbook on the basis of the results of the investigations [23, 4168].

HFCO (gas). The heat of formation of HFCO was estimated on the basis of the mean bond energies in the molecules F_2CO and H_2CO. The value thus obtained

$$\Delta H^\circ f_{298,15}(HFCO,\ \text{gas}) = -90 \pm 5\ \text{kcal/mole}$$

corresponds to the dissociation energy

$$D_0(HFCO) = 387,865 \pm 5\ \text{kcal/mole}.$$

ClCO (gas). Burns and Dainton [1029] investigated the rate of photosynthesis of phosgene and found D(Cl – CO) = 6.3 kcal/mole (see also [3915]). To this value corresponds the heat of formation adopted in the Handbook

$$\Delta H^\circ f_{298,15}(ClCO,\ \text{gas}) = -3,7 \pm 2\ \text{kcal/mole}$$

and the dissociation energy

$$D_0(\mathrm{ClCO}) = 261{,}101 \pm 2 \text{ kcal/mole.}$$

Cl_2CO (gas). Bichowsky and Rossini [813] recalculated the data of Thomsen [3981] on the combustion of phosgene and found that this heat of formation is -52.7 kcal/mole. Bychowsky and Rossini [813] also recalculated the measurement results of Thomsen [3981] and Berthelot [780] of heat of hydrolysis of Cl_2CO in alkaline solution and found ΔH_{291} = -54.4 and -60.6 kcal/mole, respectively.

The equilibrium constants of the reaction

$$\mathrm{CO}(\text{gas}) + \mathrm{Cl_2}(\text{gas}) \rightleftarrows \mathrm{COCl_2}(\text{gas})$$

have been measured several times. A calculation of the heat of this reaction on the basis of the data of Bodenstein and Duant [848], Atkinson, Heycock and Pope [587], Bodenstein and Plaut [853] and Horak [2121] (the values of the equilibrium constants found by these authors are collected in the work of Thompson [3970]), was carried out during the preparation of the Handbook and led to the value $\Delta H_0 = -24.4 \pm 0.4$ kcal/mole, to which corresponds a heat of formation of phosgene of $\Delta H°f_{293.15} = -51.8$ kcal/mole.

More reliable are the data obtained in the equilibrium investigation, hence the value

$$\Delta H°f_{293.15}(\mathrm{Cl_2CO},\ \text{gas}) = -52 \pm 2 \text{ kcal/mole,}$$

has been adopted in the Handbook for the heat of formation of phosgene, to which corresponds

$$D_0(\mathrm{Cl_2CO}) = 337{,}281 \pm 2 \text{ kcal/mole.}$$

FClCO (gas). The heat of formation of FClCO adopted in the Handbook

$$\Delta H°f_{298.15}(\mathrm{FClCO},\ \text{gas}) = -101 \pm 5 \text{ kcal/mole}$$

was estimated, using the mean bond energies in the molecules F_2CO, and Cl_2CO. To this value corresponds

$D_0(FClCO) = 376{,}043 \pm 5$ kcal/mole.

TABLE 144

Adopted Values (in cal/mole) of the Thermodynamic Values of Carbon and its Compounds with Oxygen

Вещество A	Состояние B	D_0, I или ΔHs_0 C	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{293.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
C	D Графит	169 585[а] a	0	0	0	225	234
C	E Алмаз	169 023[а]	562	455	453	118	125
C	F Газ	—	169 585	170 897	170 913	1537	1562
C^+	»	259 845[б] b	429 430	432 226	432 267	1565	1590
C_2	»	143 170	196 000	198 027	198 061	2477	2529
C_3	»	320 755	188 000	189 643	189 664	2318	2366
CO	»	255 790	— 27 218	— 26 425	— 26416	2038	2073
CO^+	»	323 179[в] c	295 961	298 210	298 243	2038	2072
CO_2	»	381 543	— 93 984	— 94 054	— 94 054	2195	2239
C_3O_2	»	635 234	— 8 505	— 8 016	— 8 000	3204	3282
HCO	»	285 596	— 5 392	— 5 296	— 5 300	2333	2373
H_2CO	»	358 660	— 26 824	— 27 700	— 27 720	2353	2395
FCO	»	292 210	— 45 138	— 45 000	— 45 000	2420	2465
F_2CO	»	414 348	— 148 776	— 149 492	— 149 500	2602	2658
HFCO	»	387 865	— 89 161	— 89 987	— 90 000	2448	2497
ClCO	»	261 101	— 3 979	— 3 705	— 3 700	2596	2647
Cl_2CO	»	337 281	— 51 609	— 52 000	— 52 000	3007	3075
FClCO	»	376 043	— 100 421	— 100 996	— 101 000	2783	2845

a) The heat of sublimation is given
b) the ionization potential of monatomic carbon is given
c) the ionization potential of carbon monoxide is given. This value corresponds to a dissociation energy

$CO^+ = C^+ + O$, $D_0 = 192{,}456 \pm 430$ cal/mole.

A) substance; B) state; C) or; D) graphite; E) diamond; F) gas.

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[Footnotes]

866* Ballik and Ramsey [630] pointed out that this value may contain an error equal to 10-20 cm^{-1} because of possible experimental errors during the determination of the molecular constants and of the fact that the magnitude of the multiplet splitting of the state $^3\Sigma_g^-$ is unknown.

866** It is specially emphasized in the work [630] that, although the state $^1\Sigma_g^+$ is the electronic ground state of the molecule C_2, it need not be the lowest state of C_2 in matrices, which agrees with the results of the experiments of Robinson and McCarthy who had shown that the lowest state of C_2 in the solid phase is the state $^3\Pi_u$.

870 According to Mulliken [2982], the molecule C_2 in the states $B^1\Delta g$, $C^1\Sigma_g^+$ and $c^3\Sigma_u^+$ dissociates into unexcited carbon atoms in the state ^3P.

878 Mulliken arrived at conclusion, on the basis of theoretical calculations of the lower electronic states of CO, that the d state of the molecule CO should be a state of the type $^3\Delta$ [3002]. In the work [3002] Mulliken also pointed out that because of the inaccuracy of numeration of the band system $d^3\Delta - X^1\Sigma^+$, the correct values of ω_e and B_e for the state $d^3\Delta$ may be larger than those found in the above-listed works and the value of T_e, correspondingly less.

879 A calculation of the potential energy curves for the lower electronic states of CO [3991a] attests to the fact that the states $X^1\Sigma^+$ and $e^3\Sigma^-$ have a common dissociation limit.

880 Calculation of the potential energy curve of CO in the state $A^1\Pi$ permits the conclusion that the potential energy curve may have a maximum (see [3991a]).

883 The vibrational levels of the $A^2\Pi$ state of CO^+, calculated on the basis of the adopted values for the constants, converge in the region of the dissociation limit.

887* The values $\nu_1 = 1300$, $\nu_2(2) = 550$ and $\nu_3 = 2200$ cm^{-1} were adopted in the work of Pitzer and Clementi [3256] for the basic frequencies of the molecule C_3 on the basis of a comparison of the respective force constants of the molecules C_3O_2, CH_2CO and C_3H_4.

887** The authors of the works [1368, 2395] emphasized that the analysis of the rotational structure carried out by them should be regarded only as preliminary, becuase the nature of the electronic states with whose transitions the observed bands are connected, is not accurately known; moreover, in the analysis of the rotational structure of the bands C_3, an error in numeration of the lines is possible, caused by the denseness of the rotational lines close to the band edges and the overlapping of different bands of the system.

888 Pitzer and Clementi [3256], on the basis of a calculation by the method of molecular orbits, arrived at the conclusion that the electronic ground state of the molecule C_3 should be a singlet state of the type $^1\Sigma_g^+$. Examination of the possible electronic configurations and the excited states corres-

ponding to them showed that bands should be present in the spectrum of C_3, connected with two forbidden transitions: $^1\Pi_u - {}^1\Sigma_g^+$ and $^1\Sigma_g^+ - {}^1\Sigma_g^+$. The authors of [3256], in accordance with the earlier proposed interpretation [2395, 1133, 1368, 2025] assumed that the bands of C_3 at λ 4050 A are due to the transition $^1\Pi_u - {}^1\Sigma_g^+$ (according to calculations, the excitation energy of the $^1\Pi_u$ state is approximately 3.1 ev, which agrees well with that found experimentally and equal to 3.06 ev).

889 Taylor, Benedict and Strong found that this relation can be described by the following empirical equation:

$$\nu^2_{0v_20} = \nu^2_0\{1 - \beta_0\sqrt{[(v_2+2)^2 - l_2^2]\,v_1} + 2\beta_2 - \beta_{2}v_2\}.$$

892 An investigation of the rotational Raman spectrum of CO_2 was carried out in the works of Houston and Lewis [2133]and Kotov, Tyulin and Tatevskiy [254]; the values of B_{000} (0.393 and 0.3895 cm^{-1}) differ from those obtained by an analysis of the infrared spectra and are evidently less accurate.

894 An analogous situation obtains with regard to the Schuman--Runge bands of the molecule O_2, which are below 1900 A in absorption, while the emission spectrum is situatied in the region of 3100-3300 A (see [142]).

896* The work of Livingston and Rao [2630] which dealt with an electron diffraction study of the structure of C_3O_2, was published in 1959. The use of the sector method of obtaining electron diffraction patterns enabled the authors of [2630] to determine with greater accuracy than in the preceding works [962, 963, 857, 2720] the values of the interatomic distances $r_{C=C} = 1.28 \pm 0.015$ and $r_{C=O} = 1.16 \pm 0.015$ A. The bond length C = C found by Livingston and Rao [2630] coincides completely with the values adopted in the present Handbook, but the interatomic distance $r_{C=C}$ is 0.03 A less than the value obtained by Mackle and Sutton [2720], although it agrees with it within the limits of error indicated in the work [2720]. It should be pointed out that the results of the electron diffraction measurements [2630] agree with the linearly symmetrical model of C_3O_2 but they do not exclude the possibility of slight (up to 5-10°) deviations from linearity. It is reported in the work [3876] that Bastiansen found for the distance C = C the value $r_{C=C} = 1.279$ A.

896** Such a molecule should have seven fundamental frequencies: four nondegenerate and three doubly degenerate frequencies. Four vibrations should be active in the infrared spectrum (ν_3, ν_4, ν_6, ν_7) and three in the Raman spectrum (ν_1, ν_2, ν_5).

897* On the basis of this hypothesis and using $r_{C=C} = 1.28$ and $r_{C=O} = 1.19$ A [2720], Rix [3446], on the basis of an analysis of the Raman bands obtained for ∠CCO the value 158°, which cannot be reconciled with the results of the electron diffraction measurements [2630] (see footnote page 896).

897** Venkateswarlu and Pillai [4085] in 1958 carried out a calculation of the force constants of the molecule C_3O_2 by the method of Wilson on the assumption that this molecule, according to the results, obtained by Rix [3446], belongs to the point group symmetry C_{2h} (∠CCO = 158°, $r_{C=C} = 1.28$ and $r_{C=O} = 1.19$ A) and has the vibrational frequencies (in cm^{-1}) of type A_g: 2185, 817, 817, 577, type A_u: 1050 and 780 and type B_u: 2258, 1670, 635 and 559, respectively. It should be pointed out that although the force constants found in the work [4085] agree within the limits of error with the constants found in the work [2640], the values of several fundamental frequencies computed by means of these constants differ considerably from those observed experimentally. This indicates that the potential constants found in the work [4085] on the assumption of a nonlinear structure of C_3O_2 do not describe the force field of this molecule correctly.

901 Spokes and Gaydon [3824a], using the burner, suggested by Hornbeck and Herman [2128], obtained bands in the region 2400-2700 A in the spectrum of the acetylene-oxygene flame when heavy water was introduced. An analysis of the vibrational structure of these bands enabled Spokes and Gaydon to find the vibrational frequencies of the bond C = O in the lower and upper electronic state, equal to 1800 and 980 cm^{-1}, respectively.
We must also draw attention to the work of Van de Forst, and Duchesne [4069a], who found, as a result of calculation, the following values for the fundamental frequencies of HCO in the excited state: $\nu_1 = 1888$, $\nu_2 = 767.5$ and $\nu_3 = 3337.1$ cm^{-1}.

902 Ewing, Thompson and Pimentel in 1960 [1517a] investigated the infrared absorption spectrum of the photolysis products of mixture of HI, HBr, DI and DBr, frozen in a matrix of solid carbon monoxide at 20°K. Comparison of the absorption spectrum in the visible region with the spectrum of the gaseous radicals HCO and DCO [2042] showed that the radicals HCO and DCO are formed during the photolysis of the abovelisted compounds. In the infrared spectrum of HCO, Ewing, Thompson and Pimentel observed two absorption regions (at 1860 and 1091 cm^{-1}), which they related to the vibration of the C = O band (ν_1) and the deformation vibration of the radical HCO (ν_2), respectively. The work [1517a] contains references to an unpublished report of Jones and Ramsay, who

found as a result of an analysis of the hot bands in the spectrum of HCO for the deformation vibrations of HCO in the ground state the frequency value ν_2 = 1083 cm^{-1}. The assignment of the frequency ν_3 in the work [1517a] is ambiguous. Ewing, Thompson and Pimentel estimated approximately the frequency ν_3 as being 3000 cm^{-1} on the assumption that the absence of this band in the spectrum is due to the low absorption coefficient for the vibration C — H. The authors did hot identify the band at 2493 cm^{-1} observed during the hydrolysis of a mixture of CO and HI because its frequency is too small compared with the corresponding vibration frequencies of the C — H bond in stable molecules. Thus, the values of the frequencies ν_1 = 1860 and ν_3 = = 3000 cm^{-1}, recommended in the work [1517a], are close to the corresponding values adopted in the present Handbookon the basis of earlier published studies. The frequency of the deformation vibration ν_1 = 1091 cm^{-1} differs considerably from the value ν_1 = 1538 cm^{-1} found by Murphy and Schoen [3008] which has been adopted in the Handbook. The existing data are insufficient to explain the cause of this discrepancy.

904 The change in the geometrical parameters within the limits of the above-indicated probable errors practically has no effect on the values of the fundamental frequencies.

905 A short review of this paper [841] has been published previously in a journal of abstracts [840].

906 The theoretical interpretation of this interaction specially for the case of H_2CO on the assumption that the molecule is completely symmetrical, has been given by Nicholson [3081] The more general case of flat molecules XYZ_2 has been examined by Silver [3724].

907 The studies of the microwave spectrum of formaldehyde and its deuterated substitution derivatives, carried out by Oka and Morino [3121a], made it possible to find the following structural parameters of the molecule H_2CC: $r_{C=C}$ = 1.21, r_{C-H} = 1.08 A and ∠HCO = 120°. It should be pointed out that although the values for the angle of HCO and the interatomic distance $r_{C=0}$ agree with the results of the electron diffraction measurements [3863] and the data of the work [2572], the interatomic distance r_{C-H} found in the works [3121a, 2572] is different. The value recommended by Oka and Morino (1.08 A) agrees better with the corresponding distances in the molecules of ethylene (1.071 A, [1646]) and ketene (1.075 A [565]) than the value 1.12 A, found in the work [2572] and which are obviously too high.

910* After the text of the present chapter had been edited, the work of Stratton and Nielsen [3887a] was published, dealing with a study of the infrared spectrum of HFCO and DFCO which had been reported previously only in brief remarks [3884, 3885, 3886 and 3887]. 9 HFCO bands and 13 DFCO bands were observed in the spectra of HFCO and DFCO, obtained in the region from 500 to 5000 cm^{-1}. An analysis of the rotational structure was carried out for five fundamental frequencies of the two molecules, as a result of which the following rotational constants were found for HFCO: $B'' = 0.3673$, $A''-B'' = 3.661$ cm^{-1} and for DFCO: $B'' = 0.3648$, $A'' - B'' = 1.806$ cm^{-1}. The work [3887a] also gives the values for the centers of the bands, connected with the fundamental frequencies for HFCO (in cm^{-1}): $\nu_1 = 2981.1$, $\nu_2 = 1836.9$, $\nu_3 = 1064.8$, $\nu_4 = 662.5$, $\nu_5 = 1342.5$ and for DFCO: $\nu_1 = 2261.7$, $\nu_2 = 1796.8$, $\nu_3 = 1073.2$, $\nu_4 = 657.5$, $\nu_5 = 967.9$ and $\nu_6 = 857.4$ and the values of the vibrational constants of HFCO (in cm^{-1}): $\omega_2^\circ = 1847.9$, $\omega_3^\circ = 1070.3$, $x_{22} = -11.0$, $x_{33} = -5.5$, $x_{53} = 10.7$, $x^{34} = -8.0$ and DFCO: $\omega_2^\circ = 1803.9$, $\omega_3^\circ = 1076.7$, $\omega_5^\circ = 970$, $x_{22} = -7.1$, $x_{33} = -3.5$, $x_{55} = -2.6$, $x_{13} = -14.9$, $x_{34} = -24.9$, $x_{36} = -2.2$, $x_{53} = -12.5$, $x_{54} = -0.9$.

910** After the work on the MS of the present chapter had been completed, the work of Favero, Mirri and Baker [1533] appeared, whose authors calculated, on the basis of the results of a study on the spectrum of HFCO in the millimeter wave region, the following rotational constants of the molecule HFCO: $A'' = 3.04055$, $B'' = 0.39228$, $C'' = 0.34680$ and $k'' = -0.96623$ cm^{-1}, to which correspond the following structural parameters: $r_{C-H} = 1.093$, $r_{C-F} = 1.093$, $r_{C-F} = 1.345$, $r_{C=O} = 1.190$ A, ∠FCO = 121°.46 and ∠FCH = 118°.14. Later on, the same authors [1553a], as a result of a study of the spectra of HFCO and DFCO, in which the centrifugal stretching was taken into account, again calculated the rotational constants of the formyl fluoride molecule and recommended slightly different values for the structural parameters of HFCO: $r_{C-H} = 1.087 \pm 0.01$, $r_{C=O} = 1.182 \pm 0.003$, $r_{C-F} = 1.342 \pm 0.003$ A, ∠FCO = 123.04 ± 0°.02, ∠FCH = 114° and ∠OCH = 123°. The values of the structural parameters obtained in the works [1533, 1533a] differ slightly from those found by Stratton and Nielsen [3887] who recommended the values $r_{C-H} = 1.080$, $r_{C-F} = 1.3428$, $r_{C=O} = 1.1857$ A and ∠FCO = 122°.14.

In 1960, Le Blanc, Laurie and Gwinn [2578a] investigated the rotational spectra of the molecules $HC^{12}OF$, $HC^{13}OF$ and $DC^{12}OF$ and found the rotational constants of these molecules. In order to eliminate the errors, due to the closeness of the C atom to the center of gravity of the molecule, it was assumed in the calculation of the structural parameters that

$r_{C-F}/r_{C=O}$ = 1.134 ± 0.005 (from electron diffraction measurements [2304]). As a result, the following values were obtained: r_{C-F} = 1.341, $r_{C=O}$ = 1.198, r_{C-H} = 1.098 A, $\angle FCO = 122°.7$, $\angle HCF = 108°$ and $\angle HCO = 129°$.
In 1961, Miller and Curl [2914a], to supplement the data obtained by Le Blanc et al [2578a], studied the microwave of $HCO^{18}F$ and, using the results of their own measurements and the data of the work [2578a] obtained: r_{C-F} = 1.338 ± ± 0.005, $r_{C=O}$ = 1.181 ± 0.005, r_{C-H} = 1.095 ± 0.008 A $\angle FCO = 122°46' \pm 30'$, $\angle HCO = 127°20' \pm 3°$ and $\angle HCF = 109°54' \pm 3°$.

911 The value of the frequency ν_5 was found by the authors of the work [3072] on the basis of observations in the Raman spectrum of a weak band with $\nu = 240$ cm^{-1}. Earlier, Thompson [3970] had estimated the frequency ν_5 as 230 cm^{-1} in analogy with the corresponding frequency of the thilophosgene molecule.

912* The methods of matrix isolation were described in the works [859, 4244, 709, 976]. Becker and Pimentel [709] showed that the vibration frequencies found in the work with matrices of inert gas, differ only slightly (not more than by 10-15 cm^{-1}) from the frequencies obtained in the absorption spectrum of the gas.

912** Catalano and Pitzer [1072] pointed out that the accuracy of the value $S_{280.66°K}$, found by Giauque and Johnson [1715] is not very high.

912*** In 1959, Overend and Evans [3157] again carried out measurements in the region 550-600 cm^{-1} in the absorption spectrum of gaseous Cl_2CO on the spectrometer with high resolution. On the basis of an analysis of the contours of the resultant absorption curve, the authors of [3157] showed that a band with a maximum at 580 cm^{-1} is present in the spectrum of Cl_2CO which overlaps with a band having its maximum at 576 cm^{-1}. Thus, the study of the spectrum of gaseous Cl_2CO confirms the assignment of the bands, carried out by Catalano and Pitzer [1072] on the basis of an analysis of absorption spectrum of Cl_2CO, obtained by the method of matrix isolation. In 1961, Stokr and Schneider [3880a] again studied the vibrational spectra of the carbonyl halogenides and also confirmed the assignment of the frequencies of Cl_2CO, proposed by Catalano and Pitzer.

914 The clearly erroneous value 1.68 A is recommended for the bond length r_{C-Cl} in the work [2662].

916 See, for example, Overstreet [3158] (Φ^*_T for T ≤ 5000°K);

Gordon [1808] (Φ^*_T for $T \leq 6000°K$); Goff, Gratch and Voorhis [1787] ($T \leq 2777°K$); Ribaud [3426] ($T \leq 4000°K$).

926 This relation is approximate because the anharmonicity of the vibrations was not allowed for in its derivation and because it was assumed that $\nu_1 = 2\nu_2$.

933 The thermodynamic functions of formyl, calculated by means of the vibrational constant of HCO, found in the work of Ewing, Thompson and Pimentel (see page 900), differ from those given in Table 142 (II) by an amount of 0.01 in $\Phi^*_{298.15}$ to 0.56 cal/mole·degree in S°_{6000}.

938* Concerning the effect of the dimensions of the graphite particles on their heat capacity at low temperatures, see also the work of Komatsu [2462a].

938** Prolonged irradiation (for 8 months) of Acheson graphite causes a destruction of its crystal lattice (displacement of the carbon atoms into the interlaminar space) and an increase in the heat capacity and entropy of the graphite ($S^\circ_{298.15} = 1.492 \pm 0.009$ cal/g-atom·degree [1324]).

939 An arithmetical error was committed by de Sorbo [1320] during the calculation of the value $H^\circ_{298.15} - H^\circ_0$ (at 250-275°K) and the value 230 ± 4 cal/g-atom was obtained.

941* Rasor and McClelland used the impulse method of measuring heat capacity [3401b] for determining the heat capacity of four samples of graphite within the range of 1200-3900°K. The results of the measurements on the investigated samples agree among themselves within the limits of the measurement error (±5% [3401a]) and also with the heat capacities, used in the present Handbook (to 3500°K). Within the range 3500-3900°K, Rasor and McClelland [3401a] found an anomalously rapidly increasing heat capacity of graphite (from $C^\circ_{p3500} = 6.6$ to $C^\circ_{p3900} = 12.0$ cal/g-atom·degree). This increase in heat capacity, in the opinion of the authors of [3401a], is only apparent and due to the marked sublimation of graphite above 3500°K.

941** References to an earlier work on the determination of the melting point of graphite can be found in the Handbooks [813, 98].

941*** At 5000°K, the partial pressures of C, C_2 and C_3 over graphite, according to the data, adopted in the present Handbook, are 4.50, 11.25 and 13.00 atmospheres, respectively and their sum is about 29 at. It is difficult to estimate the partial pressures of C_4 and C_5 at this temperature. According to the mass-spectrometric data of [1405], the sum of the partial pressures of C_4 and C_5 at 4100°K is approximately 10% of the sum of the partial pressures of C, C_2 and C_3.

941**** In 1952, Euler [1506] examined the data on the thermal conductivity of graphite electrodes within the temperature range of 3150-4000°K and found a sharp decrease in thermal conductivity above 3700°K. The author of [1506] suggested the possibility of the existence of a phase transformation in graphite in this range (melting or polymorphous transformation).

941***** Fickett and Cowan [1556] calculated the thermodynamic functions of graphite to 12,000°K without taking into account its melting point and heat of fusion.

942* According to the data of Japanese researchers, published in 1960 [3099a], carbon melts at 4020 ± 50°K in an argon atmosphere at a pressure of about 100 atmospheres. The globules of molten graphite obtained by the authors of [3099a] had the same lattice parameters as natural graphite.

942** Kubaschewski and Evans [2494] estimated ΔHm_{5000} = 33 kcal/ /g-atom or ΔSm = 6.6 cal/g-atomδdegree.

946 Until the investigations on the band system $B^1\Sigma^+ - A^1\Pi$ in the spectrum of $C^{13}O$, an accurate determination of the energy of the dissociation limit was impossible, while the corresponding data for the three vibrational levels are necessary for the calculation. On the basis of an estimate on the basis of the predissociation at the levels v = 0 and v = 1 the energy of the dissociation limit was taken as 89,620 ± ± 50 cm^{-1} (see [1668]).

948 Dworart, Burns, De Maria and Inghram [1405] carried out a mass-spectroscopic investigation of the evaporation from effusion chambers with a relative orifice of less than 10^{-5} (in the much earlier works [1113, 1111] the relative orifices were about 10^{-3}). It was found that the ratio of the ion current of C_4^+ and C_5^+ to the ion current of C^+ remained only approximately the same as in the works [1111, 1112, 1113]. This shows that the evaporation coefficients of C_4 and C_5 are close to unity.

949 Pitzer and Clementi [3256] calculated the thermodynamic properties of carbon from C_4 to C_{13}. The authors of [3256] arrived at the conclusion that the relative concentrations of the heavier molecules (C_5, C_7, etc.) should increase with temperature in saturated carbon vapor. However, experimental measurements [1405], carried out under equilibrium conditions (relative orifice of the effusion chamber smaller than 10^{-5}) showed that at temperatures up to 2700°K, heavier molecules than C_5 are not observed in carbon vapor in noticeable quantity.

950 It should be pointed out that the sole fact left unaccounted

for by this interpretation of the CO spectra, is the predissociation in the state $C^1\Sigma^+$ in the region 93,000 cm^{-1}. However, as this predissociation is observed only at a single level (v = 0) and has been little studied, it may be assumed that new studies will show that it does not contradict the adopted value of $D_0(CO)$.

951 The values given in the work [1405] were recalculated, allowance being made for the differences between the thermodynamic functions of graphite and C_2 (gas), adopted in the present Handbook, and the values, used in the work [1405].

953 Engelke [1484], on the basis of the temperature dependence of the intensities of the absorption and emission spectra of the molecule C_3, calculated values of 171 and 197 ± 10 cal/ /mole. This work is known to the authors of the Handbook only through an abstract in the Journal of Abstracts.

957 The paper [3694a] published after termination of the work on the present chapter of the Handbook, gives the results of the measurements of the potential of the occurence of R^+ ions from a series of aldehydes with the general formula RCHO. When R is n-butyl, isobutyl or phenyl, these potentials at which the ions occur lead to the coincident value $\Delta Hf(HCO) = -0.3 \pm 3$ kcal/mole. The value $\Delta Hf(HCO) = 11.2$ kcal/mole, which corresponds to $D(H - CHO) = 91$ kcal/mole, is excluded by the results of this work.

959 It was not possible to study explosiions of mixtures of CO and F_2 because the reactions between these gases began at room temperature as soon as the mixture was prepared.

Chapter 17

DERIVATIVES OF METHANE AND HALOGEN METHANE

(CX_4, CX_3Y, CX_2Y_2, CX_2YZ, CXYZV)

Methane and its halogen derivatives are very similar in their properties because of the similarity of their chemical structure. When considering these compounds, it is best to subdivide them into five groups, corresponding to the general formulae of the type CX_4, CX_3Y, CX_2Y_2, CX_2YZ and CXYZV, where X, Y, Z, V = H, F, Cl, Br, I.*

The molecular constants and thermodynamic functions of the halogensubstituted methanes are considered in the present chapter in accordance with the above-indicated groups, because different symmetry point groups** correspond to them.

The degree to which the various halogen derivatives of methane have been investigated, is uneven. In addition to compounds such as CH_4, CH_3F, CH_3Cl, CH_3Br and some others, which have been studied in detail, there are compounds which have been only little studied or never investigated at all. The least investigated are the properties of the iodine derivatives of methane because of their instability and the difficulty of their synthesis. Of the 69 halogen derivatives of methane, the fundamental vibration frequencies are known on the basis of the spectra for 40 compounds,*** the structural parameters and moments of inertia have been determined as a result of electron diffraction and spectroscopic studies for 28 compounds, and the experimental values of the heats of formation are known for 19 compounds. In view of the existence of regular changes in the properties of the halogen derivatives of methane, these data are sufficient for an approximate determination of the constants of those of them, for which the corresponding experimental investigations have not been carried out. The halogen derivatives of methane for which the fundamental frequencies have been determined on the basis of their spectra and also CH_2FI, CHF_2I, CF_2ClI, CF_2BrI and CF_2I_2, whose spectra have not yet been investigated, will be considered in the present Handbook. In the calculation of the thermodynamic functions of the latter, the vibrational components were determined by means of the vibrational components of the other halogen derivatives of methane, whose fundamental frequencies are known (see page 1082 and 1086).

For many of the halogen derivatives of methane, considered in the present Handbook, the structural parameters and heats of formation have not been determined experimentally. The problem of the approximate determination of these values on the basis of existing experimental data is discussed in §61 and in the work of Yudin and Khachkurusov [471]. The results, obtained in the last-mentioned work for the heats of formation of the halogen-substituted methanes are used in the present Handbook.

Studied in the greatest detail were the spectra of methane, its deuterium derivatives and of the halogen derivatives of methane, the spectra of CH_3F, CH_3Cl, CH_3Br, CH_3I. However, even for these compounds, the existing data are insufficient for determining reliable values of the anharmonicity constants and the constants of the vibrational-rotational interactions. Hence, the thermodynamic functions of methane and its halogen derivatives were calculated, using the approximate model of the harmonic oscillator-rigid rotator. The main error in these calculations is due to the failure to allow for the anharmonic vibrations. The errors due to the absence of any allowance being made for the excited electronic states are small because a study of the electronic spectra of methane and its halogen derivatives has shown that the energy of the excited electronic states of the molecules of these compounds exceeds 50,000 cm^{-1}. Information on the electronic spectra of methane and its halogen derivatives can be found in the reviews of Sponer and Teller [3825, 3827] and in the works [2509], (CCl_4, $CFCl_3$, $CHCl_3$, CF_2Cl_2, $CHFCl_2$, CH_2Cl_2), [1271] (CF_3Br, CF_2Br_2, $CHFBr_2$); [1231] (CF_4); [4145, 575] (CH_3I); [2380] (CCl_4); [4126] (CH_2F_2); [3879] (CH_3F, CHF_3); [4390] ($CHCl_3$, CCl_4, CCl_2F_2, CF_4); [3291, 3902a] (CF_3I); [2390] (CCl_4, CCl_2F_2).

Section 1. MOLECULAR CONSTANTS

§61. Structural Parameters

Methane and its halogen derivatives have a very similar molecular structure. The carbon atom is situated in the center of the molecule in all these compounds and around it are four other atoms (hydrogen and halogens), arranged in such a manner that the angles between the bonds are either strictly tetrahedral (109°28') or differ only slightly from the tetrahedral angle.* The bond lengths C-X for methane and its halogen derivatives have certain characteristic values. Thus, the length of the C-H bond is 1.07 to 1.11 A, the length of the bond C-F is 1.32 to 1.39 A, the length of the bond C-Cl 1.75 to 1.78 A, the length of the bond C-Br 1.91 to 1.94 A and the length of the bond C-I 2.13 to 2.16 A.

Experimental data on the structural parameters are known for methane and for 28 of its halogen derivatives.** On the basis of these data one can estimate fairly satisfactorily the structural parameters of the molecules of the other halogen derivatives of methane.

The main source of information on the experimental values of the structural parameters of the molecules of halogen-substituted methanes are the results of electron diffraction studies. The greater part of these has been obtained in the years 1935-1945, when the technique of electron diffraction investigation of molecular structure was not yet perfect and the results of the investigations inaccurate. The values of the structural parameters for several halogen derivatives of methane have been considerably improved in recent years by new electron diffractions investigations, based on the use of a more perfect technique. Moreover, highly important information was obtained on the structure of the molecules during the investigation of their infrared and microwave spectra.

The more reliable results of the experimental determination of the structural parameters of the molecules of halogen-substituted methane are used in the present Handbook for correcting inaccurate experimental data and for calculating the moments of inertia in the cases where the molecular structure of several halogen derivatives of methane has not been determined.

The influence of neighboring atoms results in variations of the length of the C-X bond in the molecules of different halogen-substituted methanes. However, in most cases these variations are of the same order of magnitude as the experimental error in the determination of the length of the C-X bond. Exceptions are only the bond lengths of C-H and C-F, whose differences in the different halogen are greater than the experimental error.

Because 16 halogen derivatives of methane for which experimental values have not been obtained for the structural parameters, are being examined in the present Handbook, it is necessary to determine the most reliable characteristic values which can be used for calculating the moments of inertia and the thermodynamic functions of the corresponding compounds. An analysis of the available experimental data for the halogen derivatives of methane and other halogen-substituted saturated hydrocarbons makes it possible to recommend for this purpose the values for the bond lengths in the molecules of the halogen derivatives of methane, given in Table 145. The angles between the bonds can be considered with sufficient accuracy to be the same, 109°28'.

The bond lengths given in Table 145 are used in the present Handbook in the cases where experimental data are lacking or have been obtained in older investigations.

An example for the considerable difference between the bond lengths of C-X, obtained in early electron diffraction studies and those of more accurate investigations, is CF_4. In 1936, Brockway found r_{C-F} 1.36 ± 0.02 A [100, 101] and in 1953-1955, $r_{C-F} = 1.322 \pm 0.005$ A [957, 428] after the technique of electron diffraction had been greatly improved.

The errors in the characteristic values for the bond lengths in the molecules of halogen-substituted methane, given in Fig. 145, may be estimated to be ±0.02 A.

TABLE 145

Characteristic Values (in A) for the Length of the C-X Bonds in Halogen Derivatives of Methane

C—X	r_{C-X}	C—X	r_{C-X}
C—H	1,10	C—Cl	1,77
C—F	$1{,}33^{a}$	C—Br	1,93
C—F	$1{,}35^{б}$ b	C—I	2,15
C—F	$1{,}38^{в}$ c	—	—

a) for molecules with three fluorine atoms
b) for molecules with two fluorine atoms
c) for molecules with one fluorine atom

§62. Molecules of the Type CX_4

The molecules of methane and its halogen derivatives of the type CX_4 have a strictly tetrahedral structure and belong to the point symmetry group $T_d(\sigma = 12)$. The molecule of these compounds have four fundamental frequencies: the frequency ν_1 of the fully symmetrical vibration of type A_1, the frequency ν_2 of the doubly degenerate vibration of the type E and two frequencies, ν_3 and ν_4, of the triply degenerate vibrations of type F_2. All four frequencies are active in the Raman spectrum. Only the frequencies ν_3 and ν_4 are active in the infrared spectrum.

The molecules of methane and its halogen derivatives of type CX_4 are spherical rotators and thus doe not have rotational spectra.

Four compounds of the type CX_4 will be examined in the present Handbook: CH_4, CF_4, CCl_4 and CBr_4. Carbon tetraiodide will not be discussed because it does not exist in the gaseous state.

CH_4. A large number of studies on the spectra of methane and its deuteron derivatives is known. The studies of the spectra of these compounds, published prior to 1945 are considered in the monographs of Herzberg [152] and Hibben [2065]. In later years, the Raman spectrum of gaseous methane has been investigated in the works [4204, 1546, 3878, 3963a] and the infrared spectrum in the works [1020, 880, 881, 4285, 1021, 3165, 509, 1054, 2722, 3040, 1053, 983, 3373a, 3286a]. The spectra of deuterated [2338, 880, 3702, 3404, 4285, 875, 2299a, 3076a] and tritiated [2301, 2302] methane were also studied. In the works [1020, 880, 881, 1021, 875, 1546, 2338, 3878, 509, 3702, 2722, 3040, 983, 3963a, 3373a, 3076a, 3286a, 3124a] the vibrational-rotational spectra of CH_4 and CD_4 were obtained on apparatus with high resolving power.

In spite of the presence of such a large number of investigations on the spectra of methane and its isotope modifications, the available data are insufficient for calculating the frequencies of the normal vibrations and the anharmonicity constants of CH_4. The literature contains approximate values for the frequencies of the normal vibrations of CH_4, calculated by means of the isotope qeuations of Teller-Redlich (see [152] page 250) and Dennison [1314] on the basis of the fundamental frequencies of CH_4, CD_4, CT_4 [1314, 2338, 2302, 2919a] and also those calculated theoretically [1966].

The infrared spectrum of CH_4 in the region 1300-1600 cm^{-1} has been investigated by Burgess [1020] by means of a vacuum spectrometer with diffraction grating. In this region are the bands ν_2 and ν_4 of methane. Burgess analyzed the fine structure of these bands and determined the position of their centers. The frequency ν_2 is not active in the infrared spectrum but the existence of a cariolis interaction between ν_2 and ν_4 makes its observation possible [152]. The band ν_2 had not been observed in earlier investigations of the infrared spectrum, because it is overlapped by a band of water vapor. The frequency ν_2, determined by Burgess [1020], on the basis of the infrared spectrum of CH_4, agrees with the value obtained by Feldman, Romanko and Welsh [1546] on the basis of an analysis of the fine structure of the corresponding band in the Raman spectrum. The frequency ν_4, found by Burgess, differs only by 0.3 cm^{-1} from the value, obtained by A. Nielsen [3076] and which has been adopted in the book of Herzberg [152].

The region 2500-3300 cm^{-1} in the spectrum of methane was studied on with large dispersion apparatus by Boyd, Thompson and Williamson [881], Stoicheff, Cumming, John and Welsh [3878] and Plyler and coworkers [509, 3286a]. This region contains the bands ν_1 and ν_3. An analysis of the rotational structure of the band ν_3 has been carried out in the works [881, 3878, 509, 3286a] which made it possible to determine the beginning of the band ν_3 with an accuracy of ±0.2 cm^{-1}. The determination of the beginning of the band ν_1 is difficult because the narrow band ν_1 is overlapped by the band ν_3. Stoicheff, Cumming, John and Welsh [3878] found the center of the band ν_1 at 2916.5 cm^{-1}. In earlier works, a value of 2914.8 cm^{-1} had been found for ν_1 [152].

The fundamental frequencies of the molecule CH_4 adopted in the present Handbook are presented in Table 146. The value found by Stoicheff, Cumming, John and Welsh [3878] from the Raman spectrum was adopted for the frequency ν_1. The values found by Burgess [1020] and Feldman, Romanko and Welsh [1546] as a result of an investigation of the infrared spectrum and the Raman spectrum was adopted for the frequencies ν_2 and ν_4. For the frequency ν_3, the value found by Allen and Plyler [509] as a result of an analysis of the rotational structure of the corresponding band in the infrared spectrum* was taken for the frequency ν_3.

TABLE 146

Adopted Values of the Molecular Constants of Methane and its Halogen Derivatives of the Type CX_4. (σ = 12)

Молекула A	ν_1	ν_2 (2)	ν_3 (3)	ν_4 (3)	$I_A I_B I_C$
	см$^{-1}$ B				10^{-117} (г·см^2)^3
CH_4	2916,5	1533,6	3018,9	1305,9	0,1523
CF_4	908,2	434,5	1272^a	632	3177,82
CCl_4	458	218	775^a	310	117350
CBr_4	268,6	122,5	671,7	181,5	2376100

A) molecule; B) g·cm^{-1}; a) the unperturbed values of the frequencies are given.

The values of the harmonics and component frequencies of CH_4, found before 1945, are given in the monograph of Herzberg [152]. In recent years, Boyd, Thompson and Williams [881] investigated the bands $2\nu_4$ and $\nu_2 + \nu_4$, Brown [983], the bands $\nu_1 + \nu_4$, $\nu_3 + \nu_4$ and $\nu_2 + \nu_4$, Rank et al. [3373a] the band $2\nu_3$.

The rotational constant B_0 of the molecule CH_4 was determined on the basis of an analysis of the fine structure of the bands in the vibrational-rotational spectra. Herzberg [152] recommended the value $B_0 = 5.252$ cm^{-1}, obtained by Childs [1098] as a result of an analysis of the fine structure of the bands ν_3 and ν_4 in the infrared spectrum of CH_4.*

After 1945, the rotational constants of methane and its deuterium derivatives were determined in the works [3878, 509, 1546, 880, 875, 2338, 3404, 3702, 3040, 2299a, 3963c]. Stoicheff, Cumming, John and Welsh [3878] studied the Raman spectrum of CH_4 and carried out an analysis of the fine structure of the band ν_3 and found $B_0 = 5.253$ cm^{-1}. As a result of the analysis of the fine structure of band ν_2 in the Raman spectrum, Feldman, Romanko and Welsh [1546] obtained $B_0 = 5.270$ cm^{-1}. Thomas and Welsh [3963c], on the basis of an analysis of the rotational structure of the bands ν_2 and ν_3, observed in the Raman spectrum of CH_4, obtained values of B_0, of 5.240 ± 0.002 and 5.2406 ± 0.0011 cm^{-1}.

The value adopted in the present Handbook for the products of the principal moments of inertia of CH_4 was calculated on the basis of the value $B_0 = 5.241$ cm^{-1}, found by Allen and Plyler [509] as a result of an analysis of the fine structure of the band ν_3 in the infrared spectrum of CH_4, in which the results of the structure analysis on band ν_3 in the Raman spectrum were utilized [3878]. To this value of the rotational constant corresponds the interatomic distance $r_0(C - H) = 1.0934$ A.

The bond length C — H in the methane molecule has been calculated in the works [152, 3878, 509, 1546, 2338, 880, 875, 3404, 3963c] on on the basis of the value of B_0 of the molecule CH_4 as well as on the basis of the rotational constants of deuterium-substituted methane. The values of r_0(C-H) obtained in earlier works differs only by 0.001 A from the above given value.

An electron diffraction investigation of the structure of the molecule CH_4 and CD_4, carried out by Bartell, Kuchitsu and de Neni [666a], led to the following effective values (r_g) of the length of the bond C-H and C-D: $r_{C-H} = 1.1070$ and $r_{C-D} = 1.1023$ A. Kuchitsu and Bartell in the work [2497a] calculated the corrections $r_g - r_e$ and $r_0 - r_e$ for the effective values of the bond lengths C-H and C-D in the molecules CH_4 and CD_4, determined as a result of electron diffraction and spectroscopic studies. Allowing for these corrections enabled the authors of the works [666a, 2497a] to determine the equilibrium value of the bond lengths in the molecules CH_4 and CD_4: $r_e =$ $= 1.085$ A. The calculations of Stevenson and Ibers [3860a], based on a method worked out by them earlier [2162a] and the values of the constant B_0 of the molecules CH_4 and CD_4, found in the works [1098, 3878, 1546, 3076a, 3702] led to a value of $r_e = 1.091$ A.

$\underline{CF_4}$. The Raman spectrum of carbon tetrachloride was studied in the works [4364, 1117], the infrared spectrum in the works [621, 3277, 4315, 1830]. The study of the spectrum of CF_4 was carried out only on apparatus with low and medium dispersion, in consequence of which the rotational structure of the bands could not be investigated.

Yost, Lassetre and Grosse [4364] investigated the Raman spectrum of liquid carbon tetrachloride (at -120°C) and determined the three fundamental frequencies: $\nu_1 = 904$, $\nu_2 = 437$, and $\nu_3 = 635$ cm^{-1}.

Baily, Hale and Thompson [621] investigated the infrared spectrum of gaseous CF_4 in the region 526-5000 cm^{-1} and observed the two fundamental frequencies ν_4 and ν_3 at 630 and 1265 cm^{-1} and also several harmonics and composite frequencies. In 1951, Plyler and Benedict [3277] again investigated the infrared spectrum of CF_4 in the region 625-3330 cm^{-1}. They observed the fundamental frequencies ν_4 and ν_3 at 630 and 1277 cm^{-1} and detected a Fermi resonance between $2\nu_4$ and ν_3. Later on, Woltz and Nielsen [4315] obtained the infrared spectrum of a more carefully purified carbon tetrachloride sample in the region 300-5000 cm^{-1}, where they observed and identified about 26 CF_4 bands. They were able to observe the frequency ν_2, which is inactive in the infrared spectrum, at 435 cm^{-1}, explaining this infringement of the selection rule by a coriolis interaction between ν_2 and ν_4. The region 1230-1285 cm^{-1} in the spectrum of CF_4 requires further investigation. Woltz and Nielsen observed five bands in this region, of which they identified the bands at 1283 and 1261 cm^{-1} with the frequencies ν_3 and $2\nu_4$. The origin of the bands at 1235, 1252 and 1275 cm^{-1} in the work [4315] remained unexplained. Some of these bands possibly belong to the frequencies of the molecule $C^{13}F_4$, to which attest the results of an investigation on the infrared spectrum of a mixture of $C^{12}F_4$ and $C^{13}F_4$, obtained by Goubeau, Bues and Kampmann [1830].

Five CF_4 bands were observed in the Raman spectrum of gaseous carbon tetrafluoride, obtained by Klassen [1117] on an apparatus with a dispersion of 15 A/mm at 4358 A and 34 A/mm at 5000 A. Of these, the sharpest and most intense band was that at 908.2 cm^{-1} which was identified with the frequency ν_1. Furthermore, two broad bands with medium intensity were observed, of which one with a sharp single maximum at 434.5 cm^{-1} was identified with the frequency ν_2 and the other with two maxima at 624 and 638 cm^{-1}, with the frequency ν_4. Two broad, weak bands with maxima at 865 and 1282 cm^{-1} were identified with the frequencies $2\nu_2$ and ν_3.

Thus, the data on the fundamental frequencies of the molecule CF_4, obtained in the study of the infrared spectrum and the Raman spectrum, are in good agreement with each other and are complementary to each other.

The values of the fundamental vibration frequencies of the molecule CF_4, adopted in the present Handbook are given in Table 146. The values found by Klassen [1117] in the Raman spectrum were taken for the frequencies ν_1 and ν_2. The Handbook adopted the hint by Plyler and Benedict [3277] concerning the existence of a Fermi resonance between the frequencies ν_3 and $2\nu_4$. Hence, Table 146 gives for the frequency ν_3 the unperturbed value which is determined approximately as the arithmetic mean of the observed frequencies ν_3 and $2\nu_4$. For the latter and also for the frequency ν_4, the values determined by Woltz and Nielsen [4315] on the basis of the infrared spectrum were adopted. The possible error in the unperturbed value of the frequency ν_3, given in Table 146, is estimated to be 5 cm^{-1} while the error in the adopted values of the other frequencies of CF_4 does not exceed 2 cm^{-1}.*

The bond length C-F in the molecule CF_4 was determined by several researchers by the method of electron diffraction. Such a study was first carried out by Brockway [100] who found the value $r_{C-F} = 1.36 \pm 0.02$ A. Later on, Hoffman and Livingston [2094] and Bowen [877] again carried out an electron diffraction investigation of the structure of CF_4, using the visual method of interpretation of the electron diffraction patterns and obtained considerably smaller values of r_{C-F}, equal to 1.317 ± 0.015 A [2094]** and 1.337 ± 0.022 A [877]. A similar value ($r_{C-F} = 1.33$ A) was found by Alcock and Hurst [497] during a study of neutron diffraction in solid carbon tetrafluoride. Brockway and coworkers [957], 428, 3986] carried out the most careful electron diffraction study of the structure of CF_4, using the sector - miccrophotometric method. The value of $r_{C-F} = 1.322 \pm 0.005$ A obtained in the works [957, 428, 3986] was recommended in the Handbook [3916] and has been used in the present Handbook for the calculation of the inertial moments of CF_4.

CCl_4. The infrared spectrum and the Raman spectrum of carbon tetrachloride has been studied by many researchers. Most of these investigations, however, dealt with the study of the spectra of liquid carbon (see [152, 2065]). On the basis of a study of the data, obtained for CCl_4 up to 1944, Herzberg [152] recommended for the fundamental frequencies of the molecule CCl_4 the values obtained by Langseth [2560] as a result of a study of the Raman spectrum of liquid carbon tetrachloride. The investigations of the infrared spectrum and the Raman spectrum of gaseous carbon tetrachloride began in 1949 and were carried out in the works [3277, 1658, 274, 2581, 4202, 1117, 275].* The rotational structure of the CCl_4 bands was not resolved in these works.

For CCl_4, the authors of the works [152, 3277, 2726, 1117, 4026, 274] found the presence of a Fermi resonance between the frequencies ν_3 and $\nu_1 + \nu_4$. It is pointed out in the work [274] that the transition from liquid to gas does not eliminate the Fermi resonance between these frequencies.

The present Handbook adopts the values of the fundamental frequencies of the CCl_4 molecules, obtained in the works [4202, 1117, 274] (see Table 146). The unperturbed value, determined approximately as the arithmetic mean of the frequencies ν_3 (794 cm^{-1}) and $\nu_1 + \nu_4$ (756 cm^{-1}) with an error of ± 10 cm^{-1} is given in Table 146 for the frequency ν_3.

The structure of the CCl_4 molecule has been investigated by electron and X-ray diffraction methods [517, 666, 433, 101, 100, 2326, 2497, 3664]. For the calculation of the products of the moments of inertia the value $r_{C-Cl} = 1.766 \pm 0.005$ A,* obtained by Bartell, Brockway and Schwendeman [666] as a result of an electron diffraction study using the microphotometric-sector method,** has been adopted in the Handbook.

$\underline{CBr_4}$. The Raman spectrum [1302, 2849, 1241, 2560] and the infrared spectrum of CBr_4 [2849, 2580, 635, 2582] were obtained for CBr_4 solutions in benzene, carbon disulfide and carbon tetrachloride. The value of the triply degenerate frequency $\nu_3 = 678$ cm^{-1} was determined by Plyler, Smith and Acquista [3285] for the gas. In view of the absence of a dipole moment in the molecule CBr_4, the values of the other frequencies of CBr_4 should not differ greatly from the values obtained on the basis of the spectra of the solutions. The scatter in the values of the fundamental frequencies of CBr_4, found by different authors by means of the spectra of solutions of carbon tetrabromide, does not exceed 5 cm^{-1}.

In the present Handbook, the values for the fundamental frequencies of the molecule CBr_4 were adopted on the basis of the data of Langseth [2560] (see Table 146). The latter studied the Raman spectrum of a solution of CBr_4 in carbon tetrachloride on a four-prism spectrograph with a dispersion of 8 A/mm.

The bond Length C-Br in the molecule CBr_4 has been determined by several investigators on the basis of electron diffraction studies and was found to be 1.91-1.94 A (see [517]). The most accurate value, 1.942 ± 0.003 A, was determined in an electron diffraction investigation by Finbak, Hassel and Olanssen [1558]. This value of r_{C-Br} was used in the present Handbook for the calculation of the product of the inertial moments of CBr_4.

§63. Molecules of the Type CX_3Y

The molecules of halogen-substituted methane of the type CX_3Y belong to the point group symmetry C_{3v} ($\sigma = 3$) and are symmetrical rotators. They have six fundamental frequencies. The frequencies ν_1, ν_2, ν_3 correspond to fully symmetrical vibrations of the type A_1, and the frequencies ν_4, ν_5, ν_6, to the doubly degenerate vibrations of type E. All fundamental frequencies are active in the infrared as well as the Raman spectra. The existence of a Fermi resonance between the frequencies ν_1 and $2\nu_5$ has been established for the molecules of halogen-substituted methane of the type CH_3X.

All the halogen-substituted derivatives of methane of the type CX_3Y, for which the vibrational spectra have been studied and the fundamental frequencies determined, are being examined in the present Handbook. Vibrational spectra were not obtained for CFI_3, $CClI_3$, $CBrI_3$, CCl_3I and CBr_3I.

CH_3F. The fundamental frequencies of the molecule CH_3F were determined as a result of an investigation of the infrared spectrum of gaseous fluoro methane [743, 4355, 3240, 546, 1318]. The Raman spectrum of fluoro methane has not been studied. Of the deuterium-substituted fluoro methanes, the vibrational spectra were investigated only for CD_3F in the works [546, 1461].

Investigations into the rotational structure of the bands in the infrared spectrum of CH_3F were carried out by Bennett and Maier [743], Yates and Nielsen [4355], Pickworth and Thompson [3240] and Andersen, Bak and Brodersen [546]. Bennett and Maier [743] investigated the infrared spectrum of CH_3F in the region 666-3330 cm^{-1}, completely resolving bands bands ν_3, ν_4, ν_5 and ν_6 and some rotational structure of bands $2\nu_5$ and ν_1. They detected an almost complete superposition of bands ν_2 and ν_5 and strong overlapping of bands ν_1, $2\nu_5$ and ν_4. The fundamental frequencies of CH_3F determined by Bennett and Maier were subsequently corrected by Herzberg [152]. The latter extended the measurement results of Bennett and Maier to vacuum and carried out an additional analysis of the data obtained by them. Herzberg found in this work that a Fermi resonance exists between the frequencies ν_1 and $2\nu_5$. Yates and Nielsen [4355] again investigated the rotational structure of the bands ν_1, ν_2, ν_3, ν_4, ν_5, $2\nu_5$ and carried out a special analysis of the overlapping bands ν_2, ν_5 and ν_1, $2\nu_5$. This analysis demonstrated the presence of a coriolis interaction between the states of CH_3F, corresponding to the bands ν_2 and ν_5, and confirmed the correctness of the remarks made by Herzberg concerning the presence of a Fermi resonance between ν_1 and $2\nu_5$. For the beginning of the bands ν_1 and $2\nu_5$, Yates and Nielsen [4355] obtained values close to those found earlier by Herzberg [152] and Bennett and Maier [743] but, in contrast to the latter, Yates and Nielsen reversed the assignment of the frequencies. This change, however, was not adopted in the subsequent investigations of the infrared spectrum of CH_3F [3240, 546, 1318]. For the beginning of the bands ν_2, ν_5 and ν_4, Yates and Nielsen [4355] obtained slightly more accurate values, than in the works [152, 743] and similar values for the beginning of the band ν_3.

The spectrum of CH_3F was obtained with the greatest resolution by Pickworth and Thompson [3240] in the region 1820-4000 cm^{-1}. They carried out a detailed analysis of the rotational structure of the bands ν_1, ν_4, $2\nu_3$ and $2\nu_5$ and determined the head of these bands with the greatest accuracy. Later on, the infrared spectrum of CH_3F was investigated using prism spectrometers with medium [546] and low [1318] dispersion. The low dispersion of the spectrometer, used in the work [546] was compensated for, however, by the use of an improved technique for recording the spectrum. In this work, carried out by Anderson, Bak and Brodersen, the rotational structure of the bands ν_4, ν_5, ν_6 was resolved and analyzed and all the fundamental frequencies of CH_3F determined again. For the frequencies ν_1 and ν_4 these authors obtained almost the same values as Pickworth and Thompson [3240] and for the frequencies ν_3, ν_5 and ν_6, values which were very close to those found earlier in the works [4355] (for ν_5) and [152] (for ν_3 and ν_6). The value of the frequency $\nu_2 = 1464$ cm^{-1} was evidently estimated by Anderson, Bak and Brodersen on the basis of the values for the frequency ν_5 adopted by them and the difference between the heads of the bands ν_2 and ν_5, found by Yates and Nielsen [4355].

The values of the fundamental frequencies of the molecule CH_3F adopted in the present Handbook are given in Table 147. For the frequency ν_1, the approximate unperturbed value is given which has been determined as the arithmetic mean of the observed values of the frequencies $\nu_1 = 2964.5$ and $2\nu_5 = 2863.2$ cm^{-1} on the basis of the data of Pickworth and Thompson [3240]. The adopted value of the frequency ν_4 had also been obtained in the work [3240]. For the frequencies ν_2, ν_5 and ν_6, values are given in Table 147, recommended by Anderson, Bak and Brodersen [546] and for the frequency ν_3, the value obtained by Herzberg [152] on the basis of the data of Bennett and Maier [743] was given. Of the adopted values the most accurate is that of the frequency ν_4, the least accurate that of the frequency ν_1, whose possible error is estimated to be approximately ± 10 cm^{-1}. The uncertainty in the adopted values of the other frequencies of CH_3F apparently does not exceed ± 3 cm^{-1}.

TABLE 147

Adopted Values of the Molecular Constants of the Halogen Derivatives of Methane of the Type CXY_3 ($\sigma = 3$)

Молекула A	ν_1 (1)	ν_2 (1)	ν_3 (1)	ν_4 (2)	ν_5 (2)	ν_6 (2)	$I_A I_B I_C$
	$см^{-1}$					B	10^{-117} $(г \cdot см^2)^3$
CH_3F	2913,85[a]	1464	1048,2	3005,8	1466,6	1197,7	5,930
CH_3Cl	2923,5[a]	1355,6	732,1	3041,8	1454,6	1015	22,0765
CH_3Br	2925[a]	1305	611	3056,7	1443,8	954,5	42,404
CH_3J	2915[a]	1251,4	533,4	3062,2	1437,8	882,5	68,818
CHF_3	3034,5	1137	699,6	1375	1152	507,6	972,95
$CHCl_3$	3032	671,1	364,8	1218	767,7	255,5	32853
$CHBr_3$	3035	539	222	1148	656	154	621340
CHJ_3	3038	437	153	1067	578	105	4483800
CF_3Cl	1105	781,7	475,8	1212	560	350	9405
CF_3Br	1085	762,5	350	1206	548	305	23743
CF_3J	1073	741	286	1185	540	265	44446
$CFCl_3$	1085	535,0	349,5	847	398	241	57740
$CFBr_3$	1069	398	218	743	306	150	808690
CCl_3Br	718	420	247	775	295	193	257310
$CClBr_3$	745	327	211	677	211	140	1214200

[a] The unperturbed ν_1 frequency is given.

A) Molecule; B) $g \cdot cm^2$. J = iodine.

The values of the rotational constants of the molecule CH_3F in the vibrational ground state were determined as a result of an analysis of the fine structure of the bands in the infrared spectrum [743, 152, 4355, 3240, 546] and on the basis of the results of an analysis of the microwave spectrum [3967, 1749]. The most accurate value of the constant $B_0 = C_0 = 0.85179$ cm^{-1} was obtained in the work [3967] on the basis of the results of a study of the microwave spectrum of CH_3F in the wavelength region 1-3 mm. Similar values for the constant $B_0 = C_0$ were found in the works [743, 4355, 3240] during an analysis of the fine structure of the bands in the infrared spectrum. The value of the rotational constant A_0 was determined by Herzberg [152] based on the data of Bennett and Maier [743] ($A_0 = 5.100$ cm^{-1}) and Anderson, Bak and Brodersen [546] ($A_0 = 5.095 \pm 0.010$ cm^{-1}) on the basis of measurements of the intervals between lines in the bands ν_4, ν_5 and ν_6.

The value given in Table 147 for the products of the main inertial moments of the molecule CH_3F was calculated from the values of the rotational constants found in the works [3967, 546].

The structural parameters of the molecule CH_3F were determined on the basis of the results of the electron diffraction investigations [517, 2627] and the results of an analysis of the fine structure of the infrared and microwave spectra of fluoromethane [152, 164, 546]. The structural parameters of CH_3F thus obtained agree with each other within the limits of the error involved in their determination. The most detailed work on the determination of the structural parameters of the CH_3F molecule was carried out by Anderson, Bak and Brodersen [546] on the basis of a simultaneous consideration of the results obtained in spectrum and electron diffraction studies. According to the calculations of these authors, the following structural parameters correspond to the rotational constants of CH_3F adopted in the present Handbook: $r_0(C-H) = 1.106 \pm 0.001$, $r_0(C-F) = 1.38527 \pm$ ± 0.00005 A, $\angle H-C-H = 109°59' \pm 3'$.

<u>CH_3Cl</u>. A large number of studies deals with the investigation of the spectra of chloromethane. The investigations of the vibrational spectra of CH_3Cl, carried out prior to 1945, were examined in the monographs by Herzberg [152] and Kohlrausch [236]. The infrared spectrum of CD_3Cl was investigated by Noether [3100], H. Nielsen and A. Nielsen, [3086] and the microwave spectrum, by Simmons and Goldstein [3730].

The infrared spectrum of gaseous chloromethane was investigated in the region 700-14,000 cm^{-1}. However, the data obtained in this are inadequate for computing the frequencies of the normal vibrations and the anharmonicity constants of the molecule CH_3Cl.* The rotational structure of the bands in the infrared spectrum of chloromethane was studied by Bennett and Maier [743] (ν_4, ν_5, ν_6), Nielsen and Barker

[3071] (ν_3), Pickworth and Thompson [3241] (ν_1, ν_2, $2\nu_5$) and Brown and Edwards [989] ($2\nu_4$). The results obtained by Bennett and Maier [743] were again analyzed and improved by Herzberg [152] who demonstrated the existence of a Fermi resonance between the frequencies ν_1 and $2\nu_5$. The most detailed analysis of the rotational structure of the bands in the infrared spectrum of CH_3Cl was carried out by Pickworth and Thompson [3241].

The Raman spectrum of gaseous chloromethane was investigated by Nielsen and Ward [3093], Welsh, Crawford, Thomas and Love [4202] on medium dispersion apparatus. Five bands corresponding to the fundamental frequencies, were observed in the work of Welsh et al [4202], and the centers of the bands determined with an accuracy of 0.6-2 cm^{-1}. The band ν_2 in the work [4202] was not observed, most likely because of its low intensity. The values of the frequencies ν_4, ν_5, ν_6, were determined on the basis of the infrared spectrum and the Raman spectrum and agree with an accuracy of 3 cm^{-1}. The differences between the values of the frequency $\nu_3 = 725.3$ cm^{-1}, found in the work [4202] and the value $\nu_3 = 732$ cm^{-1}, found from the infrared spectrum, exceeds the limits of the possible experimental error. The band ν_5 in the Raman spectrum is enormously broad and has four maxima. The wave number, corresponding to the center of this band, is 18 cm^{-1} larger than the wave number of the zero line in the infrared spectrum.

For the fundamental frequencies of the molecule CH_3Cl, values were adopted in the present Handbook, obtained by Herzberg [152] (ν_3, ν_4, ν_5, ν_6) on the basis of the data of Bennett and Maier [743] and Pickworth and Thompson [3241] (ν_1, ν_2). The adopted values of the frequencies of CH_3Cl are given in Table 147. For the frequency ν_1, the unperturbed value, determined approximately as the arithmetic mean of the observed values of the frequencies $\nu_1 = 2967.8$ and $2\nu_5 = 2879.2$

cm^{-1} [3241] between which a Fermi resonance exists, was taken.

The purely rotational infrared spectrum of CH_3Cl in the region 15-80 cm^{-1} was investigated by Palik and Rao [3168]. The microwave spectrum of CH_3Cl was studied in the works [3967, 2472, 1825, 3727, 1245] in which the frequencies, corresponding to the transitions $0 \rightarrow 1$, $2 \rightarrow 3$, $3 \rightarrow 4$, $5 \rightarrow 6$ were measured. An analysis of the microwave spectrum made it possible to determine the rotational constant B_0 for the isotope modifications of chloromethane and also the centrifugal stretching constant.* In the work of Kraitchman and Dailey [2472], the rotational constants B_0 of the molecule CH_3Cl^{35} and CH_3Cl^{37} in the excited vibrational states (corresponding to $v_3 = 1$ and $v_6 = 1$) were also determined and the constants α_3^B and α_6^B calculated.

The rotational constant B_0, determined from the infrared spectrum by Pickworth and Thompson [3241]: $B_0\ (CH_3Cl^{35}) = 0.4432$, $B_0(CH_3Cl^{37}) = 0.4366\ cm^{-1}$, are in good agreement with the more accurate values, obtained from the microwave spectrum [3967]: $B_0\ (CH_3Cl^{35}) = 0.443401$, $B_0(CH_3Cl^{37}) = 0.436572\ cm^{-1}$. The rotational constant $A_0 = 5.097\ cm^{-1}$ was calculated in the works [152, 1825] on the basis of the intervals between the lines in the perpendicular bands of the infrared spectrum (ν_4, ν_5, ν_6).

The values of the constants A_0 and $B_0 = C_0$, found as a result of the investigations on the microwave and infrared spectra in the works [3967, 152, 1825] were used in the present Handbook for computation of the products of the inertial moments of CH_3Cl.

The structural parameters of the molecule CH_3Cl were determined on the basis of the results of the electron diffraction studies in the works [517, 665] and have also been calculated in the works [164, 2915, 2406] on the basis of the rotational constants, found during investigation of the microwave and infrared spectra. The most accurate values for the structural parameters of CH_3Cl, found on the basis of the results of electron diffraction studies: $r_{C-H} = 1.11 \pm 0.01$, $r_{C-Cl} = 1.783 \pm 0.03$ A, $\angle H - C - H = 110 \pm 20°$ [665], are in close agreement with the corresponding values calculated on the basis of the microwave data: $r_{C-H} = 1.103 \pm 0.01$, $r_{C-Cl} = 1.782 \pm 0.003$ A, $\angle H - C - H = 110°20' \pm 1°$ [164].

$\underline{CH_3Br}$. The spectra of bromomethane were investigated in numerous works. The vibrational spectra of CD_3Br, CD_2HBr and CDH_2Br were investigated in the works [4199, 3100, 1198, 4266].

The investigations of the spectra of CH_3Br, carried out before the year 1945, were examined in the monographs of Herzberg [152], Kohlrausch [236] and Hibhen [2065]. In recent years, the vibrational spectra of gaseous bromomethane were investigated in the works [1198, 4202, 4199, 3377, 1553, 990]. The data thus obtained permitted a fairly reliable determination of the fundamental frequencies of the molecule CH_3Br.

The fundamental frequencies of CH_3Br, given in the monograph of Herzberg [152], are based on the results of studies on the infrared spectrum of gaseous bromomethane, obtained by Bennett and Maier [743] and Barker and Plyler [638]. Bennett and Maier [743] obtained the infrared spectrum of CH_3Br over a wide range on an apparatus with a selection of diffraction gratings and resolved the rotational structure of the bands ν_4, ν_5, ν_6. Barker and Plyler [638] carried out an accurate measurement of the frequency ν_3.* Herzberg [152] was the first to show that a Fermi resonance must exist between the frequencies ν_1 and $2\nu_5$ of the molecule CH_3Br. Later on, the most detailed investigation of the vibrational spectra of CH_3Br in the region of the fundamental frequencies were carried out by Welsh and coworkers [4202]. (Raman spectrum of the gas) and by Weissmann and coworkers [4199] (infrared spectrum of the gas). The rotational structure of several bands, corresponding to composite frequencies, was investigated in the works [3377, 990] by means of a high-dispersion spectrometer. The fundamental frequencies of the molecule CH_3Br, connected with vibrations of CH_3 groups, were also determined in the work [1318].

Weissmann and coworkers [4199] obtained the infrared spectrum of gaseous bromomethane in the region 600-3700 cm^{-1} on a double beam prism spectrometer and partially resolved the rotational structure of the bands ν_5 and ν_6. The measurements of the wavelengths of the lines in the infrared spectrum of CH_3Br in the work [4199] were compared with the results of the corresponding measurements in the works [4202, 1198] and calculations carried out to determine the positions of the zero lines of the transverse bands ν_4, ν_5, ν_6 using the data of Bennett and Maier [743].

The values recommended in the work [4199] for the fundamental frequencies of the molecule CH_3Br were adopted in the present Handbook and are presented in Table 147. For the frequency ν_1, Table 147 gives the unperturbed value, determined approximately as the arithmetic mean of the observed frequencies ν_1 (2972 cm^{-1}) and $2\nu_5$ (2878 cm^{-1}).

The rotational constants of the molecule CH_3Br $A_0 = 5.06$ cm^{-1} and $B_0 = C_0 = 0.31$ cm^{-1} were determined by Herzberg [152] on the basis of an analysis of the data of Bennett and Maier [743]. Later on, the purely rotational spectra of the isotope modifications of the molecule CH_3I were determined by the method of microwave spectroscopy and the corresponding values of the rotational constant B_0 and the centrifugal stretching constants (see [164, 416]) were determined with great accuracy. The values of the rotational constants A and B for the excited vibrational states of the molecule CH_3Br were found in the works [4199, 3377, 990] on the basis of an analysis of the fine structure of the corresponding bands in the infrared spectrum.

The following values for the rotational constants of the fundamental vibrational state of the molecule CH_3Br have been adopted in the Handbook: $A_0 = 5.082$ cm^{-1} [152], $B_0 = C_0 = 0.319160$ cm^{-1} (for CH_3Br^{79}) [3967], $B_0 = C_0 = 0.317947$ cm^{-1} (for CH_3Br^{81}) [2028]. These values were used for the computation of the products of the principal moments of inertia, given in Table 147.

The values of the structural parameters of the molecule CH_3Br were determined by means of electron diffraction measurements [517] and on the basis of the values of the rotational constant B_0 for the isotope modifications of the molecule CH_3Br, found during an analysis of the microwave spectra [164, 1825, 2406, 2915]. To the values of the rotational constants adopted in the Handbook correspond the following values of the structural parameters of the molecule CH_3Br: $r_{C-H} = 1.101$, $r_{C-Br} = 1.938$ A, $\angle H - C - H = 110°48'$ [164, 1825]. The values of the structural parameters of CH_3Br obtained in the works [2915, 2406] on the basis of microwave data, agree with those given to within ± 0.01 A for r_{C-H} $\pm$ 0.002 A for r_{C-Br} and $\pm$ 1° for $\angle H - C - H$.

CH_3I. Numerous investigations on the vibrational spectra of iodomethane are known. The most detailed studies were carried out on the infrared spectrum of gaseous iodomethane. The Raman spectrum of liquid iodomethane was obtained by several researchers on low-dispersion devices. Bands corresponding only to the fundamental frequencies of the symmetrical vibrations (ν_1, ν_2, ν_3) were observed in the Raman spectrum of gaseous iodomethane, obtained by Ball [628]. The vibrational spectra of deuterated iodomethane have not been studied.

The investigations on the vibrational spectra of CH_3I, carried out prior to 1945, were reviewed by Herzberg [152], Kohlrausch [236] and Hibben [2065].

The infrared spectrum of gaseous iodomethane in the range of the fundamental frequencies 525-3130 cm^{-1} was investigated by Bennett and Maier [743], Barker and Plyler [638], Lagemann and Nielsen [2516], Bernstein, Cleveland and Voelz [767]. The infrared spectrum of CH_3I in the region of the composite frequencies and harmonics was investigated by H. Herzberg and L. Herzberg [2028] (4000-11,800 cm^{-1}) and Wiggings, Shull and Rank [4266] (4550-6250 cm^{-1}). The data obtained in these works made a fairly reliable determination of the fundamental frequencies of the molecule CH_3I possible. However, they are insufficient for the reliable determination of the anharmonicity constants and the frequencies of the normal vibrations (see note to page 989).

The highest resolution of the fine structure of bands in the infrared spectrum of CH_3I in the domain of fundamental frequencies was obtained in the works [743, 638, 2516], in which spectrometers with diffraction gratings were used. The values of the fundamental frequencies of the CH_3I molecule given in the monograph by Herzberg [152] are based on data from these works. For the first time Herzberg [152] showed that Fermi resonance occurs between the oscillation frequencies ν_1 and $2\nu_5$ of the CH_3I molecule.

In later works [2729, 1549, 767] the infrared spectrum of CH_3I in the domain of fundamental frequencies was obtained with lower resolution making use of prism spectrometers. Values obtained earlier by Lagemann and Nielsen [2516] were chosen for the fundamental frequencies of the CH_3I molecule in the works [2729, 1549]. Bernstein, Cleveland and Voelz [767] obtained the infrared spectra (of gas and liquid) and the spectrum of Raman scattering (of liquid) of two methyl iodide specimens: of ordinary methyl iodide and of iodide with an elevated content of $C^{13}H_3I$ molecules. On the basis of their own data and the data obtained by Bennett, Meyer [743] and Lagemann and Nielsen [2516] the authors of the work [767] rendered more accurate the values of the fundamental frequencies of the $C^{12}H_3I$ molecule and determined the fundamental frequencies of $C^{13}H_3I$. In the work [767] in particular, it is noted that a slight inaccuracy in the calculations had been tolerated by Herzberg [152] when determining the values of the frequencies ν_4, ν_5, ν_6 from the data in [743, 2516].

In the present Handbook values recommended by Bernstein et al [767] were chosen for the fundamental frequencies of CH_3I observed in the spectra. For the frequency ν_1, Table 147 shows an undisturbed value chosen approximately equal to the arithmetic mean of the observed values of the frequencies $\nu_1 = 2969.0$ cm^{-1} [767] and $2\nu_5 = 2861$ cm^{-1} [152].

The values of the rotational constants A_0 and $B_0 = C_0$ of the CH_3I molecule were determined by Herzberg [152] (5.07 and 0.28 cm^{-1}, respectively) on the basis of an analysis of the spectral data obtained by Bennett and Meyer [743]. Furthermore, the purely rotational spectra of isotopic modifications of the CH_3I molecule were studied by microwave spectroscopy and the corresponding values of the rotational constant B_0 and the constants of centrifugal stretching were determined with high accuracy (see [164, 416]).

Bernstein, Cleveland and Voelz [767] re-analyzed the rotational structure of the perpendicular bands (ν_4, ν_5, ν_6) of the $C^{12}H_3I$ and $C^{13}H_3I$ molecules on the basis of data obtained from a study of the infrared spectrum in the works [743, 2516, 767] and making use of the value of B_0 found from microwave spectra. As a result of the analysis carried out in the worj [767], the values $A_0 = 5.09$ and 5.07 cm^{-1} were found for the molecules $C^{12}H_3I$ and $C^{13}H_3I$, respectively, and also the values of the constants B_1 and A_1 for the excited vibrational states of these molecules corresponding to the frequencies ν_4, ν_5, ν_6 were determined.

In the present Handbook, the following values of the rotational constants were chosen for the fundamental vibrational state of the $C^{12}H_3I$ molecule: $A_0 = 5.09$ cm^{-1} [767], $B_0 = C_0 = 0.250216$ cm^{-1} [1825], obtained from an analysis of the fine structure of bands in the infrared (A_0) and microwave spectra (B_0).* The value of the product of the principal moments of inertia of CH_3I given in Table 147 corresponds to these values of the rotational constants.

The values of the structural parameters of the CH_3I molecule were determined from electron diffraction data [101, 100] and from the results of investigating microwave spectra of isotopic modifications of the CH_3I molecule [164, 2915]. The following values of the structural parameters correspond to the values of the rotational constants of CH_3I adopted in the present Handbook: $r_{C-H} = 1.100$, $r_{C-I} = 2.139$ A, $\angle H - C - H = 110°58'$, calculated by Gordy, Simmons and Smith [1825].

$\underline{CHF_3}$. The Raman spectrum of liquid fluoroform was investigated by Glockler and Leader [1778], Glockler and Edgell [1771], Rank, Shull and Pace [3383] and that of gaseous fluoroform by Claassen and Nielsen [1118]. The infrared spectrum of gaseous fluoroform in the range from 500-4000 cm^{-1} was investigated by Price,** Plyler and Benedict [3277], Rix [3445], Morcillo, Herranz and Biarge [2946]. Single bands of the infrared spectrum of CHF_3 were investigated by Edgell and May [1459] (ν_2) and by Wiggins, Shull and Rank [4266] ($2\nu_1$). The infrared spectrum of CHF_3 in the range from 4000-14,050 cm^{-1} was investigated by Bernstein and Herzberg [762]. Using high-dispersion instruments the infrared spectrum of CHF_3 was obtained in the works [762, 4266], in which the rotational structure of the individual bands is studied. The infrared spectrum of CDF_3 was investigated by Polo and Wilson [3294].

The assignment of the frequencies observed in the spectra of the CHF_3 molecule was carried out in the works [1778, 1771, 3383, 1118, 3277, 762, 3445, 1459]. Views were divergent only about the problem of assigning the frequency ν_2 since the ν_2 band is superimposed on the intense ν_5 band. Price [762] and Rix [3445] identified the band center at 1209 cm^{-1} with the frequency ν_2, owing to the shape of the outline of this band, whereas in the works [3383, 3277, 1459] this band is assigned to the sum frequency $\nu_3 + \nu_6$, and the frequency ν_2 is determined equal to 1140 [1459] or 1150 cm^{-1} [3277]. In the Raman spectrum of liquid fluoroform Rank, Shull and Pace [3383] determined the ν_2 and ν_5 band centers at 1117 and 1160 cm^{-1}, respectively. Claassen and Nielsen [1118] observed a weak band at 1137 cm^{-1} in the Raman spectrum of the gas and assigned it to the frequency ν_2. Claassen and Nielsen did not observe the frequency ν_5 in the Raman spectrum of the gas and assumed it equal to 1152 cm^{-1} on the basis of a study on the infrared spectrum [762, 3277]. Edgell and May [1459] carried out a special investigation of the infrared spectrum of gaseous fluoroform in the range where the ν_2 band was supposed to be located. Comparing the infrared spectra of gaseous fluoroform at different temperatures Edgell and May [1459] drew the conclusion that the Q branch of the ν_2 band lies at 1140 cm^{-1} while the P and R branches lie at 1130 and 1152 cm^{-1}, respectively. The ν_5 band center was determined by them close to 1157 cm^{-1}. The work [1459] deals particularly with the problem of assigning the band at 1209 cm^{-1}, and it is found out that assigning this band to the frequency ν_2 as proposed by Price (see [762]) and Rix [3445] is weakly founded.

In the present Handbook, values based on data obtained in the works [1118, 3277, 3445, 1459] are adopted for the fundamental frequencies of the CHF_3 molecule. The values of the frequencies ν_1, ν_2,

ν_3 given in the Table 147 were obtained by Claassen and Nielsen [1118] from an investigation of the Raman spectrum. For the frequencies ν_4, ν_5, ν_6 Table 147 gives values obtained by Rix [3445] from an investigation of the infrared spectrum.

In the investigation of the infrared spectrum the rotational structure of the parallel bands $2\nu_1 + 2\nu_4$ and $3\nu_1$ [762] and $2\nu_1$ [4266] was analyzed and the values of the constant B_0 were determined equal to 0.34516 [762] and 0.3453 cm^{-1} [4266]. The purely rotational spectra of the isotopic modifications of the CHF_3 molecule were investigated with the help of microwave spectroscopy, in the works [1707, 1749, 1033]. For the $C^{12}H^1F^{19}_3$ molecule these investigations yielded a value of $B_0 = 0.34520$ cm^{-1}.

The structural parameters of the CHF_3 molecule were determined by electron diffraction [517, 2627] and calculated from the values of the rotational constant B_0 [762, 1707]. The most accurate values of the structural parameters obtained from electron diffraction investigations of the molecular structure of CHF_3 were those obtained by Brockway with the help of the sector microphotometric method. The results obtained by Brockway were published in the works [2627, 2632, 2633]: $r_{C-F} = 1.334 \pm 0.005$ A, $\angle F - C - C = 108°30' \pm 30'$. Ghosh, Trambarulo and Gordy [1707] calculated the structural parameters of the CHF_3 molecule on the basis of the values of the rotational constant B_0 of its isotopic modifications found from an analysis of the microwave spectrum. In the work [1707] the following values of the structural parameters of CHF_3 are obtained: $r_{C-F} = 1.332$, $r_{C-H} = 1.098$A, $\angle F - C - F = 108°48'$, which were used in the present Handbook to calculate the product of the principal moments of inertia of CHF_3 whose value is given in Table 147.

$\underline{CHCl_3}$. A great number of studies on the vibrational spectra of liquid chloroform and several investigations of gas spectra carried out with spectroscopes of low and medium dispersion is known. In a high-dispersion device only the $2\nu_2$ band [4266] for which a rotational analysis of fine structure was carried out was obtained.

The monograph by Herzberg [152] gives a short review of the studies carried out up to 1945. The books by Kohlrausch [236], Hibben [2065] and the works [4388, 2726] give a survey of the results of investigations carried out on the Rawan spectrum of liquid chloroform. The work by Lisitsa and Tsyashchenko [276] considers the results of studies on the infrared spectrum of liquid chloroform. In this work, an assignment of lines in the infrared spectrum of liquid chloroform lying in the range from 230 to 16,300 cm^{-1} is proposed.

Nielsen and Ward [3093], Rao [3398] and Welsh and collaborators [4202] investigated the Raman spectrum of gaseous chloroform, and the infrared spectrum was investigated by Jenkins and Straley [2238], Madigan and collaborators [2727], Plyler and Benedict [3277], Gibian and McKinney [1724], and Wiggins and collaborators [4266].

The values of all fundamental frequencies of the $CHCl_3$ molecule could be determined by investigating the Raman spectrum of the gas in the works [3093] and [4202]. With the highest resolution the Raman spectrum of gaseous chloroform was obtained by Welsh and collaborators [4202], who determined sufficiently reliable values of the fundamental frequencies of $CHCl_3$ agreeing well with the v alues of these quantities as obtained by other research workers. The values of the frequencies ν_2, ν_3, ν_5, ν_6 obtained in the work [4202] are more accurate than those found in other works by investigating the Raman spectrum and the infrared spectrum of gaseous chloroform. The values of the frequencies $\nu_4 = 1218$ and $\nu_1 = 3032\ \mathrm{cm}^{-1}$ found in the work [4202] practically coincide with the somewhat more accurate values $\nu_4 = 1218.9$

and $\nu_1 = 3034.4\ cm^{-1}$, found by Jenkins and Straley [2238] by studying the infrared spectrum.

In the present Handbook, the values obtained by Welsh and collaborators [4202] from a study on the Raman spectrum and given in Table 147 were adopted for the fundamental frequencies of the $CHCl_3$ molecule. A comparison with analogous results of other studies on the spectrum of $CHCl_3$ permits us to assume that the error of the adopted values of the fundamental frequencies varies within the limits of ±1 to ±3 cm^{-1}.

The vibrational spectra of liquid and gaseous deuterotrichloromethane ($CDCl_3$) were investigated by Bernstein and his collaborators in the works [2728, 768].

Single ranges of the rotational spectra of several isotopic modifications of the $CHCl_3$ molecule were determined by the methods of microwave spectroscopy in the works [1707, 3798, 4037, 4309], and the values of the rotational constant B_0* (see also [164, 416]) corresponding to them were determined with great accuracy.

The structural parameters of the $CHCl_3$ molecule were determined by Brockway [100, 101] from the results of electron diffraction studies and, more accurately, in the works [1707, 4309] as a result of calculations based on the values of the rotational constants of the isotopic modifications of the $CHCl_3$ molecule found by analyzing the microwave spectrum. Ghosh, Trambarulo and Gordy [1707] used the values of the rotational constant B_0 of the molecules $C^{12}HCl^{35}_3$, $C^{12}HCl^{37}_3$ and $C^{12}DCl^{35}_3$ found from the microwave spectrum and calculated the following values of the structural parameters of the $CHCl_3$ molecule: $r_{C-H} = 1.073$, $r_{C-Cl} = 1.767$ A, $\angle Cl - C - Cl = 110°24'$, which are used in the present Handbook to calculate the product of the principal moments of inertia of $CHCl_3$, given in Table 147. Wolfe [4309] calculated the values of r_{C-Cl} and $\angle Cl - C - Cl$, on the basis of the values of the rotational constants of the $CHCl_3^{35}$ and $CHCl_2^{35}Cl^{37}$ molecules he had obtained and the value of $r_{C-H} = 1.073$ A found in the work [1707]. Thus, Wolfe found $r_{C-Cl} = 1.762$ A and $\angle Cl - C - Cl = 110°55$ in agreement with the values of the corresponding parameters found in the work [1707].

$CHBr_3$. The vibrational spectra of liquid bromoform were studied by many research workers. In the monographs by Kohlrausch [236] and Hibben [2065] there are surveys on Raman spectrum studies. In a work by Meister, Rosser and Cleveland [2849] the results of studies on the Raman and infrared spectra of liquid bromoform published up to 1950 are considered and compared with the results obtained by the authors of this work. The work [2849] gives an interpretation of the vibrational spectra of liquid bromoform and on the basis of considering the results of studies on these spectra the most probable values of the fundamental frequencies of $CHBr_3$ are recommended. Among the studies on the vibrational spectra of liquid bromoform carried out in the following in order to make the values of the fundamental frequencies more accurate and to assign them only the investigation of the infrared spectrum of $CHBr_3$ carried out by Plyler and Benedict [3277] is of interest.

Jenkins and Straley [2238] and Plyler and Benedict [3277] obtained the infrared spectrum of gaseous bromoform in the range from 660--5000 cm^{-1} using instruments with low dispersion. The ν_1 and ν_4 bands are situated in the mentioned spectral range. The bands corresponding to other fundamental oscillation frequencies of the $CHBr_3$ molecule lie in the longer-wave range of the infrared spectrum studied only for liquid bromoform. The Raman spectrum of gaseous bromoform was not investigated.

Thus, mainly the vibrational spectra of liquid bromoform enable us to draw conclusions as to the fundamental frequencies of the $CHBr_3$ molecule. We have, however, to note that in the transition from liquid to gas the most remarkable difference in the values of the fundamental frequencies must be expected for the frequencies ν_1 and ν_4 corresponding to totally symmetric and deformation vibrations of the C-H bond. According to the data of Plyler and Benedict [3277] this difference amounts to 18 cm^{-1} for ν_1 and 7 cm^{-1} for ν_4. For the rest of frequencies, its order of magnitude is close to the error committed in determining their values from the vibrational spectra of liquid bromoform.

Table 147 shows the values of the fundamental frequencies of the $CHBr_3$ molecule, adopted in the present Handbook. The adopted values of the frequencies ν_2, ν_3, ν_5, ν_6 are based on the results of studies on the vibrational spectra of liquid bromoform, given in the works [2849, 3277]. For the frequency ν_4 Table 147 gives a value based on the results of measuring the position of the center of the corresponding band in the infrared spectrum of gaseous bromoform [2238, 3277]. The values of the frequency ν_1 obtained in the works [2238] (ν_1 = 3049.2 cm^{-1}) and [3277] (ν_1 = 3058 cm^{-1}) cannot be considered reliable. The value of the frequency ν_1 obtained from studies on the vibrational spectra of liquid bromoform [2849, 3277] also cannot be regarded as precisely established. On the other hand, this frequency is characteristic of the C-H bond in the CHX_3 molecules, where X = F, Cl, Br, I. Owing to this fact, for the frequency ν_1 of the $CHBr_3$ molecule a value equal to 3035 cm^{-1} whose error was estimated in the limits of ±20 cm^{-1} was adopted.

Ferigle, Cleveland, Boyer and Bernstein [1553] studied the vibrational spectra of $CDBr_3$. More early studies are considered in the work [2849].

The rotational constant B_0 of the isotopic $CHBr_3$ modifications was determined from the microwave spectrum [4282, 2459, 2011, 4281]. Making use of the values of the rotational constant B_0 of the $CHBr_3^{79}$, $CHBr_3^{81}$, $CDBr_3^{79}$, $CDBr_3^{81}$ molecules, Williams, Cox and Gordy [4281] calculated the following values of the structural parameters of the bromoform molecule: $r_{C-H} = 1.068 \pm 0.01$, $r_{C-Br} = 1.930 \pm 0.003$ A, $\angle Br - C - Br = 110°48'$, which were used to calculate the product of the moments of inertia in the present Handbook (see Table 147).

An electron diffraction study of the structure of $CHBr_3$ carried out by Levy and Brockway [2599] led to the values $r_{C-Br} = 1.91$ A and $\angle Br - C - Br = 111°$.

$\underline{CHI_3}$. The fundamental frequencies of the CHI_3 molecule are well-known on the basis of studies on the vibrational spectra of solid iodoform and its solutions in different solvents.

The individual bands corresponding to vibrations of the CHI_3 molecule were in the infrared spectrum of iodoform dissolved in $CHCl_3$ [1482], CS_2 and CCl_4 [3277, 3326] and in the spectrum of a CHI_3 suspension in paraffin [635]. A spectroscopic study of molecular iodoform monocrystals was carried out by Hexter and Cheung [2063] who investigated the polarized infrared spectrum in a wide range and by Goypiron and Mathieu [1835] who studied the Raman spectrum. In the works [2063, 1835] all fundamental frequencies of the CHI_3 molecule were assigned. Stammreich and Forneris [3837] studied the Raman spectrum of iodoform solutions in solvents of different polarity [$(C_2H_5)_2O$, $CHBr_3$, CH_2Br_2, C_5H_5N] and found that the frequencies of the sharpest lines in the spectra of the different solutions vary within the limits of ± 1 cm^{-1}. The difficulties in studying the Raman spectrum of CHI_3 are connected with the photochemical instability of iodoform and the presence of intense fluorescence proceeding from the decomposition products. Stammreich and Forneris mention the relative stability of iodoform dissolved in pyridine. The helium lines λ = 5875.6 and λ = 6678.2 A were used to excite the Raman spectrum in the work [3837], since for photochemically unstable molecules an excitation in the region of longer waves is preferable.

The values of the fundamental frequencies of CHI_3 obtained in the work [3837] are adopted in the present Handbook and given in Table 147. The values of the frequencies ν_6, ν_3, ν_5, ν_4 obtained in the work [3837] coincide with the values given in the works [3277, 2063, 1835] within the limits of 3-5 cm^{-1}. The values of the frequencies of the totally symmetric valence vibrations ν_2 and ν_1 are, respectively, by 11 and 60 cm^{-1} higher than those obtained from the spectrum of crystalline iodoform.

The molecular structure of iodoform was studied by the methods of X-ray diffraction [232] and electron diffraction [675, 2953, 100, 101]. The following values were obtained for the C-I bond length and the valence angle of I – C – I: $r_{C-I} = 2.12 \pm 0.04$ A [675, 100, 101], $\angle I - C - I = 113°$ [675], $r_{C-I} = 2.16$ A [2953]..

The value of the product of the principal moments of inertia of the CHI_3 molecule given in Table 147 was calculated under the assumption of tetrahedral arrangement of the bonds and of C-H and C-I bond lengths as adopted in Table 145. In the limits of the errors indicated on page 975 the latter agree with the aforementioned results of determining the structural parameters of the CHI_3 molecule by electron diffraction.

CF_3Cl. The Raman spectrum of liquid chlorotrifluoro methane was investigated by Kahovec and Wagner [2318], Delwaulle and Francois [1303, 1305]. The values of the fundamental frequencies of the CF_3Cl molecule determined by these authors are close to the values of these quantities obtained later on by studying the vibrational spectra of the gas.

The infrared spectrum of gaseous chlorotrifluoro methane was obtained with the help of prism spectrometers by Thompson and Temple [3974] in the range from 780-5000 cm^{-1} and by Plyler and Benedict [3277] in the range from 400-5000 cm^{-1}. In these works the bands of CF_3Cl are assigned and the values of the frequencies ν_1, ν_2, ν_4 and ν_5 are determined.

The Raman spectrum of gaseous chlorotrifluoro methane was studied by Claassen [1117] by means of a spectrograph with three prisms. The Raman spectrum of CF_3Cl was also obtained by Taylor [3955] who used a spectrometer with lower dispersion and a less perfect method of registration. Practically coinciding values were obtained for the fundamental frequencies of the CF_3Cl molecule in the works [1117, 3955]. The values of the frequencies of CF_3Cl obtained by Claassen [1117] must, however, be considered more accurate, for reasons indicated above. In particular, Claassen succeeded in observing two separate maxima of the ν_3 band corresponding to the isotopic molecules CF_3Cl^{37} and CF_3Cl^{35} whereas Taylor did not achieve such a resolution.

On the basis of a comparison of all data obtained for the fundamental frequencies of the CF_3Cl molecule in the works [3974, 3277, 1117, 3955] a choice of the values of those quantities that are adopted in the present Handbook was carried out. In doing so, account was taken of the fact that the ν_1 and ν_4 bands are considerably sharper in the infrared spectrum of CF_3Cl than in the Raman spectrum, for which reason the values of the centers of these bands found from the infrared spectrum are more reliable than those found from the Raman spectrum. The values of the frequencies ν_2, ν_3, ν_5, ν_6 given in Table 147 were obtained by Claassen [1117] from studies on the Raman spectrum, and the values of the frequencies ν_1 and ν_4 were obtained by Plyler and Benedict [3277] from an investigation of the infrared spectrum.

The purely rotational spectrum of the CF_3Cl molecule was studied with the help of microwave spectroscopy by Coles and Hughes [1156] who determined the values of the rotational constant B_0 for CF_3Cl^{35} (0.111262 cm^{-1}) and CF_3Cl^{37}(0.108458 cm^{-1}). On the basis of these data Coles and Hughes calculated the bond lengths of C-F (1.323 A) and C-Cl (1.765 A) in the CF_3Cl molecule assuming that all angles between the bonds are tetrahedral. In the following, Sheridan and Gordy [3704] recalculated the bond lengths of C-F (1.328 ± 0.005 A) and C-Cl (1.740 ± 0.018 A) from values of B_0 for CF_3Cl^{35} and CF_3Cl^{37} found in the work [1156], assuming $\angle F - C - F = 108 \pm 1°$ on the basis of electron diffraction data and the structural parameters of the CF_3Br CF_3I and CF_3CN molecules found by them from microwave spectra.

The values of the structural parameters of the CF_3Cl molecule were also determined on the basis of results of electron diffraction studies [877, 665]. Bowen [877] applied a visual method of analyzing an electron diffraction pattern with 11 maxima and obtained the following values of the structural parameters of CF_3Cl: $r_{C-F} = 1.323 \pm 0.032$, $r_{C-Cl} = 1.747 \pm 0.4$ A, $\angle F - C - F = 108°30'$. Bartell and Brockway [665] applied the sectio microphotometric method and obtained data on the structure of CF_3Cl that are essentially more accurate: $r_{C-F} = 1.328 \pm 0.002$, $r_{C-Cl} = 1.751 \pm 0.004$ A, $\angle F - C - F = 108°36' \pm 24'$. In the work [665] it was shown that the values of the structural parameters of the CF_3Cl molecule found from electron diffraction measurements are in very good agreement with the values of these quantities as calculated from the rotational constants B_0 of the CF_3Cl^{35} and CF_3Cl^{37} molecules found by Coles and Hughes [1156] if $\angle F - C - F = 108°36'$, is assumed.

The value of the product of the principal moments of inertia of the CF_3Cl molecule given in Table 147 was calculated from the structural parameters found by Bartell and Brockway [665].

$\underline{CF_3Br}$. The infrared spectrum of gaseous bromotrifluoro methane was investigated by Plyler and Acquista [3271] with the help of prism spectrometers in the range from 330-5000 cm^{-1}, by Polo and Wilson [3293] in the range from 625-4000 cm^{-1} and by McGee, Cleveland et al [2705, 2706], in the range from 400-2220 cm^{-1}. The assignment of the observed bands given by these research workers was rendered more precise and supplemented in the following by studies on the infrared spectrum of gaseous bromotrifluoro methane and the Raman spectrum of liquid bromotrifluoro methane carried out by Edgell and May [1460, 1458], and by a study on the Raman spectrum of gaseous bromotrifluoro methane carried out by Taylor [3955].

The whole set of values of the fundamental frequencies of the CF_3Br molecule was obtained in studies on the Raman spectra [1460, 3955]. The lowest fundamental frequencies ν_6 and ν_3 were not observed in the investigation of the infrared spectrum*; in the works [3293, 2705, 1460] they were calculated from the frequencies of the corresponding overtones. Nevertheless, the values of the corresponding fundamental frequencies of the CF_3Br molecule found in the aforementioned investigations are slightly different. Table 147 shows the values of the fundamental frequencies of the CF_3Br molecule adopted in the present Handbook. For the frequencies ν_6 and ν_3 the values obtained by Edgell and May [1460] and Taylor [3955] from studies of the Raman spectra of bromotrifluoro methane were adopted. For the frequency ν_5 a value obtained by Polo and Wilson [3293] in the investigation of the infrared spectrum of the gas and by Edgell and May [1460] from studies on the Raman spectrum of the liquid was adopted. The values of the frequency ν_5 obtained in other investigations of the vibrational spectra of CF_3Br differ from the adopted value in the limits of ±2 cm^{-1}. For the frequency ν_2 a value was adopted that had been obtained in the Raman spectrum of the gas by Taylor [3955] who used a three-prism spectrometer with a dispersion in 15 A/mm. Plyler and Acquista [3271] and Edgell and May [1460] found the Q branch of this band at 761 cm^{-1} in the infrared spectrum of the gas. The values of the frequencies ν_4 and ν_1 adopted in Table 147 were determined by Edgell and May [1460] and Plyler and Acquista [3271] by studies on the infrared spectrum of the gas. The errors of the adopted values of the fundamental frequencies of the CF_3Br molecule can be estimated within ±3 cm^{-1}.

An investigation of the purely rotational spectrum of the CF_3Br molecule by the methods of microwave spectroscopy was carried out by Sharbaugh, Pritchard and Madison [3692] and by Sheridan and Gordy [3704]. In the mentioned studies the values of the rotational constant B_0 of the CF_3Br^{79} (0.699836 cm^{-1}) and CF_3Br^{81} (0.693312 cm^{-1}) molecules were determined with high accuracy. On the basis of these data Sheridan and Gordy [3704] determined the following values of the structural parameters of the CF_3Br molecule: $r_{C-F} = 1.330 \pm 0.005$, $r_{C-Br} = 1.908 \pm 0.018$ A, $\angle F - C - F = 108 \pm 1°$ which are used to calculate the product of the principal moments of inertia of the CF_3Br molecule in the present Handbook (see Table 147).

The structural parameters of the CF_3Br molecule were also determined by Bowen [877] and Anderson [552] on the basis of results of electron diffraction studies carried out by them. The values of the structural parameters CF_3Br($r_{C-F} = 1.343 \pm 0.01$, $r_{C-Br} = 1.911 \pm$ $\pm\ 0.033$ A, $\angle F - C - F = 109.5 \pm 2°$ [877] and $r_{C-F} = 1.325 \pm 0.005$, $r_{C-Br} = 1.910 \pm 0.06$ A, $\angle F - C - F = 109.2 \pm 0.5°$) obtained in these works are in agreement with each other and with the values found by Sheridan and Gordy [3704].

CF_3I. The infrared spectrum of gaseous iodotrifluoro methane was studied in the works [3271, 2706, 3293, 2705, 1460, 1452]. The Raman spectrum was investigated only for liquid iodotrifluoro methane in the works [1460, 3955].

The fundamental frequencies ν_3 and ν_6 in the infrared spectrum of CF_3I were not observed immediately. The values of these frequencies were estimated equal to 286 cm^{-1} [1460, 2705] and 290 cm^{-1} [3293] for ν_3 and 265 cm^{-1} [1460, 3293] and 260 cm^{-1} [2705] for ν_6 from the overtones and the composite frequencies. In the limits of 2 cm^{-1} these values coincide with those found from the Raman spectrum of liquid CF_3I. The values of other fundamental frequencies obtained in the works of various authors are in good agreement with each other.

In the present Handbook the values determined from the infrared spectrum of gaseous iodotrifluoro methane by Edgell and May [1460] are adopted for the fundamental frequencies of the CF_3I molecule (see Table 147).

The purely rotational spectrum of the $C^{12}F_3^{19}I^{129}$ molecule was studied by the methods of microwave spectroscopy by Sheridan and Gordy [3704] and Sterzer [3849], who determined the value of the rotational constant $B_0 = 1523.23$ Mc or 0.0508093 cm^{-1}.

For the first time, the structural parameters of the CF_3I molecule were determined by Sheridan and Gordy [3704] on the basis of results of a study on the microwave spectra of CF_3I and other compounds. In the work [3704] $r_{C-F} = 1.332$ A, $\angle F - C - F = 108 \pm 1°$ was adopted for CF_3I and on the basis of the value of B_0 given above $r_{C-I} = 2.134 \pm 0.016$ A was calculated. These values of the structural parameters were soon verified by electron diffraction investigations carried out by Bowen [877](r_{C-F} = 1.328 ± 0.026, r_{C-I} = 2.122 ± 0.037 A, ∠F – C – – F = 108°18' ± 2°), Anderson [552] (r_{C-F} = 1.332 ± 0.004, r_{C-I} = = 2.130 ± 0.008 A, ∠F – C – F = 108.3 ± 1°) and by Wong and Schomaker [4316] (r_{C-F} = 1.334, r_{C-I} = 2.137 A, ∠F – C – F = 108°12'). In the work [4316] a rotating sector and the value of the constant B_0 found from the microwave spectrum were used.

The values of the structural parameters that were found by Sheridan and Gordy [3704] were adopted for CF_3I in the Handbook; with the help of these parameters the product of the principal moments of inertia of the CF_3I molecule given in Table 147 was calculated.

$\underline{CFCl_3}$. The Raman spectrum of gaseous chlorotrifluoro methane was studied by Claassen [1117] and that of liquid one by Delwaulle and Francois [1303], Glockler and Leader [1774], and By Zietlow, Cleveland and Meister [4388].

The infrared spectrum of gaseous $CFCl_3$ obtained in prism spectrometeers was investigated in the range from 300-3200 cm^{-1} [3974, 3277, 769]. In the works by Thompson and Temple [3974], Bernstein, Zietlow and Cleveland [769] the fundamental frequencies ν_1, ν_2 and ν_3 were measured. Plyler and Benedict [3277] succeeded in measuring two low frequencies ν_3 and ν_5 in the infrared spectrum of $CFCl_3$. The fundamental frequency ν_6 was determined only from the Raman spectrum.

The values of the fundamental frequencies of $CFCl_3$ found from studies on the infrared spectrum and the Raman spectrum by various authors agree in the limits of 75 cm^{-1}. In the present Handbook the values of the fundamental frequencies of $CFCl_3$ recommended by Claassen [1117] (see Table 147) are adopted.

The microwave spectrum of $CFCl_3$ was investigated by Long, Williams and Weatherly [2643]. On the basis of the very accurately measured frequencies of the purely rotational transitions of the $CFCl_3^{35}$ (I = 1 →

→ 2) and $CFCl_2^{35}Cl^{37}$ ($I_\tau = 1_0 \rightarrow 2_1$ and $I_\tau = 1_{-1} \rightarrow 2_0$) molecules, the authors calculated the values of the rotational constants A_0 and B_0 of these molecules (for $CFCl_3^{35}$ $A_0 = B_0 = 2465.39$ Mc $= 0.0822364$ cm^{-1} and for $CFCl_2^{35}Cl^{37}$ $A_0 = 2463.22$ Mc $= 0.0821640$ cm^{-1}, $B_0 = 2398.50$ Mc $= 0.0800052$ cm^{-1}).

The structural parameters of the $CFCl_3$ molecule were determined by analyzing the results of electron diffraction studies [955, 956, 4333] and investigating the microwave spectrum [2643]. In these works the same values were obtained for the C-Cl bond length (1.76 A) but different values for the C-F bond lengths and the angle of Cl-C-Cl. Electron diffraction studies led to the values $r_{C-F} = 1.40 \pm 0.04$ A [955, 956] and 1.44 ± 0.04 A [4333] and to the values $\angle Cl - C - Cl = 111.5 \pm 1°$ [955, 956] and 113°18' [4333]. The results of studies on the microwave spectrum of $CFCl_3$, however, led to the values $r_{C-F} = 1.33$ A and $\angle Cl - C - Cl = 109°40'$. The value of the C-F bond length in the $CFCl_3$ molecule obtained in the work [2643] is not more reliable than the values found as a result of electron diffraction studies. In order to obtain the value of r_{C-F} in the work [2643] the slight dependence of the constants A_0 and B_0 on the $CFCl_2^{35}Cl^{37}$ molecule on this quantity and the assumption that the structural parameters of the $CFCl_3^{35}$ and $CFCl_2^{35}Cl^{37}$ molecules are identical were used. The latter assumption would be rigorous if the equilibrium values of the rotational constants were known. A C-F bond length equal to 1.38 A is characteristic of molecules of halogen substitution products of methane with one fluorine atom (see Table 145). Consequently, the values of the structural parameters of the $CFCl_3$ molecule found by Brockway as a result of an electron diffraction study must be considered most satisfactory [955, 956]: $r_{C-F} = 1.40 \pm 0.04$, $r_{C-Cl} = 1.76 \pm 0.02$ A, $\angle Cl - C - Cl = 111.5 \pm 1°$.

The value of the product of the principal moments of inertia of $CFCl_3$ given in Table 147 was calculated by means of the value of the rotational constant B_0 of the $CFCl_3^{35}$ molecule (in the calculation of $I_A = I_B$) obtained in the work [2643] and by means of the values of the structural parameters, obtained by Brockway [955, 956] (in the calculation of I_C).

$\underline{CFBr_3}$. The values of the fundamental frequencies of the $CFBr_3$ molecule are well-known from a work by Delwaulle and Francois [1303] who studied the Raman spectrum of liquid fluorotribromo methane. The correctness of the frequency assignment carried out in the work [1303] is verified by polarization measurements, a comparison with the fundamental frequencies of other fluorine and bromine substitution products of methane, but also by calculating the frequencies by means of the force constants as were carried out in the work [2849]. The values of the fundamental frequencies of the $CFBr_3$ molecule found in the work [1303] were adopted in the present Handbook and are given in Table 147.

An electron diffraction investigation of the $CFBr_3$ molecule structure was carried out by Wouters and de Hemptinne [4333] who obtained $r_{C-F} = 1.44 \pm 0.06$, $r_{C-Br} = 1.91 \pm 0.02$ A, $\angle Br - C - Br = 113°48'$. The method of studying the molecular structure of $CFBr_3$ by electron diffraction in the work [4333] was not perfect, for which reason the values of the structural parameters of $CFBr_3$ obtained in this work are not accurate. The data on the structural parameters of the molecules of halogen substitution products obtained later on by more reliable methods permit the determination of more satisfactory values of these quantities for $CFBr_3$. The calculation of the product of the principal moments of inertia of $CFBr_3$ given in Table 147 was carried out under the assumption that the angles between the bonds in the $CFBr_3$

molecule are tetrahedral and the C-F and C-Br bond lengths are equal to (see Table 145): $r_{C-F} = 1.38 \pm 0.03$, $r_{C-Br} = 1.93 \pm 0.03$ A.

$\underline{CCl_3Br}$. The vibrational spectrum of CCl_3Br was only studied for liquid bromotrichloro methane and its solutions. The Raman spectrum of CCl_3Br was studied by Wouters [4332], Delwaulle and Francois [1302] Zietlow, Cleveland and Meister [4388]. The infrared spectrum of CCl_3Br was studied in the range from 300-2300 cm^{-1} in the works [2582, 3277, 2726].

The values of the fundamental frequencies of the CCl_3Br molecule obtained by various authors agree in the limits of 10 cm^{-1}. Without giving the preference to anyone of the works the mean values of the fundamental frequencies obtained in the works [3277, 2726, 4388, 1302] are adopted in the Handbook (see Table 147). We must point out the possibility of a Fermi resonance between the frequencies $\nu_2 + \nu_5$ and ν_4, as mentioned by Zietlow et al [4388].

The structural parameters of the CCl_3Br molecule were determined by electron diffraction studies [1057, 61]. In the work [1057] less accurate values of these quantities are obtained than in the work [61]. In the last work carried out by Akishin et al. under the assumption that $r_{C-Cl} = 1.76$ A, $r_{C-Br} = 1.93 \pm 0.02$ A and $\angle Cl - C - Cl = 109.5 \pm \pm 2°$ was obtained. These values of the structural parameters of CCl_3Br are adopted in the present Handbook, taking into account the fact that the inaccuracy of the value of r_{C-Cl} adopted in the work [61] amounts to ±0.01 A, such that the inaccuracies of the given values of r_{C-Br} and $\angle Cl - C - Cl$ amount to ±0.03 A and ±2.5°, respectively. The values of the structural parameters of CCl_3Br recommended in the work [61] were used to calculate the product of the moments of inertia whose value is given in Table 147.

$\underline{CClBr_3}$. The Raman spectrum [2582, 1302, 2849] and the infrared spectrum [2582, 3285, 2849] were only obtained for liquid chlorotribromo methane and its solutions in CS_2, CCl_4 and C_6H_6.

The infrared spectrum of $CClBr_3$ was studied in the range of wave numbers higher than 300 cm^{-1}, on account of which the frequencies ν_3, ν_5 and ν_6 in the infrared spectra of liquid chlorotribromo methane were not observed.

Six intense lines which Delwaulle and Francois [1302] identified with six fundamental frequencies were found in the Raman spectrum of $CClBr_3$. According to calculations carried out by Simanouti [3725] and Meister and Voelz [2850] two fundamental frequencies * must, however, have values close to 211 cm^{-1}. Meister, Rosser and Cleveland [2849] mention the great width of the line at 211 cm^{-1} as well as the fact that the degree of depolarization of this line is abnormally high for a totally symmetric vibration. For all these reasons, Meister, Rosser and Cleveland ascribed the value of 211 cm^{-1} to the fundamental frequencies ν_3 (A_1) and ν_5 (E). The authors of the work [2849] identified the line observed in the Raman spectrum at 269 cm^{-1} with the overtone frequency $2\nu_6$. The values of the fundamental frequencies of $CClBr_3$ recommended in the works [2849, 2850] are adopted in the present Handbook and given in Table 147.

Experimental determinations of the structural parameters and rotational constants of the $CClBr_3$ molecule were not carried out.

The product of the principal moments of inertia of $CClBr_3$ given in Table 147 was calculated on the basis of the following values of the structural parameters: $r_{C-Cl} = 1.77 \pm 0.03$, $r_{C-Br} = 1.93 \pm 0.03$ A, $\angle Br - C - Br = \angle Cl - C - Br = 109°28' \pm 4°$ (see Table 145).

§64. MOLECULES OF THE CX_2Y_2 TYPE

The CX_2Y_2 type molecules of the halogen substitution products of methane belong to the point group symmetry C_{2v} ($\sigma = 2$) and prove to be asymmetric gyroscopes. Such molecules have nine fundamental frequencies: four frequencies of totally symmetric vibrations of the type A_1 (ν_1, ν_2, ν_3, ν_4), one frequency of an antisymmetric vibration of the A_2 (ν_5) type, two frequencies of vibrations of the B_1 (ν_6, ν_7) type, and two frequencies of the B_2 (ν_8, ν_9) type. None of the vibrations are degenerate. All nine fundamental frequencies are active in the Raman spectrum: in the infrared spectrum all frequencies are active except for the frequency ν_5. In the Raman spectrum, polarized lines correspond to vibrations of the A_1 type, and depolarized ones to the other vibrations.

In the present Handbook, only CCl_2I_2 and CBr_2I_2 are not considered among the CX_2Y_2 type halogen substitution products of methane since these compounds are unstable and have not as yet been investigated.

$\underline{CH_2F_2}$. The infrared spectrum of gaseous methylene fluoride was studied by Stewart and Nielsen [3865] in the range from 1000-4000 cm^{-1} Plyler and Benedict in the range from 408-5000 cm^{-1} and Porto [3310] in the range from 4000-10,000 cm^{-1}. Rank, Shull and Pace [3383], Delwaulle and Francois [1305], Glockler and Leader [1775] and Wagner [4124] investigated the Raman spectrum of liquid methylene fluoride. The Raman spectrum of gaseous methylene fluoride was not investigated. The vibrational spectra of the deuteron substitution products of methylene fluoride were also not studied. The fundamental frequencies of the $CHDF_2$ and CD_2F_2 molecules were calculated by Meister et al [2848] by making use of the force constants obtained from the fundamental frequencies of the CH_2F_2 molecule and other molecules of the halogen substitution products of methane.

Stewart and Nielsen [3865] resolved the rotational structure of the ν_4, ν_6, ν_7, ν_8 and ν_9 bands of CH_2F_2 molecule using instruments with Wood difrraction gratings and determined the positions of the centers of these bands. Owing to the fact that the ν_1 and ν_3 bands are partly overlapped by other bands the positions of their centers were determined less accurately by Stewart and Nielsen. The frequencies $\nu_5 = 1262$ and $\nu_2 = 1508$ cm^{-1} in the work [3865] were adopted on the basis of data [3383] on the Raman spectrum since the corresponding bands in the infrared spectrum were not observed. The band at 1508 cm^{-1}, which according to polarization measurements carried out by Rank, Shull and Pace [3383] belongs to a totally symmetric vibration must be active in the infrared spectrum. Plyler and Benedict [3277] remark that probably has a low intensity in the infrared spectrum and is masked in this range by the absorption of water vapor. The 1262 cm^{-1} line in the Raman spectrum [3383] is strongly depolarized and belongs to the frequency ν_5, which is not active in the infrared spectrum. Plyler and Benedict [3277] observed a weak band at 1262 cm^{-1} and explained this fact by a violation of the selection rule either on account of a Coriolis interaction between the frequencies ν_5 and ν_7 or on account of a strong intermolecular interaction. The assignment of frequencies adopted in the works [3277, 3383] is verified by a calculation of the frequencies of CH_2F_2 with the help of the force constants [2848].

Table 148 shows the values of the fundamental frequencies of the CH_2F_2 molecule adopted in the present Handbook. The values found by Rank et al [3383] by investigating the Raman spectrum of liquid methylene fluoride were adopted for ν_2 and ν_5, whereas the values found by Stewart and Nielsen [3865] from a study on the infrared spectrum of gaseous methylene fluoride were adopted for the rest of the fundamental frequencies.

Stewart and Nielsen [3865] and Nielsen [3310] carried out an approximate analysis of the rotational structure of the bands in the infrared spectrum of CH_2F_2. The purely rotational transitions of the CH_2F_2 molecule in the fundamental vibrational state were analyzed by Lide [2610, 2609] on the basis of the microwave spectrum. The values of the rotational constants (A_0 = 1.63908, B_0 = 0.35371, C_0 = 0.30851 cm^{-1}) found by Lide [2610] were used to calculate the product of the principal moments of inertia of CH_2F_2, the value of which is given in Table 148.

TABLE 148

Adopted Values of the Molecular Constants of the Halogen Substitution Products of Methane of Type CX_2Y_2 ($\sigma = 2$)

A Молекула	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	$I_A I_B I_C$ B
	$см^{-1}$									10^{-117} $(г\cdot см^2)^3$
CH_2F_2	2949	1508	1116	528,6	1262	3015,2	1176,1	1435,4	1089,7	122,58
CH_2Cl_2	2995,7	1430,1	712,9	281,5	1153	3040	893	1262	748	1870,5
CH_2Br_2	3008	1402	591	174	1091	3061	810	1195	648	15998
CH_2J_2 C	2967	1350	486	121	1030	3050	716	1107	572	74877
CF_2Cl_2	1098	667,2	454,2	261,5	322	922	435,3	1159	447,4	25848
CF_2Br_2	1090	623	340	165	282	1153	367	831	330	169320
CF_2J_2	—	—	—	—	—	—	—	—	—	676170
CCl_2Br_2	746	380	242	154	175	698	230	731	262	582650

A) Molecule; B) $(g\cdot cm^2)^3$; C) J = Iodine.

The structural parameters of the CH_2F_2, molecule were calculated by Lide [2610] on the basis of the results of analyzing the microwave spectrum of $C^{12}H_2F_2$ and $C^{13}H_2F_2$: r_{C-F} = 1.358 ± 0.001, r_{C-H} = 1.092 ± ± 0.003 A, ∠F – C – F = 108°17' ± 6', ∠H – C – H = 111°52' ± 25'. Similar values of r_{C-F} and ∠F – C – F were found by electron diffraction studies on the structure of the CH_2F_2 molecule in the works [2627, 1941] and on the basis of an analysis of the rotational structure of the bands in the infrared spectrum [3310].

$\underline{CH_2Cl_2}$. The vibrational spectra of methylene chloride were investigated by Plyler and Benedict [3277, 3278] (infrared spectrum) and Nielsen and Ward [3093], Rao [3398], Welsh et al [4202] (Raman spectrum). The results of the studies on the vibrational spectra of liquid methylene chloride carried out up to 1945 are considered in a monograph by Herzberg [152]. The vibrational spectra of the deuteron substitution products of methylene chloride were not studied.

Only three bands corresponding to the frequencies ν_1, ν_3 and ν_4 were observed in earlier investigations of the Raman spectrum of gaseous methylene chloride carried out by Nielsen and Ward [3093] and Rao [3398]. The differences in the values of the frequencies ν_3 and ν_4 found in these works do not exceed 5 cm^{-1}, whereas the difference in the values of the frequency ν_1 amounts to 14 cm^{-1}. A more perfect investigation of the Raman spectrum of gaseous methylene chloride was carried out by Welsh, Crawford, Thomas and Love [4202]. They observed bands corresponding to eight fundamental frequencies of CH_2Cl_2 (only the band ν_8 was not observed), and studied the shape of the band outlines, which in connection with the results of polarization measurements permitted a more accurate assignment of the bands to the oscillation frequencies of the CH_2Cl_2 molecule. The authors of the work [4202] estimate the accuracy of the determined values of the fundamental frequencies of CH_2Cl_2 between ± 0.4 and ± 2 cm^{-1}.

Plyler and Benedict studied the infrared spectrum of gaseous methylene chloride in the range from 500-5000 cm^{-1} with a prism spectrometer [3277] and in the range from 4340-6250 cm^{-1} with a diffraction grating spectrometer [3278]. In the work [3277] the values of all fundamental frequencies of the CH_2Cl_2 molecule were determined from the spectrum of the liquid and the values of the frequencies ν_2, ν_4, ν_5 and ν_9 from the spectrum of the gas. The latter values are not accurate since they differ by 10-30 cm^{-1} from the values of the corresponding frequencies as determined in the works [3097, 3398, 4202] from the Raman spectrum of gaseous methylene fluoride.

Table 148 shows the values of the fundamental frequencies of the CH_2Cl_2 molecule adopted in the present Handbook. For the frequency ν_8 a value found by Plyler and Benedict [3277] from a study on the infrared spectrum of liquid methylene fluoride was adopted. For the rest of the frequencies the values found by Welsh et al [4202] from a study on the Raman spectrum of gaseous methylene fluoride were adopted.

On the basis of an investigation of the rotational structure of the bands in the infrared spectrum of CH_2Cl_2 in the range from 4340--6250 cm^{-1} Plyler and Benedict [3278] determined the magnitude of $A'' - B'' + C'' = 0.955\ cm^{-1}$.

The values of the rotational constants of seven isotopic modifications of the CH_2Cl_2 molecule were determined with high accuracy by Myers and Gwinn [3015] on the basis of a careful investigation of the microwave spectrum. Using all these data Myers and Gwinn calculated the values of the structural parameters of the CH_2Cl_2 molecule and with the help of diagrams picked out the set values of these parameters whose dependence on the character of the isotopic substitution would be minimum owing to the zero-point vibrations. The effective value of the structural parameters of the CH_2Cl_2 molecule found in this way in the work [3015] are equal to: $r_{C-Cl} = 1.7724 \pm 0.0005$, $r_{C-H} = 1.068 \pm 0.005$ A, $\angle Cl - C - Cl = 111°47' \pm 1$, $\angle H - C - H = 112°0' \pm 20'$. These values of the structural parameters of the CH_2Cl_2 molecule agree with the results of electron diffraction studies on the molecular structure of methylene chloride [100, 101]: $r_{C-Cl} = 1.77 \pm 0.02$ A, $\angle Cl - C - Cl = 112 \pm 2°$. The value of the valence angle Cl – C – Cl found in the work [3015] from the rotational constants of the isotopic modifications of CH_2Cl_2 was verified by calculations of Myers and Gwinn based on the use of the correlation between the structures of the $CH_2Cl^{35}_2$ and $CD_2Cl^{35}_2$ molecules and on the use of the value of the constants of the quadrupole bond between the chlorine nuclei in these molecules as found by them from the microwave spectrum.

The value of the product of the principal moments of inertia of the CH_2Cl_2 molecule given in Table 148 was calculated with the help of the values of the structural parameters found in the work [3015].

$\underline{CH_2Br_2}$. The vibrational spectra of liquid methylene bromide were studied in the works [595, 1299, 4124, 1784, 2458, 4024] (Raman spectrum) and [632, 3285, 635, 3278, 1482] (infrared spectrum). The Raman spectrum of gaseous methylene bromide was investigated by Nielsen and Ward [3093], and the infrared spectrum of gaseous methylene bromide by Plyler et al [3277, 3285, 3278]. The studies on the vibrational spectra of methylene bromide were carried out with low-dispersion instruments. An exception is only the investigation of the infrared spectrum of gaseous methylene bromide in the range from 4340-6250 cm^{-1}, carried out by Plyler and Benedict [3278] with a diffraction grating spectrometer. The vibrational spectra of the deuteron substitution products of methylene bromide were not studied. The values of the fundamental frequencies of the isotopic $CHDBr_2$ and CD_2Br_2 molecules were calculated by Dowling and Meister [1397] from the force constants obtained from the experimental values of the fundamental frequencies of CH_2Br_2 and other halogen substitution products of methane.

The values of the fundamental frequencies of the CH_2Br_2 molecule found in various works are in good agreement with each other. Dowling and Meister [1397] considered the results of studies on the vibrational spectra of methylene bromide obtained by different authors and indicated the most probable values, by their opinion, of the fundamental frequencies of the CH_2Br_2 molecule.

Table 148 shows the values of the fundamental frequencies of the CH_2Br_2 molecule adopted in the present Handbook. The values of the frequencies ν_1, ν_2, ν_3, ν_7, ν_8, ν_9 were obtained in the works [3093, 3285] from a study on the vibrational spectra of gaseous methylene bromide. For the frequencies ν_4, ν_5, ν_6, Table 148 shows mean values from the results of studies on the vibrational spectra of liquid methylene bromide.

The C-Br bond lengths and the angle between these bonds in the CH_2Br_2 molecule were determined by electron diffraction studies, carried out by Levy and Brockway [2599]($r_{C-Br} = 1.91 \pm 0.02$ A, $\angle Br - C - Br = 112 \pm 2°$) and Morino et al [2953 ($r_{C-Br} = 1.90 \pm 0.03$ A, $\angle Br - C - Br = 116 \pm 2°$). Assuming, according to [2599] $\angle Br - C - Br = 112°$, Plyler and Benedict [3278] calculated $r_{C-Br} = 1.907$ A on the basis of an analysis of the rotational structure of the bands in the infrared spectrum of CH_2Br_2. The electron diffraction investigation of the structure of the CH_2Br_2 molecule was, however, carried out by imperfect methods in the works [2599, 2953], for which reason the values of r_{C-Br} and $\angle Br - C - Br$ are not accurate. Studies on the molecular structure of the halogen substitution products of methane and the halogen substitution products of other hydrocarbons carried out in the following showed that for these compounds the C-Br bond length must have a value close to 1.93 A (see [3916] and §61).

The following values of the structural parameters are adopted in the present Handbook for CH_2Br_2, in accordance with Table 145: $r_{C-Br} = 1.93 \pm 0.03$, $r_{C-H} = 1.10 \pm 0.03$ A, $\angle Br - C - Br = \angle H - C - H = 109°28' \pm 4°$, which are used in the calculation of the product of the principal moments of inertia, given in Table 148.

<u>CH_2I_2</u>. The vibrational spectra of liquid methylene iodide were investigated with low-dispersion prism spectrometers. The Raman spectrum was investigated in the works [595, 4124, 2458, 4024, 4114] and the infrared spectrum in the works [3277, 635, 1482, 632, 4114]. The vibra-

tional spectra of the deuteron substitution products of methylene iodide were not studied. The results of the studies on the vibrational spectra of methylene iodide in various works were analyzed by Voelz, Cleveland and Meister [4114] and compared with the results of their own investigation. The differences in the values of the fundamental frequencies of the CH_2I_2 molecule, obtained by various investigations, do not exceed 5 cm^{-1}. A comparison of the fundamental frequencies of the CH_2Br_2 molecule obtained by investigating the vibrational spectra of liquid and gaseous methylene bromide shows that the influence of the intermolecular interaction in liquid methylene iodide on the values of the oscillation frequencies is smaller than the accuracy in the determination of these quantities from the existing spectra data.

Table 148 shows the values of the fundamental frequencies of the CH_2I_2 molecule adopted in the present Handbook. The results of an investigation of the vibrational spectra of methylene iodide obtained in the works [4114, 4124, 1482, 3277] were the basis on which these values were adopted. The errors in the adopted values of the fundamental oscillation frequencies of the CH_2I_2 molecule may be estimated within the limits of ± 2 cm^{-1} for frequencies below 1000 cm^{-1} and within ± 4 cm^{-1} for frequencies above 1000 cm^{-1}.

The structure of the CH_2I_2 molecule was studied using electron diffraction methods by Brockway [100, 101] and Bastiansen [675]. Brockway [100, 101] was aware of the fact that the value of the C-I bond length equal to 2.28 A he had obtained was very inaccurate. Bastiansen [675] carried out a more perfect investigation of the molecular structure of CH_2I_2 making use of a rotating sector and obtained $r_{C-I} = 2.14 \pm 0.04$ A, $\angle I - C - I = 114°42'$. But also Bastiansen's reseults are not exact anough and require verification.

In the present Handbook the values of the C-H and C-I bond lengths given in Table 145 were used to calculate the product of the principal moments of inertia of the CH_2I_2 molecule given in Table 148, and the angles between the bonds were assumed to be identical and equal to 109°28'.

$\underline{CF_2Cl_2}$. The Raman spectrum of liquid Freon-12 was studied by Bradley [886] and that of gaseous Freon-12 by Claassen [1117]. The infrared spectrum of gaseous Freon-12 was studied by Thompson and Temple [3974] in the range from 600-1800 cm^{-1}, Plyler and Benedict [3277] in the range from 400-3400 cm^{-1} and Hadni [1921] in the range from 420-480 cm^{-1}.

For the first time, an interpretation of the vibrational spectra of CF_2Cl_2 and an assignment of the fundamental frequencies were given by Thompson and Temple [3974] on the basis of Bradley's data [886] on the Raman spectrum of liquid Freon-12 and using their own data on the infrared spectrum of the gas. In the following, it turned out that the assignment of the fundamental frequencies of the CF_2Cl_2 molecule proposed in the work [3974] required essential corrections.

On the basis of a calculation of the frequencies from the force constants Plyler and Benedict [3277] showed that five fundamental frequencies must be smaller than 500 cm^{-1}, and only four fundamental frequencies must be greater than 600 cm^{-1}. An intense band at 882 cm^{-1} was interpreted as a composite frequency $\nu_3 + \nu_7$ in the work [3277], and its high intensity was ascribed to a Fermi resonance with a frequency $\nu_6 = 922$ cm^{-1}. In the range from 400-500 cm^{-1} Plyler and Benedict [3277] observed three weak bands at 437, 446 and 473 cm^{-1}, which they identified with the frequencies ν_7, ν_3 and ν_9. In the Raman spectrum Claassen [1117] observed intense lines at 433 and 457.5 cm^{-1}, which he identified with the frequencies ν_7 and ν_3. In view of the fact that in the Raman spectrum a line at 473 cm^{-1} was not observed, in the work [1117] Claassen adopted a value equal to 446 cm^{-1} for the frequency ν_9, it had been calculated from the force constants of CF_2Cl_2 by Dowling [1395], in accordance with a value of ν_9 calculated previously by Masey [2796] on the basis of experimental values of the specific heat of gaseous Freon-12.

In 1955, Hadni [1921] obtained the infrared spectrum of CF_2Cl_2 in the range from 420-480 cm^{-1} with a diffraction grating spectrometer. The great resolving power of the spectrometer permitted him to observe the rotational structure of the bands and to assign them more accurately. Hadni obtained the following values of the frequencies: $\nu_7 = 435.3$, $\nu_9 = 447.4$, $\nu_3 = 454.2$, $\nu_6 - \nu_4 = 472$ cm^{-1}; thus, he verified the interpretation of the vibrational spectra of CF_2Cl_2 given in the works [1117, 1395].

Table 148 shows the values of the fundamental frequencies of the CF_2Cl_2 molecule adopted in the present Handbook. For the frequencies ν_3, ν_7, ν_9 the values obtained by Hadni [1921], for the frequency ν_8 the value obtained by Plyler and Benedict [3277], and for the rest of the frequencies the values found from the Raman spectrum by Claassen [1117] were adopted.

Electron diffraction studies on the structure of the CF_2Cl_2 molecule were carried out by Brockway [955, 956], Livingston and Lyon [2629] and Kristoff [2488]. The least complete and accurate data on the structure of CF_2Cl_2 were obtained by Brockway [955, 956]: $r_{C-F} = 1.35 \pm 0.03$, $r_{C-Cl} = 1.74 \pm 0.03$ A. Livingston and Lyon [2629] applied the sector-visual method of electron diffraction and obtained: $r_{C-F} = 1.335 \pm 0.02$, $r_{C-Cl} = 1.775 \pm 0.02$ A, $\angle F - C - F = 109.5 \pm 3°$, $\angle Cl - C - Cl = 108.5 \pm 2°$. The values of the structural parameters of the CF_2Cl_2 molecule obtained in the work [2629] were used in the present Handbook to calculate the product of the principal moments of inertia (see Table 148).

In 1958, the values of the structural parameters of the CF_2Cl_2 molecule were made somewhat more accurate by Kristoff [2488], who applied the sector microphotometric method of measurements. In the work [2488] the following values of the structural parameters of the CF_2Cl_2 molecule are given: $r_{C-F} = 1.338 \pm 0.013$, $r_{C-Cl} = 1.775 \pm 0.013$ A, $\angle F - C - F = 109.5 \pm 2°$, $\angle Cl - C - Cl = 109.5 \pm 1°$.

<u>CF_2Br_2</u>. The fundamental frequencies of the CF_2Br_2 molecule are known on the basis of an investigation of the Raman spectrum of liquid dibromodifluoro methane [1776, 1303, 1284] and of the infrared spectrum of gaseous dibromodifluoro methane [1284, 1282, 3271] in the range from 400-4000 cm^{-1}. The values of the fundamental frequencies of the CF_2Br_2 molecule obtained by different authors differ from each other within the limits of 3 cm^{-1}.

The values of the fundamental frequencies of the CF_2Br_2 molecule adopted in the present Handbook and given in Table 148 were determined by Decker, Meister, Cleveland and Bernstein [1284] on the basis of studies on the Raman spectrum of liquid dibromodifluoro methane (ν_3, ν_4, ν_5, ν_7, ν_9) and on the basis of studies on the infrared spectrum of gaseous dibromodifluoro methane (ν_1, ν_2, ν_6, ν_8).

The structural parameters of the CF_2Br_2 molecule were not determined experimentally. The value of the product of the principal moments of inertia of CF_2Br_2 given in Table 148 was calculated with the help of the following values of the structural parameters: $r_{C-F} = 1.35$, $r_{C-Br} = 1.93$ A, $\angle F - C - F = \angle Br - C - Br = 109°28'$ (see §61, Table 145). The errors in the adopted values of the C-F and C-Br bond lenghts are estimated within the limits of ± 0.03 A and those of the valence angles within $\pm 4°$.

<u>CF_2I_2</u>. The spectra and the structure of the diododifluoro methane

molecule were not studied. The values of the fundamental frequencies of the CF_2I_2 molecule can only be estimated very roughly. The thermodynamic functions of gaseous diiodo-difluoro methane can, however, be estimated without carrying out such estimates (see page 1082).

Using the results of studies on the molecular structure of the remaining halogen substitution products of methane it can be verified that the C-F and C-I bond lengths in the CF_2I_2 molecule have values close to those shown in Table 145, and that the angles between the bonds are close to tetrahedral ones. The value of the product of the principal moments of inertia of the CF_2I_2 molecule given in Table 148 was calculated under the assumption of the following values of the structural parameters: $r_{C-F} = 1.35$, $r_{C-I} = 2.15$ A, $\angle F - C - F = \angle I - C - I = 109°28'$. The errors in the adopted values of the C-F and C-I bond lengths can be estimated within the limits of ±0.03 A and those of the angles between the bonds within ±4°.

$\underline{CCl_2Br_2}$. The fundamental frequencies of the CCl_2Br_2 molecule were determined on the basis of studies on the Raman spectrum [2582, 1302, 1273] and on the infrared spectrum of liquid dichloro-dibromo methane [2582, 3269, 3277], but also on the infrared spectrum of gaseous dichloro-dibromo methane [1273]. The vibrational spectra obtained for dichloro-dibromo methane and their interpretation were considered by Davis, Cleveland and Meister [1273].

The values of the fundamental frequencies of the CCl_2Br_2 molecule obtained by the authors of the works [1302, 1273, 3277] are in good agreement with each other. In the work [2582] clearly too low values were obtained for the fundamental frequencies of CCl_2Br_2, which is explained (see [1273]) by insufficient purification of the dichloro-dibromo methane specimen under investigation.

The values of the fundamental frequencies of the CCl_2Br_2 molecule recommended by Davis, Cleveland and Meister [1273] and given in Table 148 are adopted in the present Handbook. For the frequencies ν_1, ν_6 and ν_8 the values determined from the infrared spectrum of gaseous dichloro-dibromo methane, and for the rest of frequencies the values determined from the spectra of liquid dichloro-dibromo methane were adopted.

An electron diffraction investigation of the structure of the CCl_2Br_2 molecule was carried out in 1936 by Capron and Perlinghi [1058] who obtained: $r_{C-Cl} = 1.75$ and $r_{C-Br} = 1.93$ A.

The value of the product of the principal moments of inertia of CCl_2Br_2 given in Table 148 was calculated on the basis of the following values of structural parameters: $r_{C-Cl} = 1.77$, $r_{C-Br} = 1.93$ A, $\angle Cl - C - Cl = \angle Br - C - Br = 109°28'$ – in accordance with the data adopted in Table 145. The errors in the adopted values of the C-Cl and C-Br bond lengths may be estimated within ±0.03 A and those of the angles between the bonds within ±4°.

§65 MOLECULES OF THE CX_2YZ AND CXYZV TYPES

The molecules of the halogen substitution products of methane of the CX_2YZ and CXYZV types belong to the lower symmetry classes C_s and C_1 ($\sigma = 1$). They are asymmetric gyroscopes and have nine normal vibrations active both in the infrared spectrum and in the Raman spectrum.

The fundamental frequencies of the molecules of the CX_2YZ type belong to the A' and A" symmetry types: the frequencies ν_1, ν_2, ..., ν_6 belong to the A' symmetry type, and the rest to the A" symmetry type. In the Raman spectrum the lines corresponding to the fundamental frequencies of the A' type are polarized, and the other lines are depolarized.

In the present Handbook 18 halogen substitution products of methane of the CX_2YZ and one halogen substitution product of the CXYZV type

(CHFClBr) are considered.

CH_2FCl. The Raman spectrum of liquid fluoro-chloro methane was studied by Glockler and Bachman [1770] and Delwaulle and Francois [1305]. The infrared spectrum of gaseous fluoro-chloro methane was investigated by Plyler and Lamb [3282] and Porto [3310].

Plyler and Lamb [3282] obtained the infrared spectrum of CH_2FCl with a prism spectrometer in the range from 330-5000 cm^{-1} and with a diffraction grating spectrometer in the range from 3840-6600 cm^{-1}. Using the results of studies on the Raman spectrum of CH_2FCl obtained earlier and on the infrared spectra of CH_2F_2 and CH_2Cl_2, Plyler and Lamb assigned 25 bands observed in the infrared spectrum of CH_2FCl and determined the values of all fundamental frequencies of the molecule. In the work [3282] it is shown that the band at 1236 cm^{-1}, which has not been observed previously in the Raman spectrum, belongs to the fundamental frequency ν_8. Except for the frequencies ν_4 and ν_5, the values of the fundamental frequencies of the CH_2FCl molecule as determined from the infrared spectrum of the gas and from the Raman spectrum of the liquid coincide. The frequencies ν_4 and ν_5 corresponding to the valency and deformation vibrations of the CH_2 radical vary by about 20 cm^{-1} if liquid fluoro-chloro methane goes over into the gaseous state.

The values of the fundamental frequencies of the CH_2FCl molecule recommended by Plyler and Lamb [3282] on the basis of an analysis of the results obtained from a study on the infrared spectrum and the Raman spectrum of fluoro-chloro methane and adopted in the present Handbook are given in Table 149.

Porto [3310] investigated the rotational structure of three bands of CH_2FCl lying in the range from 4000-10,000 cm^{-1} and determined the value of A_0 as $1/2\ (B_0 + C_0) = 1.208 \pm 0.004$ cm^{-1}. Mueller [2970] studied the microwave spectrum of the CH_2FCl^{35} and CH_2FCl^{37} molecules. The values of the rotational constants of the molecules CH_2FCl^{35} (A_0 = = 1.39463, B_0 = 0.190655, C_0 = 0.173273 cm^{-1}) and CH_2FCl^{37} (A_0 = = 1.39223, B_0 = 0.186145, C_0 = 0.169503 cm^{-1}) are used in the present Handbook to calculate the product of the principal moments of inertia of CH_2FCl given in Table 149.

TABLE 149

Adopted Values of the Molecular Constants of the Halogen Substitution Products of Methane of the CX_2YZ and CXYZV Types (σ = 1)

Молекула [1]	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	$I_A I_B I_C$
	cm^{-1}									10^{-117} (г·см²)³ [2]
CH_2FCl [3]	2993	1470	1351	1068	760	385	3048	1236	1004	481,62
CH_2FBr	2993	1461	1313	1050	641	314	3053	1227	939	1160,6
CH_2FJ	—	—	—	—	—	—	—	—	—	2048,0
CH_2ClBr	2986	1421	1235	737	618	227	3053	1139	854	4727,8
CH_2ClJ	2979	1392	1126	718	527	194	3048	1183	801	8998,1
CH_2BrJ	2978	1374	1065	616	517	144	3053	1150	754	33267
CHF_2Cl	3023	1311	1178	809	595	422	1347	1116	365	3585,3
CHF_2Br	3013	1280	1135	718	577	240	1344	1108	323	8832,7
CHF_2J	—	—	—	—	—	—	—	—	—	15940
$CHFCl_2$	3023	1310	1079	742	458	276	1242	804	368	11708
$CHFClBr$	3023	1299	1060	655	426	220	1202	772	313	29648
$CHFBr_2$	3016	1294	1063	620	359	172	1170	704	296	86536
$CHCl_2Br$	3028	1177	734	597	330	220	1217	773	215	81521
$CHClBr_2$	3023	1191	756	576	279	168	1149	669	201	222280
CF_2ClBr	1102	872	648	400	380	200	1150	440	300	63976
CF_2ClJ	—	—	—	—	—	—	—	—	—	118400
CF_2BrJ	—	—	—	—	—	—	—	—	—	331470
$CFCl_2Br$	1069	779	501	334	303	215	825	390	203	142270
$CFClBr_2$	1063	790	462	340	267	160	746	306	195	345720

1) Molecule; 2) $(g \cdot cm^2)^3$; 3) J = Iodine.

The values of the structural parameters of the CH_2FCl molecule were determined by electron diffraction [955, 956] and from the results of an analysis of the microwave spectrum [2970]. The electron diffraction investigation of the molecular structure of CH_2FCl carried out by Brockway [955, 956] led to the following results: r_{C-F} = 1.40 ± ± 0.03, r_{C-Cl} = 1.76 ± 0.02 A, $\angle F-C-Cl$ = 110 ± 2°. By far more accurate values of the structural parameters of CH_2FCl were obtained by Mueller [2970] as a result of calculations based on the use of the afore-indicated values of the rotational constants of the CH_2FCl^{35} and CH_2FCl^{37} molecules and carried out on the assumption that the angle between the C-H bonds in the CH_2FCl molecule is equal to 111°56' (the mean of the values of the H – C – H angles in the CH_2F_2 and CH_2Cl_2 molecules). Thus, in the work [2970] Mueller obtained the following values of the structural parameters of the CH_2FCl molecule: $r_{C-H} = 1.078 \pm 0.005$, $r_{C-F} = 1.378 \pm 0.006$, $r_{C-Cl} = 1.759 \pm 0.003$ A, $\angle F - C - Cl = 110°1' \pm 2'$.

CH_2FBr:. The Raman spectrum of liquid bromo-fluoro methane was investigated by Delwaulle and Francois [1299, 1305]. On the basis of polarization measurements and a comparison of the observed frequencies of CH_2FBr with the values of the frequencies of the halogen substitution products of methane studied earlier the values of all fundamental frequencies of the CH_2FBr molecule were determined in the work [1299]. The infrared spectrum of bromo-fluoro methane was not studied.

The values of the fundamental oscillation frequencies of the CH_2FBr molecule obtained in the work [1299] are adopted in the present Handbook and given in Table 149. The errors in the values of these quantities are estimated within ± 5 cm^{-1}.

The values of the structural parameters of the CH_2FBr molecule were not determined experimentally. In order to calculate the product of the principal moments of inertia of the CH_2FBr molecule (see Table 149) the following values of the structural parameters were used in the present Handbook: $r_{C-H} = 1.10$, $r_{C-F} = 1.38$, $r_{C-Br} = 1.93$ A, $\angle H - C - H = \angle F - C - Br = 109°28'$, adopted on the basis of the results of a study on the molecular structure of other halogen substitution products of methane (see Table 145). The errors in the adopted values of the bond lengths of the CH_2FBr molecule may be estimated within ±0.03 cm A and the errors in the angles between the bonds within ±4°.

CH_2FI. The spectra and the structure of the CH_2FI molecule were not studied. Consequently, the values of the fundamental frequencies of this molecule can only be estimated very roughly. The thermodynamic functions of this molecule were, however, calculated without such an estimate (see page 1086).

The value of the product of the principal moments of inertia of the CH_2FI molecule given in Table 149 was calculated on the basis of a use of the following values of the structural parameters: $r_{C-H} = 1.10$, $r_{C-F} = 1.38$, $r_{C-I} = 2.15$ A, $\angle H - C - H = \angle F - C - I = 109°28'$. The latter values are based on the results of a study on the molecular structure of other halogen substitution products of methane (see Table 145). The errors in the values of the bond lengths adopted for CH_2FI may be estimated within ±0.03 A and those in the angles between the bonds within ±4°.

CH_2ClBr. The Raman spectrum of liquid bromo-chloro methane was studied in the works [595, 1299, 4190] and the infrared spectrum in the works [1482, 3285, 4190]. The infrared spectrum of gaseous bromo-chloro methane was investigated by Weber, Meister and Cleveland [4190] in the range from 600-1450 cm^{-1} with a prism spectrometer and by Plyler and Benedict [3278] in the range from 3125-6250 cm^{-1} with a diffraction grating spectrometer.

The results of a determination of the values of the fundamental frequencies of the CH_2ClBr molecule obtained by various authors were considered by Weber, Meister and Cleveland in the work [4190]. The values of the fundamental frequencies of the CH_2ClBr molecule recommended by these authors are adopted in the present Handbook and given in Table 149.*

Plyler and Benedict [3278] analyzed the rotational structure of several lines in the infrared spectrum of CH_2ClBr and from the results of this analysis found $A_0 - 1/2\ (B_0 + C_0) = 0.898\ cm^{-1}$. Using this value and assuming that $r_{C-H} = 1.093$ A and $\angle H - C - H = 109°28'$, Plyler and Benedict calculated the values of the rest of the structural parameters: $r_{C-Cl} = 1.766$, $r_{C-Br} = 1.911$ A, $\angle Cl - C - Br = 112°$. The values of the structural parameters of the CH_2ClBr molecule obtained in the work [3278] were used to calculate the product of the principal moments of inertia of CH_2ClBr adopted in the Handbook (see Table 149).

$\underline{CH_2ClI,\ CH_2BrI}$. The Raman spectra of liquid chloro-iodo methane and bromo-iodo methane were studied by Bacher and Wagner [595, 4124]. In these studies the values of the fundamental frequencies of the CH_2ClI and CH_2BrI molecules were determined, but the problem of how to assign them was not solved quite uniquely.

The fundamental frequencies of the CH_2ClI and CH_2BrI molecules adopted in the present Handbook on the basis of results of a study on the Raman spectrum of these compounds in the works [595, 4124] are given in Table 149.

The products of the principal moments of inertia of the CH_2ClI and CH_2BrI molecules given in Table 149 were calculated using the following values of the bond lengths: $r_{C-H} = 1.10$, $r_{C-Cl} = 1.77$, $r_{C-Br} = 1.93$, $r_{C-I} = 2.15$ A and on the assumption that all angles between the bonds are identical and equal to 109°28'. The adopted values of the structural parameters of the CH_2ClI and CH_2BrI molecules are based on the results of experimental investigations of the molecular structure of the halogen substitution products of methane (see Table 145). The errors in the adopted values of the bond lengths of the CH_2ClI and CH_2BrI molecules may be estimated within ± 0.03 A and those of the angles between the bonds within $\pm 4°$.

CHF_2Cl. The Raman spectrum of liquid chloro-difluoro methane was investigated by Glockler and Bachman [1769] and Glockler and Leader [1778]. The infrared spectrum of gaseous chloro-difluoro methane was obtained with prism spectrometers and studied in the works [3277] (350-4200 cm^{-1}) and [4200] (270-4000 cm^{-1}). A summary of the main results of these studies is given in the work [4200].

Similar values are obtained for the fundamental frequencies of the CHF_2Cl molecule in the works [1769, 1778, 3277, 4200]. In the present Handbook the values obtained by Plyler and Benedict [3277] are adopted for the fundamental frequencies of the CHF_2Cl molecule. These values are given in Table 149. The errors in these values are estimated within ±5 cm^{-1}.

An electron diffraction study of the molecular structure of CHF_2Cl was carried out by Brockway [955, 956] in 1937 when the methods of such investigations were still imperfect. In the works [955, 956] the following values of the structural parameters of CHF_2Cl were obtained: $r_{C-F} = 1.36 \pm 0.03$, $r_{C-Cl} = 1.73 \pm 0.03$ A, $\angle F - C - F = \angle Cl - C - F = 110°30'$.

The product of the principal moments of inertia of the CHF_2Cl molecule given in Table 149 was calculated on the assumption that all angles between the bonds are identical and equal to 109°28', and the C-H and C-F, and C-Cl bond lengths are, respectively, equal to 1.10; 1.35 and 1.77 A (see Table 145).* The errors in the adopted values of the bond lengths may be estimated within ± 0.03 A and those of the angles between the bonds within ±4°.

CHF_2Br. The infrared spectrum of gaseous bromo-difluoro methane was investigated by Plyler and Acquista [3271] in the range from 320-4300 cm^{-1} and by Palm, Voelz and Meister [3169] in the range from 600-3800 cm^{-1} with low dispersion prism spectrometers. The Raman spectrum of bromo-difluoro methane was not studied.

Plyler and Acquista [3271] interpreted their own infrared spectrum and determined the values of all fundamental frequencies of the CHF_2Br molecule. The values of eight fundamental frequencies were determined immediately from the spectrum in the work [3271]. The value of the minimum frequency ν_6 was determined equal to 240 cm^{-1} on the basis of data obtained for the composite frequencies. The assignment of the frequencies in the infrared spectrum of CHF_2Br, and also their values obtained in the work [3271] were verified by Palm, Voelz and Meister [3169] who re-investigated the infrared spectrum of CHF_2Br and calculated the values of the frequencies by making use of a potential function with a great number of force constants.* The same values as in the work [3271] were adopted by the authors of the work [3169] for the fundamental frequencies of the CHF_2Br molecule. A value equal to 244 cm^{-1} was obtained for the frequency ν_6 by calculating the frequencies from the force constants, in the work [3169].

Previously, the values of the fundamental frequencies of CHF_2Br had been determined approximately by Glockler and Leader [1778] by comparing the values of the corresponding frequencies of the various molecules of the CHX_2Y type, where X, Y = F, Cl, Br and by Stepanov [391] on the basis of approximate calculations with the help of the force constants of CH_4, CF_4, CCl_4 and CBr_4. The values of the high frequencies of CHF_2Br (higher than 1000 cm^{-1}) estimated in the works [1778, 391] are close to the corresponding experimental values obtained in the works [3271, 3169]. The values of the low frequencies of CHF_2Br (lower than 1000 cm^{-1}) estimated in the works [1778, 391] are, however, very considerably different from the experimental ones. For the frequency ν_6, in particular, Stepanov obtained a value equal to 380 cm^{-1} which was adopted in the following by Pitzer and Gelles [3258].

For the remaining fundamental frequences of CHF_2Br the values determined from the infrared spectrum by Plyler and Acquista [3271] were adopted in the work [3258].

The fundamental frequencies of the CHF_2Br molecule determined from studies on the infrared spectrum of gaseous bromo-difluoro methane [3271, 3169] were adopted in the present Handbook and are given in Table 149.

The molecular structure of CHF_2Br was not studied by electron diffraction.

The product of the principal moments of inertia of the CHF_2Br molecule given in Table 149 was calculated on the assumption that all angles between the bonds are identical and equal to 109°28', and that the C-H and C-F and C-Br bond lengths are, respectively, equal to 1.10; 1.35 and 1.93 A (see Table 145). The errors in the values adopted for the bond lengths are estimated within ± 0.03 A and those of the angles between the bonds within $\pm 4°$.

$\underline{CHF_2I}$. Experimental studies on the spectra and the structure of iodo-difluoro methane were not carried out. Consequently, the values of the fundamental frequencies of the CHF_2I molecule can only be estimated very roughly. For the present Handbook, however, such estimates need not be made.

The value of the product of the principal moments of inertia of the CHF_2I molecule given in Table 149 was calculated on the assumption that all angles between the bonds are identical and equal to 109°28', and that the C-H, C-F, and C-I bond lengths are, respectively, equal to 1.10; 1.35 and 2.15 A. The adopted values of the structural parameters of the CHF_2I molecule are based on the results of a study on the molecular structure of other halogen substitution products of methane (see Table 145). The errors in the adopted values of the bond lengths may be estimated within ±0.03 A and those of the angles between the bonds within ±4°.

CHFCl$_2$. The Raman spectrum of liquid fluoro-dichloro methane was studied by Bradley [886], Glockler, Edgell and Leader [1773] and Delwaulle [1298]. The infrared spectrum of gaseous fluoro-dichloro methane was obtained with prism spectrometers and investigated in the works [3974] (550-3050 cm^{-1}), [3277] (360-4400 cm^{-1}) and [4200] (270--4000 cm^{-1}). A summary of the principal results of studies on the vibrational spectra of CHFCl$_2$ is given in the work [4200]. The most comprehensive data on the Raman spectrum of liquid fluoro-dichloro methane and on the assignment of the bands observed in it to the fundamental frequencies of the CHFCl$_2$ molecule are obtained in the work by Delwaulle [1298], in which, in contrast to the studies carrie out earlier [886, 1773], the degree of polarization of the individual lines were determined. The informations obtained from a study on the Raman spectra of liquid fluoro-dichloro methane facilitated the interpretation of the infrared spectrum.

Similar values were obtained for the fundamental frequencies of the CHFCl$_2$ molecule in the works [886, 1773, 1298, 3277, 4200]. In the present Handbook the values recommended by Plyler and Benedict [3277] and given in Table 149 were adopted for the fundamental frequencies of the CHFCl$_2$ molecule. The errors of these values are about ±1%.

An electron diffraction investigation of the molecular structure of CHFCl$_2$ was carried out by Brockway [955, 956] in 1937 when the method of such studies was still imperfect. In the works [955, 956] the following values of the structural parameters of CHFCl$_2$ were obtained: $r_{C-F} = 1.41 \pm 0.03$, $r_{C-Cl} = 1.73 \pm 0.04$ A, $\angle Cl - C - Cl = 112 \pm 2°$, $\angle F - C - Cl = 109 \pm 2°$.

The product of the principal moments of inertia of CHFCl$_2$ given in Table 149 was calculated on the assumption that all angles between the bonds are identical and equal to 109°28', and that the C-H, C-F and C-Cl bond lengths are, respectively, equal to 1.10; 1.38 and 1.77 A (see Table 145). The errors in the adopted values of the bond lengths are estimated within ±0.03 A and those of the angles between the bonds within ±4°.

CHFClBr. The values of the fundamental frequencies of the CHFClBr molecule were determined on the basis of studies on the Raman spectrum [1777, 1298] and the infrared spectrum [3283] of liquid fluoro-chloro-bromo methane. Plyler and Lamb [3283] investigated also the infrared spectrum of gaseous fluoro-chloro-bromo methane and found that the frequency shifts in the infrared spectra of liquid and gaseous CHFClBr do not exceed 10 cm^{-1}. The difference between the values of the fundamental frequencies of the CHFClBr molecule, which were determined from the Raman spectrum [1777] and from the infrared spectrum [3283], does not exceed 3 cm^{-1}, except for the frequencies ν_6 and ν_1, for which this difference is 5 cm^{-1}. The frequency ν_6 was determined equal to 225 cm^{-1} from the Raman spectrum [1777], whereas it was not observed in the infrared spectrum and determined equal to 220 cm^{-1} [3283] from data obtained on the composite frequencies.

In the present Handbook the values obtained by Plyler and Lamb [3283] as a result of their own interpretation of the infrared spectrum of liquid fluoro-chloro-bromo methane were adopted for the fundamental frequencies of the CHFClBr molecule. The values of the fundamental frequencies of CHFClBr obtained in the work [3283] are given in Table 149. The errors in the adopted values of the fundamental frequencies of CHFClBr are estimated within the limits of ±5 to ±10 cm^{-1}.

The structural parameters of the CHFClBr molecule were not determined experimentally.

The product of the principal moments of inertia of the CHFClBr molecule given in Table 149 was calculated on the assumption that all angles between the bonds are identical and equal to 109°28', and that the C-H, C-F, C-Cl and C-Br bond lengths are, respectively, equal to 1.10; 1.38; 1.77 and 1.93 A (see Table 145). The errors in the adopted values of the bond lengths are estimated within the limits of ±0.03 A and those of the angles between the bonds within ±4v.

$\underline{CHFBr_2}$. The values of the fundamental frequencies of the $CHFBr_2$ molecule were determined on the basis of studies on the Raman spectrum of liquid fluoro-dibromo methane, which were carried out by Glockler and Bachman [1768], Glockler and Leader [1778] and Delwaulle and Francois [1307, 1298]. In the work [1307] Delwaulle and Francois measured the polarization of the lines in the Raman spectrum, which permitted the frequencies to be assigned more accurately.

The values of the fundamental frequencies of the $CHFBr_2$ molecule adopted in the present Handbook on the basis of data obtained in the works [1778, 1298] are given in Table 149. Practically identical values of the fundamental frequencies of $CHFBr_2$ were adopted by Pitzer and Gelles in the work [3258]. The errors in the adopted values of the fundamental frequencies of the $CHFBr_2$ molecule are estimated from ±3 cm^{-1} (for low frequencies) to ±8 cm^{-1} (for high frequencies).

The structural parameters of the $CHFBr_2$ molecule were not determined experimentally.

The product of the principal moments of inertia of the $CHFBr_2$ molecule given in Table 149 was calculated on the assumption that all angles between the bonds are identical and equal to 109°28', and that the C-H, C-F and C-Br bond lengths are, respectively, equal to 1.10; 1.38 and 1.93A (see Table 145). The errors of the adopted values of the bond lengths are estimated within ±0.03 A and those of the angles between the bonds within ±4°.

$CHCl_2Br$. The Raman spectrum of liquid bromo-dichloro methane was studied in several works. A survey of the results of these studies is given in the monographs by Hibben [2065], Kohlrausch [236] and in the work [3292]. The infrared spectrum of liquid and gaseous bromo-dichloro methane was investigated by Plyler and Benedict [3277] and Polo with collaborators [3292]. In the work [3292] also the vibrational spectra of $CDCl_2Br$ were studied.

The infrared spectra of $CHCl_2Br$ were obtained with prism spectrometers. The infrared spectrum of liquid dichloro-bromo methane, which was obtained in the work [3277] in the range from 290-5000 cm^{-1} and in the work [3292] in the range from 400-4000 cm^{-1}, was studied most completely. Several ranges of the infrared spectrum located within the range from 490-3200 cm^{-1} were obtained for gaseous bromo-dichloro methane.

Plyler and Benedict [3277] interpreted the infrared spectrum of liquid bromo-dichloro methane by using earlier obtained data on the Raman spectrum and comparing the infrared spectra of gaseous and liquid bromo-dichloro methane found the shifts of the frequencies ν_2, ν_3, ν_7 and ν_8 due to the change of the state of aggregation. The values of the fundamental frequencies of the $CHCl_2Br$ molecule recommended by Plyler and Benedict [3277] were adopted by Pitzer and Gelles in the work [3258].

Using their own results of a study on the Raman spectrum of liquid bromo-dichloro methane and on the infrared spectra of liquid and gaseous bromo-dichloro methane and taking account of the results of studies carried out earlier Polo and collaborators [3292] determined the values of the fundamental frequencies of the $CHCl_2Br$ molecule. In this case, the difference in the values of the frequency ν_1 obtained in the works [3277] and [3292] (from the spectra of liquid bromo-dichloro methane) proved to be equal to 19 cm^{-1}, which is to be ascribed to the less careful measurements of the band center positions in the spectrum of $CHCl_2Br$ in the work [3277]. In view of the fact that the infrared spectrum of gaseous bromo-dichloro methane was studied less thoroughly than that of the liquid, values of only six frequencies(ν_1, ν_2, ν_3, ν_4, ν_7, ν_8)* differing from the values of the corresponding frequencies of the $CHCl_2Br$ molecule in liquid bromo-dichloro methane within the limits of 3 to 7 cm^{-1} were obtained for the $CHCl_2Br$ molecule in the gaseous phase in the work [3292]. The frequencies ν_5, ν_6 and ν_9 were determined only for liquid bromo-dichloro methane. The difference of the values of the frequencies ν_5, ν_6 and ν_9 obtained in the work [3292] from the corresponding values of the frequencies of the free $CHCl_2Br$ molecule, evidently, does not exceed 3 cm^{-1}.

Table 149 shows the values of the fundamental frequencies of the $CHCl_2Br$ molecule adopted in the present Handbook. For the frequencies ν_1, ν_2, ν_3, ν_4, ν_7, ν_8 the values found by the authors of the work [3292] from the infrared spectrum of gaseous bromo-dichloro methane, and for the frequencies ν_5, ν_6, ν_9 the values determined from the vibrational spectra of liquid bromo-dichloro methane in the work [3292] were adopted. The errors in the adopted values of the fundamental frequencies of the $CHCl_2Br$ molecule are estimated with the limits of ± 3 cm^{-1}.

The structural parameters of the $CHCl_2Br$ molecule were not determined experimentally.

The product of the principal moments of inertia of the $CHCl_2Br$ molecule given in Table 149 was calculated on the assumption that all angles between the bonds are identical and equal to 109°28', and that the C-H, C-Cl and C-Br bond lengths are, respectively, equal to 1.10;

1.77 and 1.93 A (see Table 145). The errors in the adopted values of the bond lengths are estimated within ±0.03 A and those of the angles between the bonds within ±4°.

$CHClBr_2$. The Raman spectrum of liquid chloro-dibromo methane was studied in the works [1776, 1298, 3297] and the infrared spectrum in the works [1482] (550-1200 cm^{-1}), [1658, 3277] (278-4280 cm^{-1}) and [3297] (550-3600 cm^{-1}). The individual bands of $CHClBr_2$ were observed in the infrared spectrum of gaseous chloro-dibromo methane [3277, 3297]. The Raman spectrum of gaseous chloro-dibromo methane was not studied. A survey of the principal results of studies on the vibrational spectra of chloro-dibromo methane is given in the work by Pontarelli et al. [3297]. The vibrational spectra of $CDClBr_2$ were investigated in the work [3297].

Using the results of a study on the vibrational spectra of liquid chloro-dibromo methane in the works [1298, 3277. 3297] the values of all fundamental frequencies of the $CHClBr_2$ molecule which practically coincide with each other for the corresponding frequencies were determined. An exception is only the frequency ν_1, for which Plyler and Benedict [3277] determined a value equal to 3034 cm^{-1} from the infrared spectrum of liquid chloro-dibromo methane whereas in the rest of the studies on the vibrational spectra of liquid chloro-dibromo methane [1298, 3297] values within the limits from 3020 to 3023 cm^{-1} were obtained for this frequency. On the basis of a comparison of the infrared spectra of liquid and gaseous chloro-dibromo methane Plyler and Benedict in the work [3277] determined also the shifts of the frequencies ν_2, ν_3, ν_7 and ν_8 of the $CHClBr_2$ molecule due to intermolecular interaction in the liquid. The values of the corresponding frequencies of the free $CHClBr_2$ molecule obtained in the work [3297] are by 2-3 cm^{-1} lower than those calculated from the data of Plyler and Benedict

[3277]. In the work [3297] for the free $CHClBr_2$ molecule (in the gas) also the frequency ν_4 was determined.

The values of the fundamental frequencies of the $CHClBr_2$ molecule adopted in the present Handbook are given in Table 149. For the frequencies ν_2, ν_3, ν_4, ν_7, ν_8 the values obtained in the work [3297] from the infrared spectrum of gaseous chloro-dibromo methane were adopted. The errors in the values of these frequencies are estimated within ± 3 cm^{-1}. For the rest of the $CHClBr_2$ frequencies the values recommended in the work [3927] on the basis of results of a study on the vibrational spectra of liquid chloro-dibromo methane are given in Table 149. The errors in the values of these frequencies are estimated within the limits from ± 5 to 10 cm^{-1}.

The structural parameters of the $CHClBr_2$ molecule were not determined experimentally. The value of the product of the principal moments of inertia of the $CHClBr_2$ molecule given in Table 149 was calculated on the assumption that all angles between the bonds are identical and equal to 109°28', and that the C-H, C-Cl, and C-Br bond lengths are, respectively, equal to 1.10; 1.77 and 1.93 A (see Table 145). The errors in the values adopted for the bond lengths are estimated within ± 0.03 A and those of the angles between the bonds within $\pm 4°$.

CF_2ClBr. Stepanov [391] was the first to obtain values of the fundamental frequencies of the CF_2ClBr molecule as a result of calculations carried out on the basis of his own calculated values of the force constants of the CF_4, CCl_4 and CBr_4 molecules. In the following the results of these calculations facilitated the interpretation of the infrared spectrum of gaseous difluoro-chloro-bromo methane obtained by Plyler and Acquista [3271] with a prism spectrometer in the range from 264--5000 cm^{-1}. Immediately from the infrared spectrum of CF_2ClBr Plyler and Acquista [3271] determined the values of the frequencies ν_1, ν_2,

ν_3, ν_7 and ν_8. The values of the remaining fundamental frequencies of the CF_2ClBr molecule were estimated by Plyler and Acquista with the help of the composite frequencies, on the basis of the results of calculations carried out by Stepanov [391] and of a comparison with the values of the corresponding frequencies of the CF_2Br_2 and CF_2Cl_2 molecules.

The values of the fundamental frequencies of the CF_2ClBr molecule determined in the work [3271] are adopted in the present Handbook and given in Table 149. The errors in the adopted values of the frequencies ν_1, ν_2, ν_3, ν_7 and ν_8 are estimated within the limits of ± 3 cm^{-1} and those of the frequencies ν_4, ν_5, ν_6, ν_9 within the limits of ± 10 cm^{-1}.

The structural parameters of the CF_2ClBr molecule were not determined experimentally. The value of the product of the principal moments of inertia of the CF_2ClBr molecule given in Table 149 was calculated on the assumption that the angles between the bonds are identical and equal to 109°28', and that the C-F, C-Cl and C-Br bond lengths are equal to 1.35; 1.77 and 1.93 A respectively (see §61). The errors in the adopted values of the bond lengths are estimated within 0.03 A and those of the angles between the bonds within ±4°.

CF_2ClI, CF_2BrI. Experimental studies on the spectra and the molecular structure of CF_2ClI and CF_2BrI were not carried out. The values of their fundamental frequencies can only be estimated very roughly. The thermodynamic functions of both gases can, however, be calculated without estimating the fundamental frequencies (see page 1086).

With the help of the results of experimental studies on the molecular structure of the halogen substitution products of methane it is possible to verify the fact that the C-F, C-Cl, C-Br and C-I bond lengths in the CF_2ClI and CF_2BrI molecules have values close to those shown in Table 145 and that the angles between the bonds are almost tetrahedral. The values of the product of the principal moments of inertia of these molecules given in Table 149 were calculated on the assumption that the angles between the bonds are identical and equal to 109°28' , and that the C-F, C-Cl, C-Br and C-I bond lengths are, respectively, equal to 1.35; 1.77; 1.93 and 2.15 A (see §61 and Table 145). The errors in the adopted values of the bond lengths may be estimated within ±0.03 A and those of the angles between the bonds within ±4°.

$CFCl_2Br$, $CFClBr_2$. The values of the fundamental frequencies of the $CFCl_2Br$ and $CFClBr_2$ molecules were determined by Delwaulle and Francois [1303] as a result of a study on the Raman spectra of liquid fluoro-dichloro-bromo methane and fluoro-chloro-dibromo methane. The infrared spectra of these compounds were not studied. The assignment of the bands in the obtained spectra of the $CFCl_2Br$ and $CFClBr_2$ molecules was carried out by Pitzer and Gelles [3258] with the help of the generalized Teller-Redlich product rule.

The values of the fundamental frequencies of the $CFCl_2Br$ and $CFClBr_2$ molecules obtained by Delwaulle and Francois in the work [1303] are adopted in the present Handbook and given in Table 149.* The errors in the adopted values of these quantities are estimated within ±5 cm^{-1}.

The structural parameters of the $CFCl_2Br$ and $CFClBr_2$ molecules were not determined experimentally.

The values of the products of the principal moments of inertia of these molecules given in Table 149 were calculated on the assumption that the angles between the bonds are identical and equal to 109°28', and that the C-F, C-Cl and C-Br bond lengths are, respectively, equal to 1.38; 1.77 and 1.93 A (see §61). The errors in the adopted values of the bond lengths are estimated within ±0.03 A and those of the angles between the bonds within ±4°.

DIVISION 2. THERMODYNAMIC FUNCTIONS OF THE GASES

The thermodynamic functions of methane and of 45 of its halogen substitution products calculated in the approximate harmonic-oscillator-rigid rotator model are given in Volume II of the Handbook (Tables 141, 147, 152, 154, 155, 160, 163-168, 170-203). The calculations were carried out with the help of the values of the molecular constants given in the Tables 146-149, without taking account of the influence of the intermolecular interaction. In the Tables 408-417 of Volume II of the Handbook the values of the virial coefficients and their derivatives are given for CH_4, CF_4, CH_3F, CCl_4, CH_2Cl, $CHCl_3$, $CHFCl_2$, $CFCl_3$, CH_3Br and CH_3I, by means of which the nonideality corrections in the values of the thermodynamic functions of these gases may be taken into account. The thermodynamic functions of methane and of 32 of its halogen substitution products were calculated in the temperature interval from 293.15-6000°K. For 13 gases which are most unstable at high temperatures (CBr_4, CH_2Br_2, CH_2I_2, CCl_2Br_2, CH_3I, $CHBr_3$, CHI_3, CCl_3Br, $CClBr_3$, CH_2ClI, CH_2BrI, $CHCl_2Br$, $CHClBr_2$), the thermodynamic functions were calculated in the temperature interval from 293.15-4000°K.

Among the 69 halogen substitution products of methane 24 compounds containing iodine are not considered*; the experimental values needed to calculate the thermodynamic functions were not obtained for them, nor could the values of the functions be determined by the method which had been applied to CF_2I_2, CH_2FI, CHF_2I, CF_2ClI and CF_2BrI (see §68 and 69). The halogen substitution products that are not considered in the Handbook are compounds which have been studied insufficiently owing to their low stability and the difficulty of being obtained in pure form. Many of them are unknown in the gaseous state (e.g., $CBrI_3$,

CI_4).

The thermodynamic functions of methane and its halogen substitution products were calculated with the help of the molecular constants in the approximation of the harmonic-oscillator-rigid rotator model, in many works. A survey of the results published up to 1953 for 35 compounds of this class is given in the Handbook by Zeise [4384]. Subsequently, the most comprehensive surveys of tables of the thermodynamic functions of the halogen substitution products of methane were compiled by Gelles and Pitzer [1678] (for 39 compounds),* Sverdlin [359-361] (for 18 compounds) and Albright, Galegar and Innes [496] (for 5 compounds). In all these works, the thermodynamic functions of the halogen substitution products of methane were calculated up to 1000°K, and only Gelles and Pitzer [1678] calculated up to 1500°K.

The values of the thermodynamic functions of the halogen substitution products of methane given in the Handbook by Zeise [4384] were calculated by various authors in the course of the years 1935-1952 making use of informations on the molecular constants of these compounds which have become out of date. In particular, the calculations of the thermodynamic functions of the gaseous halogen substitution products of methane carried out at that time were, for the most part, based on values of the molecular fundamental frequencies determined from the Raman spectra of the corresponding substances in liquid state, but also on inaccurate values of the structural parameters of the molecules obtained by earlier electron diffraction investigations.

In the calculations of Gelles and Pitzer [1678] more reliable data for the fundamental frequencies obtained from an analysis of the infrared spectra were used. It is, however, by no means all halogen substitution products of methane considered in the work [1678] for which infrared spectra were obtained in a sufficiently wide range. Besides, the assignments of the fundamental frequencies proposed in the original works had to be verified for many halogen substitution products of methane. Consequently, in the work [3258] Pitzer and Gelles verified the correctness of the assignment of the fundamental frequencies of the halogen substitution products of methane with the help of the generalized Teller-Redlich rule. Using this semiempiric method Gelles and Pitzer succeeded in correcting the assignment of the fundamental frequencies of several halogen substitution products of methane and in taking account of these corrections in the calculation of the thermodynamic functions. For the majority of the halogen substitution products of methane the values of the fundamental frequencies adopted by Gelles and Pitzer were made more accurate in the following, a fact, that, however, exerted only an unimportant influence on the results of the calculations of the thermodynamic functions. The most significant drawback of the calculations carried out by Gelles and Pitzer is the use of inaccurate values of the product of the principal moments of inertia of the molecules of several halogen substitution products of methane. Besides, errors were tolerated in the calculation of the thermodynamic functions in the work [1678].

In Sverdlin's works [359-361] the values of the fundamental frequencies calculated by Stepanov [392]* and Maslov [293]** were used to calculate the thermodynamic functions of the halogen substitution products of methane rather than the experimental ones. This proved to be the source of additional errors, since for all compounds considered in the works [359-361] (except for CI_4) sufficiently reliable values of the fundamental frequencies were known on the basis of the experimental data.

Albright, Galegar and Innes [496] calculated tables of the thermodynamic functions of CCl_4, $CFCl_3$, CF_2Cl_2, CF_3Cl and CF_4 in the temperature interval from 100-1000°K, taking the corrections to the anharmonicity of the vibrations into account, according to an empirical formula given by McCullough and his collaborators [2698] on the assumption that the proportionality coefficient in this formula is the same for all fluorine and chlorine substitution products of methane.* In the work [496] the latter quantity was found from the experimental data obtained for the specific heat of CF_2Cl_2 [2796].

The attempt to make the values of the thermodynamic functions of CCl_4, $CFCl_3$, CF_2Cl_2, CF_3Cl and CF_4 more accurate in the temperature interval from 100-1000°K undertaken by Albright et al [496] by approximately allowing for the anharmonicity of the molecular vibrations cannot be considered satisfactory since in this temperature interval the anharmonicity corrections are insignificant and their values of the same order as the errors due to the inaccuracy of the structural parameters of the molecules. The vibrational anharmonicity corrections to the values of the thermodynamic functions of the gases are essential at temperatures above 1000°K. The anharmonicity constants of the molecular vibrations are needed to take account of these corrections. Their values for methane and its halogen substitution products were, however, not determined.

For halogen substitution products used as working substances in refrigerating plants** tables of the thermodynamic properties in the low-temperature range (for the liquid and gaseous states) are given in Handbooks [3417, 79, 480].

§66. CX_4-Type Halocarbons

The thermodynamic functions of CH_4, CF_4, and CCl_4 and CBr_4 given in the tables 141, 147, 160, and 173 in Volume II of this Handbook have been calculated for the corresponding ideal gases by means of Eqs. (II.243) and (II.244) in the harmonic-oscillator-rigid-rotator approximation with the molecular constants from Table 146. The values of the constants $\vartheta_n(d_n)$, C'_{Φ} and C'_{S} used in the calculations are given in Table 150.

TABLE 150

The Constants for Calculating the Thermodynamic Functions of Gaseous CH_4, CF_4, CCl_4, and CBr_4

Вещество 1	θ_1 (1)	θ_2 (2)	θ_3 (3)	θ_4 (3)	C'_{Φ}	C'_{S}
	2 *град*				3 *кал/моль·град*	
CH_4	4196,2	2206,5	4343,6	1878,9	−8,8339	−0,8848
CF_4	1306,7	625,2	1830	909	6,1226	14,0717
CCl_4	659	314	1115	446	11,3733	19,3224
CBr_4	386,5	176,3	966,4	261,1	16,6522	24,6013

1) Substance; 2) deg; 3) cal/mole·deg.

The errors in the values of the thermodynamic functions of CH_4, CF_4, CCl_4 and CBr_4 given in the above-mentioned Tables of Volume II of the Handbook are due mainly to inaccurate molecular constants and to the anharmonic vibrations of the molecules, which have not been taken into consideration. The former reason is predominant at $T < 1000°K$, the latter at higher temperatures. The overall error in Φ^*_{3000} for CH_4, CF_4 CCl_4, and CBr_4 has been estimated to be 0.7, 2.6, 2.4, and 3.5 cal/mole·degree, respectively.

In Volume II of the Handbook, tables of the virial coefficients and of their products for CH_4, CCl_4 and CF_4, can be found, by means of which the corrections required in the thermodynamic functions of the corresponding gases owing to intermolecular interaction can be calculated (see Tables 407, 408, 410).

Below we shall continue considering the required calculations of the thermodynamic functions of CH_4, CF_4, CCl_4, and CBr_4, and we shall compare the results of these calculations with the results of the corresponding calculations carried out during the preparation of this edition of the Handbook.

$\underline{CH_4}$. The results of calculations of the thermodynamic functions of methane in a gaseous state, published up to 1954, have been reviewed by Frost [425, 426] and Justi [2312]. In the following years, the thermodynamic functions of methane have been calculated in the publications [2450, 1079, 1078, 420, 2489, 2302] from the molecular constants of CH_4, and in the paper [1933] with the aid of calorimetric measurements. The thermodynamic functions of methane given in the paper [4122], in the Handbooks [3680, 3426, 3507, 137, 418, 2363, 149], and in the monographs [119, 119a] for the temperature range of 298.15--1500°K are based on the corresponding calculations carried out by Pitzer [3254].

The thermodynamic functions of CH_4 in the temperature range of 100-1000°K have been calculated in papers by Cerny and Erdos [1079, 1078]. In the first edition of the Handbook, the thermodynamic functions of CH_4 were calculated for the same temperatures as in this edition, but they were based on somewhat different values of the molecular and physical constants. The values of Φ_T^* in the temperature range of 1000-6000°K have been calculated in the paper [2489]. Jones and McDowell [2302] have calculated the thermodynamic functions of gaseous methane and of 11 of its deuterium and tritium substitutes* in the harmonic-oscillator-rigid rotator approximation with the nuclear spin taken into consideration at temperatures ranging from -80 to +1000°C.**

The thermodynamic functions of gaseous methane calculated from the molecular constants of CH_4 in different papers differ slightly from one another and from the values of the respective quantities in Table 141 (II). The discrepancies of the order of a few hundredths cal/mole·degree in Φ_T^* and S_T° are due to the differences in the molecular and physical constants used in the calculations.

A survey on the results for $S_{298.15}^\circ$ of gaseous methane obtained by calorimetric measurements is given in the Handbook [98] where a value of $S_{298.15}^\circ = 44.5 \pm 0.2$ cal/mole·degree has been obtained on the basis of measurements by Frank and Clusius [1596]; this value agrees with that given in Table 141 (II).

The results of calorimetric measurement of the specific heat of methane in a gaseous state are given in a monograph by Justi [2312] for temperatures ranging from -70 to +208°C and in the Handbook [418] for temperatures of 0-600°C. Halford and Miller [1933] have precisely measured the specific heat of gaseous methane at $T = 279°K$ and $p \sim 10^{-3}$ mm Hg and have obtained $C_{v_{279}}^\circ = 6.36 \pm 0.06$ cal/mole·degree. Within the limits of error, the results of all these measurements are in accordance with the corresponding quantities calculated from the molecular constants in the harmonic-oscillator-rigid rotator approximation.

$\underline{CF_4}$. The first attempt to determine the values of the thermodynamic functions of gaseous carbon tetrafluoride was made by Eucken and Bertram [1499]. They calculated C_v° of CF_4 in the temperature range of 0-300°C with $\nu_1 = 1000$, $\nu_2 = 503$, $\nu_3 = 1350$, and $\nu_4 = 653$ cm^{-1} on the basis of the CF_4 infrared spectrum which they have taken in the range of 600-1500 cm^{-1}, and by comparing the fundamental frequencies of the CBr_4, CCl_4, and CF_4 molecules with one another. In the paper [1499], the specific heat of gaseous CF_4 has been measured also at T = 113, 173, and 199°K.

Later, Eucken and Schroder [1505] measured the specific heat of carbon tetrafluoride in the temperature range of 12-145°K, determined the heat of phase conversion and the heat of fusion of CF_4 and on this basis calculated $S^\circ_{298.15}$ (CF_4 gaseous) = 62.43 cal/mole•degree* which is in excellent agreement with the value calculated by means of the molecular constants of CF_4 taken from this Handbook (see Volume II, Table 147). A calorimetric examination of the thermodynamic properties of carbon tetrafluoride in the temperature range of 12-95°K has been conducted by Kostryukov, Samorukov, and Strelkov [252]. The temperature of the triple point, the heat and entropy of phase conversion, and the heat and entropy of fusion of carbon tetrafluoride have been determined with greater precision in the paper [252]. The value of $S^\circ_{298.15}$ of gaseous CF_4 has not been calculated in the paper [252].

Eucken and Schroder [1505] have also calculated $S^c_{298.15} = 62.81$ cal/mole•degree with the aid of the molecular constants of CF_4, taking $\nu_1 = 903$, $\nu_2 = 427$, $\nu_3 = 1350$, $\nu_4 = 652$ cm^{-1} and $I = 62.81 \times 10^{-40}$ g•cm^2. At the same time, Yost [4358] calculated $S^\circ_{298.15}$ of CF_4 on the basis of the following values of the molecular constants: $\nu_1 = 904$, $\nu_2 = 437$, $\nu_3 = 1350$, $\nu_4 = 635$ cm^{-1} and $r_{C-F} = 1.36$ A. The values of the molecular constants of CF_4 used by Yost in his calculations have further been used by Kelley [2363] in the calculation of the thermodynamic functions of gaseous CF_4 in the temperature range of 400-1200°K.

After 1950, the thermodynamic functions of CF_4 were calculated in the papers [1283] (at T = 100-1000°K), [361] (at T = 298.2-1000°K), [1678] (at T = 100-1500°K), [496] (at T = 100-1000°K), and during the preparation of the first edition of this Handbook (at T = 293.16-6000°K). In all these calculations, except in the paper [496], the thermodynamic functions of CF_4 have been calculated in the approximation using the harmonic-oscillator and the rigid-rotator as a combined model.

The thermodynamic functions of CF_4 have been calculated in [496] with the harmonic-oscillator-rigid-rotator model with approximate consideration of the anharmonicity of the vibrations according to the empirical formula of McCullough and collaborators [2698] and with the specific heat values of CF_2Cl_2 as found experimentally by Masi [2796]. However, these corrections are small (about 0.05 cal/mole•degree for Φ^*_{1000}) at the temperatures for which the calculations have been made. These corrections are considerably smaller than the error caused by inaccurate values of the molecular constants.

The main discrepancy among the values of the thermodynamic functions of CF_4 calculated in the papers [1283, 361, 1678, 496], in the first as well as in this edition of the Handbook is due to the different values of the interatomic distance r_{C-F} used in these treatises. A value of $r_{C-F} = 1.36$ A has been used in the calculations of Decker, Meister, Cleveland [1283], and Sverdlin and Godnev [361]. In the papers [1678] and [496], identical values of the product $I_A I_B I_C = 3240. \times 10^{-117}$ g^3•cm^6 have been used; this value is near to the one used in this Handbook.* The thermodynamic functions of CF_4 obtained in the paper [1678] are practically the same as the values of the respective quantities in Table 147 (II). Any slight deviations from the corresponding quantities given in the paper [496] must be attributed to corrections accounting for the anharmonicity of the vibrations. Owing to the different values of r_{C-F} used in the papers [1283, 361] and in this Handbook, the corresponding values of Φ^*_T and S°_T differ by about 0.2 cal/mole•degree.

On the basis of the results of an electron diffraction study carried out by Hoffmann and Livingston [2094], $r_{C-F} = 1.317$ A was taken in the first edition of the Handbook. This is the main reason why the values of the thermodynamic functions of CF_4 obtained in the first edition of the Handbook were slightly smaller than the ones in this edition (the difference in Φ_T^* amounts to 0.03 to 0.07 cal/mole·degree).

CCl_4. The thermodynamic functions of carbon tetrachloride in a gaseous state have been calculated in many papers. A list of the results of these calculations is given in Table 151. This Table also quotes reference books which contain the results of the calculations of the corresponding original papers. In all the papers listed in Table 151, the thermodynamic functions of CCl_4 have been calculated in the harmonic-oscillator-rigid-rotator approximation. The only exception is the work by Albright, Galegar, and Innes [496] in which approximate corrections have been adopted accounting for the anharmonicity of the vibrations of the CCl_4 molecule. The differences among the values of the thermodynamic functions of CCl_4 calculated by various authors, are not great (in the case of Φ_T^*, they move within the limits of ± 0.2 at T = 1000°K and ± 0.8 cal/mole·degree at T = 6000°K compared to the values given in Table 160 (II)). They are due chiefly to the different values of the fundamental frequencies and of the C-Cl bond length in the CCl_4 molecule that have been used in the calculations.

The fundamental frequencies of the CCl_4 molecule, used in this Handbook, are approximate to those used in the papers [3857, 3856, 3858, 2726, 1079, 1078, 1678]. However, the r_{C-Cl} values used in these papers are smaller than the ones used in this Handbook. $r_{C-Cl} = 1.76$ A in the papers [3857, 3858, 3856, 2726, 1678], and $r_{C-Cl} = 1.755$ A in the papers [1079, 1078]. It must be said that Gelles and Pitzer [1678] have made a mistake in calculating the thermodynamic functions of CCl_4. Hence, from a comparison of the Φ_T^* values calculated in the papers [2726, 1079, 1678, 359, 496] and in this Handbook and the values of the molecular constants used for CCl_4 it can be seen that the value obtained for Φ_{1000}^* in the paper [1678] is by 0.1 cal/mole·degree greater than the one that should be in conformity with the constants used.

The values of the thermodynamic functions of CCl_4 differing mainly from the values listed in Table 160 (II) have been obtained by Sverdlin [359] and Gordon [1816]. The Φ^*_{1000} value obtained from paper [359] is about 0.2 cal/mole·degree smaller and the Φ^*_{1000} value from [1816] is by about the same amount greater than in Table 160 (II). The difference can be explained by the fact that the paper [359] obviously used the somewhat high values of the frequencies $\nu_1 = 480$ and $\nu_3 =$ ν 787 cm^{-1} calculated in the paper [392] (see the first footnote on page 1048), and the value $r_{C-Cl} = 1.755$ A which is smaller than the one used in this Handbook. At the same time, Gordon [1816] purposely used lower fundamental frequencies of CCl_4*in his calculations in order to "partly make up for neglecting the anharmonicity of the vibrations in the calculations, the centrifugal elongation, and the vibrational-rotational interaction". Gordon assumed a C-Cl bond length of 1.76 A.

Likewise in the first as well as in this edition of the Handbook, the calculations in a paper by Albright et al. [496] have been carried out with CCl_4 frequencies found by Claassen [1117] (cf. page 981). The calculation in this edition of the Handbook differs from that in the first edition and the one in [496] in that the undisturbed value 775 cm^{-1} of this quantity has been used for the frequency ν_3 instead of the observed value of 794 cm^{-1}. For this reason and owing to the different r_{C-Cl} and physical constants used, the Φ^*_T values for CCl_4 given in the first and in this edition of the Handbook differ by 0.042 0.150, and 0.165 cal/mole·degree at T = 298.15, 3000, and 6000°K, respectively.

In the calculations of Albright et al [496], an attempt was made to consider approximately the anharmonicity of the CCl_4 vibrations with the help of an empirical formula deduced in the paper [2698] on the basis of experimental data on the specific heat of CF_2Cl_2. However, this attempt cannot be called justified (cf. page 1049.

TABLE 151

List of Data on the Thermodynamic functions of Carbon Tetrachloride in a Gaseous State

Авторы 1	Год опубликования 2	Термодинамические функции 3	Справочники и монографии 4
Йост и Блэр [4361]	1933	S°_{298}	—
Волд [4120][а]	1935	C°_{p} ^{5}для $T = 373{,}15 - 773{,}15^{\circ}K$	[2312,98]
Лорд и Бланчард [2649][б] b	1936	S°_{T} ^{5}для $T = 298{,}15$ и $348{,}5^{\circ}K$	—
Стивенсон и Бич [3856, 3857, 3858]	1938	$S^{\circ}_{298,1}$, Φ°_{T}, $H^{\circ}_{T} - H^{\circ}_{0}$ ^{5}для $T = 291{,}1 - 600^{\circ}$ K	[100,149]
Йост [4358]	1938	$S^{\circ}_{298,1}$	[98,2364]
Коб и Лонг [2450]	1950	Φ°_{T}, S°_{T}, C°_{p}, $H^{\circ}_{T} - H^{\circ}_{0}$ ^{5}для $T = 273 - 1500^{\circ}$ K	—
Мадиган и Кливленд [2726]	1951	Φ°_{T}, S°_{T}, C°_{p}, $H^{\circ}_{T} - H^{\circ}_{0}$ ^{5}для $T = 298 - 1000^{\circ}$ K	[4384,119a]
Черный и Эрдеш [1079, 1078]	1953	Φ°_{T}, S°_{T}, C°_{p}, $H^{\circ}_{T} - H^{\circ}_{0}$ ^{5}для $T = 100 - 1000^{\circ}$ K	—
Геллес и Питцер [1678]	1953	Φ°_{T}, S°_{T}, C°_{p}, $H^{\circ}_{T} - H^{\circ}_{0}$ ^{5}для $T = 100 - 1500^{\circ}$ K	[119a]
Свердлин [359]	1954	Φ°_{T}, S°_{T}, C°_{p}, $H^{\circ}_{T} - H^{\circ}_{0}$ ^{5}для $T = 298{,}2 - 1000^{\circ}$ K	—
Олбрайт и др. [496]	1954	Φ°_{T}, S°_{T}, C°_{p}, $H^{\circ}_{T} - H^{\circ}_{0}$ ^{5}для $T = 100 - 1000^{\circ}$ K	—
Первое издание Справочника	1956	Φ°_{T}, S°_{T}, $H^{\circ}_{T} - H^{\circ}_{0}$ ^{5}для $T = 293.16 - 6000^{\circ}$ K	—
Гордон [1816]	1958	Φ°_{T}, S°_{T}, C°_{p}, $H^{\circ}_{T} - H^{\circ}_{0}$ ^{5}для $T = 298{,}16 - 2000^{\circ}$ K	—

1) Authors: 2) year of publication; 3) thermodynamic functions; 4) reference books and monographs; 5) for.
a) On the basis of the C°_{p} values calculated by Vold, the corresponding empirical formulas have been deduced in [3821, 2363]. The formula for C°_{p} obtained by Kelley [2363] has been used by the same author in connection with the given papers [3856, 3857, 3858, 4358] for calculating $H^{\circ}_{T} - H^{\circ}_{298.16}$ and $S^{\circ}_{T} - S^{\circ}_{298.16}$ in the range of T = 400--1000°K. b) The values of S°_{298} and $S^{\circ}_{348.5}$ have been calculated in [2649] for all isotopic varieties of CCl_4 and for a natural blend of isotopic molecules.

The $S^{\circ}_{298.15}$(CCl_4, gaseous) values have been calculated on the basis of the results of calorimetric measurements in several studies. The most precise result was obtained by Hildenbrand and McDonald in

1959 [2071]. A survey on the results of earlier calorimetric investigations of the thermodynamic properties of carbon tetrachloride at low temperatures can be found in the Handbooks [98, 2364] and in the paper [2071]. Hildenbrand and McDonald [2071] measured the specific heat of carbon tetrachloride in the temperature range of 17-298°K. From these data and by extrapolating the specific heat of CCl_4 to 0°K the authors of [2071] found $S^\circ_{298.15}(CCl_4, \text{liquid}) = 51.67 \pm 0.15$ cal/ /mole•degree. Using furthermore the data they had obtained for the heat of fusion of CCl_4, corrections accounting for non-ideal behavior, and a conversion to standard conditions, Hildenbrand and McDonald found $S^\circ_{298.15}(CCl_4, \text{gaseous}) = 73.92 \pm 0.20$ cal/mole•degree which is in accordance with the value calculated in various papers from the molecular constants, and with the value of $S^\circ_{298.15} = 74.107$ cal/mole• •degree given in Table 160 (II).

The specific heat of carbon tetrachloride in a gaseous state was measured by Eucken and Sarstedt [1504] at T = 465°K and by Aihara [494] at T = 279°K. The results of these measurements agree, within the limits of error, with the CCl_4 specific heat calculated with the molecular constants used in this Handbook, when corrections accounting for non-ideal behavior are taken into consideration.

$\underline{CBr_4}$. From the molecular constants, the thermodynamic functions of carbon tetrabromide have been calculated by Stevenson and Beach [3857, 3856, 3858] (Φ^*_T and $H^\circ_T - H^\circ_0$ at T = 291.1-600°K and $S^\circ_{298.1}$), by Sverdlin and Godnev [361] (Φ^*_T, S°_T, C°_p and $H^\circ_T - H^\circ_0/T$ at T = 298.2-1000°K) and by Gelles and Pitzer [1678] (Φ^*_T, S°_T, C°_p, $H^\circ_T - H^\circ_0$ at T = 100-1500°K). The Φ^*_T and S°_T values of CBr_4 from the papers [3858, 3857, 3856, 361, 1678] and from Table 173 (II) agree among one another within 0.05 cal/ /mole•degree. Discrepancies, if any, are due to differences in the molecular and physical constants used.

The first edition of the Handbook did not deal with the thermodynamic functions of CBr_4.

§67. CX_3Y-Type Halocarbons

The tables 152, 155, 163, 165, 166, 168, 174, 176, 177, 179, 183, 185, 193 195, 196 of Volume II of the Handbook give the thermodynamic functions of 15 CX_3Y-type halogen substitutes of methane, calculated for the corresponding ideal gases in the harmonic-oscillator-rigid-rotator approximation, and with the molecular constants of Table 147. The values of the constants $\theta_n(d_n)$, C'_Φ and C'_S used in the calculations are given in Table 152.

TABLE 152

Constants for Calculating the Thermodynamic Functions of Gaseous CX_3Y,Type Halocarbons

Вещество 1	$\theta_1(1)$	$\theta_2(1)$	$\theta_3(1)$	$\theta_4(2)$	$\theta_5(2)$	$\theta_6(2)$	C'_Φ	C'_S
	град 2						кал/моль·град 3	
CH_3F	4192,42	2106	1508,1	4324,7	2110,1	1723,2	−0,1983	7,7508
CH_3Cl	4206,3	1950,4	1053,3	4376,5	2092,9	1460,4	2,2835	10,2326
CH_3Br	4208	1878	879	4397,9	2077,3	1373,3	4,8147	12,7638
CH_3J 4	4194	1800,5	767,4	4405,9	2068,7	1269,7	6,4943	14,4434
CHF_3	4366	1636	1006,6	1978	1657	730,3	7,0198	14,9689
$CHCl_3$	4362	965,6	524,9	1752	1104,6	367,6	12,1076	20,0567
$CHBr_3$	4367	776	319	1652	944	222	17,2646	25,2137
CHJ_3	4371	629	220	1535	832	151	20,5496	28,4987
CF_3Cl	1590	1124,7	684,6	1744	806	504	10,4670	18,4161
CF_3Br	1561	1097	504	1735	788	439	12,4439	20,3930
CF_3J	1544	1066	411	1705	777	381	13,8844	21,8335
$CFCl_3$	1561	770	502,9	1219	573	347	13,0863	21,0354
$CFBr_3$	1538	573	314	1069	440	216	17,7313	25,6804
CCl_3Br	1033	604	355	1115	424	278	15,6651	23,6142
$CClBr_3$	1072	470	304	974	304	201	18,3112	26,2603

1) Substance; 2) deg; 3) cal/mole•degree; 4) J = Iodine.

The errors in the values of the thermodynamic functions of the CX_3Y-type halogen substitutes of methane are caused mainly by inaccurate values of the molecular constants used and by not considering the anharmonicity of the vibrations. At temperatures lower than 1000°K, the error in the thermodynamic functions is due chiefly to inaccurate molecular constants, and it amounts to 0.05 to 0.1 cal/mole•degree with $\Phi^*_{298.15}$. At higher temperatures, the error in the thermodynamic functions is due chiefly to a neglecting of the anharmonicty of the vibrations; it has been estimated to be from 1 to 3 cal/mole•degree with Φ^*_{3000}.

Tables of the virial coefficients and of their derivatives of six CX_3Y-type halocarbons (CH_3F, CH_3Cl, $CHCl_3$, $CFCl_3$, CH_3Br, CH_3I) are given in Volume II of the Handbook; with their help it is possible to consider the corrections for non-ideal behavior (see Volume II, Tables 409, 411, 412, 414-416).

Below, the results of earlier calculations of the thermodynamic functions of the individual CX_3Y-type halocarbons are considered, and the results of these calculations are compared with the values of the thermodynamic functions of the same compounds given in Volume II of the Handbook.

$\underline{CH_3F}$. The thermodynamic functions gaseous fluoromethane have been calculated by Edgell and Glockler [1455] ($S^\circ_{298.1}$ and C°_p at T = 298.1--600°K), by Sverdlin and Godnev [361] (Φ^*_T, S°_T, C°_p, $H^\circ_T - H^\circ_0/T$ at T = = 298.2-1000°K), and by Gelles and Pitzer [1678] (Φ^*_T, S°_T, C°_p, $H^\circ_T - H^\circ_0$ at T = 100-1500°K). The thermodynamic functions of the deuterium substitutes of fluoromethane have not been taken into consideration.

The values of the thermodynamic functions of CH_3F given in the papers [1455, 361, 1678] and in Table 152 (II) differ insignificantly though different values of the molecular and physical constants have been used in these papers. Despite the fact that different values of the structural parameters of the CH_3F molecule have been used in these calculations, this is explained by practically identical products of the principal moments of inertia having been obtained, the differences in the values of the individual frequencies obviously having been compensated during the calculation of the vibrational components of the thermodynamic functions.

$\underline{CH_3Cl}$. The thermodynamic functions of chloromethane in a gaseous state have been calculated by Vold [4120] (C_p° and $E_T^\circ - E_0^\circ$ at T = 0--500°C), Stevenson and Beach [3858, 3856, 3857] ($S_{298.16}^\circ$, Φ_T^* and $H_T^\circ - H_0^\circ$ at T = 291.1-1200°K), Cerny and Erdos [1080] (Φ_T^*, S_T°, C_p°, $H_T^\circ - H_0^\circ/T$ at T = 100-1000°K), Gelles and Pitzer [1678] (Φ_T^*, S_T°, C_p°, $H_T^\circ - H_0^\circ$ at T = 100-1500°K) and Sverdlin [359] (Φ_T^*, S_T°, $H_T^\circ - H_0^\circ/T$, C_p° at T = 298.2-1000°K). The thermodynamic functions of CH_3Cl given in the Handbook by Zeise [4384] are based on the results of calculations performed in the papers [4120, 3856, 3857, 3858]. The CH_3Cl specific heat values calculated by Vold [4120] are rendered in a monograph by Justi [2312] and have been used in the paper [3821] for to present the temperature dependence of C_p° in analytical form. The results of the calculations made by Cerny and Erdos [1080] and by Gelles and Pitzer [1678] are given in a monograph by Vvedenskiy [119a]. The thermodynamic functions of the deuterium substitutes of chloromethane have not been considered.

Earlier calculations of the thermodynamic functions of CH_3Cl were based on obsolete values of the molecular constants. However, the differences in the values of the fundamental frequencies had little effect upon the results of the calculations. The greatest influence was found to be exerted by differences in the products of the principal moments of inertia. For this quantity, values very close to the one used in this Handbook have been used in the papers [3857, 3858, 3856, 1080, 359]. The results of these calculations are therefore in good agreement with the data of Table 163 (II). The value of $I_A I_B I_C = 17.9 \cdot 10^{-117}$ $g^3 \cdot cm^6$, which was taken by Gelles and Pitzer in their calculations [1678], has been calculated for a tetrahedral molecular model on the assumption that r_{C-H} = 1.10 and r_{C-Cl} = 1.75 A, but it differs greatly from the $I_A I_B I_C$ value used in this Handbook (see Table 147). This explains the systematic discrepancies in the values of the thermodynamic functions of CH_3Cl given in the paper [1678] and in Table 163 (II). For Φ^*_T and S°_T they amount to about 0.23 cal/mole•degree.

From the results of calorimetric measurements, Messerly and Aston [2860] obtained the value $S^\circ_{298.15}$ (CH_3Cl, gaseous) = 55.94 ± 0.15 cal/mole•degree, which is in agreement with the value $S^\circ_{298.15}$ = 56.021 cal/mole•degree given in Table 163 (II).

<u>CH_3Br.</u> The thermodynamic functions of gaseous methyl bromide have been calculated by Stevenson and Beach* [3856, 3857, 3858] ($S^\circ_{298.15}$, Φ^*_T and $H^\circ_T - H^\circ_0$ at T = 291.1-1200°K), Sverdlin and Godnev [361] (Φ^*_T, S°_T, C°_p, $H^\circ_T - H^\circ_0/T$ at T = 298.2-1000°K), Gelles and Pitzer [1678] (Φ^*_T, S°_T, C°_p, $H^\circ_T - H^\circ_0$ at T = 100-1500°K), and by Weissman et al [4199] (Φ^*_T, S°_T, $H^\circ_T - H^\circ_0$, C°_p at T = 100-1550°K). The thermodynamic functions of the deuterium substitutes of methyl bromide have been calculated by Weissman et al [4199] (for CD_3Br) and by Dowling [1396] (for CH_2DBr and CHD_2Br).

The differences among the values of the thermodynamic functions of CH_3Br in the papers [3858, 3857, 3856, 361, 1678, 4199] and in Table 174 (II) are small desoite the considerable discrepancies in the values of the molecular and physical constants used for the calculations. The differences in the Φ^*_T and S°_T values do not exceed 0.05 cal/mole•degree. The results obtained by Sverdlin and Godnev [361] are the ones agreeing best with the data in this Handbook. Slight systematic discrepancies between the values of the thermodynamic functions of CH_3Br given in Table 174 (II) and in the papers [3858, 3857, 3856, 1678, 4199] are caused mainly by differences in the values of the product $I_AI_BI_C$. This quantity was taken to be somewhat smaller in the papers [3858, 3857, 3856, 4199] than in this Handbook, corresponding to $r_{C-Br} = 1.91$ A, whereas in the paper [1678] the greater value of $44.6 \cdot 10^{-117}$ $g^3 \cdot cm^6$.

Egan and Kemp [1467] have calculated the value $S^\circ_{298.15}(CH_3Br$, gaseous) = 58.61 ± 0.2 cal/mole·degree from their results of calorimetric measurements of the specific heat of the heat of fusion of methyl bromide. The entropy of CH_3Br at 298.15°K, determined from the calorimetric data agrees with the value of $S^\circ_{298.15} = 58.767$ cal/mole·degree given in the Table 174 (II).

<u>CH_3I</u>. The thermodynamic functions of methyl iodide have been calculated by Edgell and Glockler [1455]* ($S^\circ_{298.1}$ and C°_p at T = 198.1--600°K), Fenlon et al [1549]** (Φ^*_T, S°_T, C°_p and $H^\circ_T - H^\circ_0$ at T = 200--1000°K), Gelles and Pitzer [1678] (Φ^*_T, S°_T, C°_p, $H^\circ_T - H^\circ_0$ at T = 100--1500°K), and by Sverdlin [359] (Φ^*_T, S°_T, C°_p, $H^\circ_T - H^\circ_0/T$ at T = 298.2--1000°K).

The values of the thermodynamic functions of CH_3I given in the papers [1549, 359] and in Table 193 (II) differ slightly from one another. The Φ^*_T and S°_T values from the paper [1678] are systematically lower by 0.20 cal/mole·degree than the values of the corresponding quantitites in Table 193 (II). The $S^\circ_{298.15}$ value given in the paper [1455] is greater than the $S^\circ_{298.15}$ value in Table 193 (II) by exactly this amount. These deviations are due to the fact that the low value of $55.1 \cdot 10^{-117}$ $g^3 \cdot cm^6$ has been taken for $I_AI_BI_C$ in paper [1678]*** whereas a higher value of this quantity has been taken in the paper [1455] owing to obsolete data on the structure of the CH_3I molecule.

<u>CHF_3</u>. The thermodynamic functions of gaseous trifluoromethane have been calculated by Glockler and Edgell [1771] (C°_p at T = 256-650°K)

Decker, Meister, Cleveland [1283] (T = 298.2-1000°K), Sverdlin, Godnev, [361] (T = 298.2-1000°K), and Gelles and Pitzer [1678] (T = 100-1500°K). The thermodynamic functions of CD_3F have been calculated in the papers [1283]* (at T = 298.2-1000°K) and [3294] (at T = 200-1500°K).

Owing to the insignificant discrepancies between the values of the molecular constants of CHF_3 used in the papers [1283, 361, 1678] and in this Handbook, the differences among the corresponding values of the thermodynamic functions of trifluoromethane do not exceed 0.02 cal/mole•degree.

Vanderkooi and De Vries [4055] conducted precise experimental measurements of the specific heat of gaseous trifluoromethane at low pressure, and they obtained $C_{v300} = 10.23 \pm 0.13$ cal/mole•degree; this agrees well with the value of this quantity calculated from the molecular constants (10.25 cal/mole•degree).

$\underline{CHCl_3}$. The thermodynamic functions of trichloromethane in a gaseous state have been calculated by Vold [4120]** (C_p° at T = 0-500°C) Stevenson and Beach [3857, 3856, 3858] ($S^\circ_{298.1}$, Φ_T^* and $H_T^\circ - H_0^\circ$ at T = 291.1-800°K), Madigan and Cleveland [2726]*** (T = 298.16-1000°K), Kobe and Long [2450] (T = 273.15-1500°K), Cerny and Erdos [1079] (T = 100-1000°K), Gelles and Pitzer [1678] (T = 100-1500°K), and by Sverdlin [359] (T = 298.2-1000°K). The thermodynamic functions of $CDCl_3$ have been calculated by Madigan et al in the paper [2728]*** (T = 298.16-1000°K).

The values of the thermodynamic functions calculated in the papers [3858, 3857, 3856, 2726, 2450, 1079, 1678, 359] for $CHCl_3$ agree within ±0.1 cal/mole•degree with the values of the corresponding quantities given in Table 165 (II). Any slight differences are due to differences in the molecular and physical constants that have been used.

An experimental measurement of the specific heat of gaseous trichloromethane, conducted by Aihara [494], led to the value of C_{v279} = = 13.8 cal/mole·degree. Within the limits of error, this agrees with the value calculated from the molecular constants.

$CHBr_3$. The thermodynamic functions of gaseous tribromethane have been calculated by Stevenson and Beach* [3856, 3857, 3858] ($S^\circ_{298.1}$, Φ^*_T and $H^\circ_T - H^\circ_0$ at T = 291.1-600°K), Sverdlin and Godnev [361] (T = = 298.2-1000°K), and Gelles and Pitzer [1678] (T = 100-1500°K). The thermodynamic functions of $CDBr_3$ have been calculated in the paper [1553] (at T = 298.16-1000°K).**

The values of the thermodynamic functions of $CHBr_3$ given in the papers [3858, 3857, 3856, 361, 1678] and in Table 176 (II) agree with each other within 0.2 cal/mole·degree. The Φ^*_T and S°_T values calculated by Gelles and Pitzer [1678] are about 0.05 cal/mole·degree smaller than the corresponding values of these quantities of Table 176 (II); this is due mainly to the fact that a smaller value (1.91 A) of the C-Br bond length was used in the paper [1678] than in this Handbook. The Φ^*_T and S°_T values calculated by Sverdlin and Godnev [361] are about 0.2 cal/mole·degree greater than the corresponding quantities of Table 176 (II). This discrepancy is due mainly to the fact that the authors of the paper [361] have not used the fundamental frequencies observed in the vibrational spectra of tribromethane but instead have taken value calculated by Stepanov [392] from obsolete data on the vibrational spectra of the halogen substitutes of methane (see footnote original page 1048). The values of the two doubly generate ν_6 and ν_4 in this case were found to be much lower than the frequencies observed in the vibrational spectra of $CHBr_3$.

Experimental measurement of the specific heat of gaseous tribromomethane conducted by Aihara [494] led to the value $C_{v_{279}}$ = 15.8 cal/mole·degree. Without any correction accounting for intermolecular interaction, this quantity amounts to 14.7 cal/mole·degree.

$\underline{CHI_3}$. The thermodynamic functions of gaseous iodoform have been calculated by Sverdlin [359, 360] in the temperature range of 298.2--1000°K. The calculations were carried out on the basis of the molecular constants of CHI_3 the values of which differed considerably from those used in this Handbook; this gave rise to great differences between the thermodynamic functions of CHI_3 given in these papers and those of Table 195 (II).

For calculating the thermodynamic functions of CHI_3 the approximate fundamental frequencies evaluated by Maslov [293] by means of the influence factors and the structural parameters determined by Brockway in one of his earlier electron diffraction studies [956] have been used in the paper [359]. The somewhat too high values of 131 and 350 cm^{-1}, respectively were in this case taken for the doubly degenerate frequencies ν_6 and ν_3, and for the C-I bond length the value of 2.12 A which is smaller than that used in this Handbook. The thermodynamic functions of CHI_3 calculated in the paper [359] from these constants differ from those of Table 195 (II) by 1.48 and 2.08 cal/mole·degree, respectively, with $\Phi^*_{298.15}$ and Φ^*_{1000}.

In a recalculation of the thermodynamic functions of CHI_3 [360] Sverdlin used better values of the fundamental frequencies based on his estimates made with the partial frequency method [362]. The values of the thermodynamic functions of CHI_3 obtained in the paper [360] unlike those of the paper [359], are somewhat greater than the corresponding quantities of Table 195 (II) which must be attributed to the lower frequency values ν_2, ν_4, and ν_6 used in the paper [360] in the calculation of the thermodynamic functions of CHI_3.

$\underline{CF_3Cl, CFCl_3}$. The thermodynamic functions of CF_3Cl and $CFCl_3$ in their gaseous state have been calculated by Justi and Langer [2314]

(C_v°, C_p° at T = 173.15-473.15°K), Thompson and Temple [3974] (T = 250--600°K for CF_3Cl and T = 298.16-600°K for $CFCl_3$), Gelles and Pitzer [1678] (T = 100-1500°K), and by Albright, Galegar, Innes [496] (T = = 100-1000°K). The thermodynamic functions of CF_3Cl have been calculated also by Decker, Meister, and Cleveland [1283] (T = 100-1000°K), and the thermodynamic functions of $CFCl_3$ by Bernstein, Zietlov, and Cleveland [769] (T = 298.16-1500°K). Zeise's Handbook [4384] renders the thermodynamic functions of CF_3Cl as calculated in the paper [1283] and those of $CFCl_3$ as calculated in the paper [3974].

In this Handbook as well as in all the papers with the exception of [496] - the thermodynamic functions of CF_3Cl and $CFCl_3$ have been calculated in the harmonic-oscillator-rigid-rotator approximation. Approximate corrections for the anharmonicity of the vibrations of the CF_3Cl and $CFCl_3$ molecules have been adopted in the paper [496]. This was accomplished with the aid of an empirical formula proposed in the paper [2698] and experimental data on the specific heat of CF_2Cl_2 from the paper [2796].

As a result of the anharmonicity of the vibrations having been considered, the thermodynamic functions of CF_3Cl and $CFCl_3$ obtained from [496] are somewhat greater than the corresponding quantities given in the other papers and in the Tables 166 (II) and 168 (II). In the temperature range examined in [496], however, the corrections accounting for the anharmonicity of the vibrations are small amounting to about 0.13 cal/mole·degree with Φ_{1000}^* (CF_3Cl) and to about 0.30 cal/mole·degree with Φ_{1000}^* ($CFCl_3$). They should be more essential at higher temperatures. Yet, the procedure of considering the anharmonicity of the vibrations, used in the paper [496], cannot be applied at high temperatures.

The differences between the corresponding values of the thermodynamic functions of CF_3Cl and $CFCl_3$ given in the papers [3974, 1678, 1283, 769] and in the Tables 166 (II) and 168 (II) do not exceed 0.1 cal/mole·degree with both Φ_T^* and S_T°; they are due to the differences among the values of the molecular and physical constants used in the calculations. The differences among the values of the fundamental frequencies of the CF_3Cl and $CFCl_3$ molecules, used in the calculations, are insignificant. Greater are the differences among the values of the structural parameters and the products of the principal moments of inertia corresponding to them. The values used for these quantities in the papers [1283, 769] are close to the ones used in this Handbook. The thermodynamic functions of CF_3Cl and $CFCl_3$ obtained in these papers are therefore close to the values given in the Tables 166 (II) and 168 (II). In their calculations, Thompson and Temple [3974] used inaccurate values of the structural parameters of the CF_3Cl and $CFCl_3$ molecules which had been found in an earlier electron diffraction investigation carried out by Brockway [956]. From these data, higher $I_AI_BI_C$ values than those in this Handbook have been obtained. In relation to this, the Φ_T^* and the S_T° values obtained from the paper [3474] were higher than those in the Tables 166 (II) and 168 (II). In the paper [1678] by Gelles and Pitzer, the same values of the product $I_AI_BI_C$ of CF_3Cl and $CFCl_3$ are given also in the paper [3974]. When, however, the Φ_T^* and S_T° values of CF_3Cl given in the paper [1678] are greater than the corresponding values of these functions in Table 166 (II), the values of these functions of $CFCl_3$ given in the paper [1678] will be smaller than in Table 168 (II). This is evidence of the values of the thermodynamic functions of $CFCl_3$ given in [1678] not being in accord with the molecular constants of $CFCl_3$ used in the same paper.*

Along with calculations from molecular constants, some values of the thermodynamic functions of gaseous CF_3Cl and $CFCl_3$ have been found by experiment. Vanderkooi and De Vries [4055] measured the specific heat of trifluorochloromethane at an extremely low pressure by the "incandescent wire" method and found $C^\circ_{v300} = 14.10 \pm 0.38$ cal/mole••degree, to be in agreement with the results of the corresponding calculations from the molecular constants.* Osborn, Garner, Doescher, and Yost [3148] measured the specific heat of fluorotrichloromethane in the temperature range of 14-298°K as well as the heat of fusion and the vapor pressures, and found the value $S^\circ_{298.15}(CFCl_3, \text{gaseous}) = = 74.07 \pm 0.1$ cal/mole•degree; from these data by calculation; this agrees well with the value $S^\circ_{298.15} = 74.007$ cal/mole•degree from Table 168 (II).*

$\underline{CF_3Br, CF_3I}$. The thermodynamic functions of gaseous CF_3Br and CF_3I have been calculated by McGee, Cleveland et al [2705] (T = 100--1000°K) and by Gelles and Pitzer [1678] (T = 100-1500°K). The results of the calculations in [2705] are rendered in the Handbook [4384], and the results from [1678] in the monograph [119a].

The values of the thermodynamic functions of CF_3Br and CF_3I given in the papers [2705, 1678] and in the Tables 177 (II) and 196 (II) are close to one another**. Any discrepancies are due to differences in the molecular and physical constants used.

$\underline{CFBr_3}$. The thermodynamic functions of gaseous fluorotribromomethane had been calculated earlier by Gelles and Pitzer [1678] in the temperature range of 100-1500°K. The difference between the corresponding values of Φ^*_T and S°_T of [1678] and of Table 179 (II) is 0.04 cal//mole•degree. This is due to the difference between the values of the structural parameters of $CFBr_3$ used in the calculations. Apparently in their calculations, Gelles and Pitzer [1678] used the structural parameters as found by Wouters and Hemptinne [4333] in an electron diffraction investigation of the molecular structure of fluorotribromomethane (see page 1013).

CCl_3Br, $CClBr_3$. The thermodynamic functions of CCl_3Br and $CClBr_3$ had been calculated earlier by Glockler and Edgell [1772] (C_p° at T = = 250-600°K) and by Gelles and Pitzer [1678] (T = 100-1500°K). The thermodynamic functions of CCl_3Br also have been calculated by Madigan and Cleveland [2726] (T = 298.2-1000°K). The values of the thermodynamic functions of CCl_3Br and $CClBr_3$ given in the Handbook by Zeise are based on the results of the calculations made by Glockler and Edgell [1772] and by Madigan and Cleveland [2726]. The monograph [119a] contains the results of the calculations of [2726, 1678].

The difference between the corresponding values of Φ_T^* and S_T° of CCl_3Br from the paper [2726] and from Table 183 (II) is not greater than 0.02 cal/mole·degree in spite of the considerable differences among the values of the molecular and physical constants used. In their calculations, Glockler and Edgell [1772] obtained too high a specific heat C_p° of CCl_3Br which exceeds the corresponding quantities in the papers [2726, 1678] by about 0.22 cal/mole·degree. The discrepancies are due to inaccurate values of the fundamental frequencies of the CCl_3Br molecule having been used in the paper [1772]. The Φ_T^* and S_T° values given in the paper [1678] are approximately 2 cal/mole·degree lower than in the paper [2726] and in Table 183 (II). The cause of such a sharp discrepancy is apparently an error in the calculations of Gelles and Pitzer.

The Φ_T^* and S_T° values of gaseous chloro-tribromomethane given in the paper [1678] are about 0.1 cal/mole·degree below the corresponding values of these quantities in Table 185 (II). This difference is due to inaccurate calculations made by Gelles and Pitzer. The C_p° values of $CClBr_3$ obtained from the papers [1772, 1678] at $T \leq 3000$°K differ greatly from one another; this is due to different fundamental frequencies of the $CClBr_3$ molecule having been used.

§68. CX_2Y_2-Type Halocarbons

The Tables 154, 164, 167, 175, 178, 184, 194, 197 of Volume II of the Handbook show the values of the thermodynamic functions of CX_2Y_2--type halogen substitutes of methane calculated for the corresponding ideal gases in the harmonic-oscillator-rigid-rotator approximation with the molecular constants from Table 148. The values of the constants θ_n, C'_Φ and C'_S used in the calculations are shown in Table 153.

TABLE 153

The Constants for the Calculation of the Thermodynamic Functions of Gaseous CX_2Y_2-type Halocarbons

Вещество 1	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7	θ_8	θ_9	C'_Φ	C'_S
	град 2									3 кал/моль·град	
CH_2F_2	4243	2170	1606	760,5	1816	4338,2	1692,2	2065,2	1567,8	4,8818	12,8309
CH_2Cl_2	4310,2	2057,6	1025,7	405,2	1659	4374	1285	1816	1076	9,0509	17,0000
CH_2Br_2	4328	2017	850	250	1570	4404	1165	1719	932	13,3187	21,2678
CH_2J_2 4	4269	1942	699	174	1482	4388	1030	1593	823	16,1404	24,0895
CF_2Cl_2	1580	960,0	653,5	376,2	463	1327	626,3	1668	643,7	12,7130	20,6621
CF_2Br_2	1568	896	489	237	406	1659	528	1196	475	16,2237	24,1728
CF_2J_2	—	—	—	—	—	—	—	—	—	18,7028	26,6519
CCl_2Br_2	1073	547	348	222	252	1004	331	1124	377	17,8859	25,8350

1) Substance; 2) deg; 3) cal/mole•degree; 4) J = Iodine.

The errors in the calculation of the thermodynamic functions of the CX_2Y_2-type halocarbons are due mainly to inaccurate values of the molecular constants and to the anharmonicity of the vibrations not having taken into consideration. At temperatures below 1000°K, the errors in the thermodynamic functions are due chiefly to inaccurate molecular constants, amount to 0.05 to 0.1 cal/mole•degree with $\Phi^*_{298.15}$ at higher temperatures than are due to the anharmonicity of the vibrations not having been considered, and they are estimated at 1 to 3 cal/mole•degree with Φ^*_{3000}.

What follows is a discussion of earlier calculations of the thermodynamic functions of the individual CX_2Y_2-type halocarbons and a comparison of the results of these calculations with the corresponding values of the thermodynamic functions of these substances given in Volume II of the Handbook.

CH_2F_2. The thermodynamic functions of gaseous methylene fluoride have been calculated by Glockler and Edgell [1772] (C°_p at T = 250--600°K), Sverdlin and Godnev [361] (T = 298.2-1000°K), Gelles and Pitzer [1678] (T = 100-1500°K), and Meister, Dowling and Bielecki [2848 (T = 100-1000°K). In the paper [2848], the thermodynamic functions of $CDHF_2$ and CD_2F_2 have been calculated, too.

The values of the thermodynamic functions of CH_2F_2 given in the papers [1678, 361] and in Table 154 (II) differ slightly from one another owing to slight differences in the molecular and physical constants. The differences between the corresponding values of Φ^*_T and S°_T do not exceed 0.03 cal/mole•deg. The difference between the corresponding values of Φ^*_T and S°_T given in the paper [2848] and in Table 154 (II) is 0.15 cal/mole•degree at T = 298.15°K, and 0.12 cal/mole•degree at T = 1000°K. This difference is due to the fact that in the paper [2848] obsolete values of the fundamental frequencies of the CH_2F_2 molecule and an inaccurate value of the C-F bond length (1.32 A) have been used.

CH_2Cl_2. The thermodynamic functions of gaseous methylene chloride have been calculated by Vold [4120] (C°_p, $E^\circ_T - E^\circ_0$ at T = 0-500°C), Stevenson and Beach [3858, 3857, 3856] ($S^\circ_{298.1}$, Φ^*_T, and $H^\circ_T - H^\circ_0$ at T = = 291.1-800°K), Justi and Langer [2313] (C°_v, C°_p from -50 to +150°C), Glockler and Edgell [1772] (C°_p at T = 250-600°K), Kobe and Long [2450] (at T = 273.15-1500°K), Gelles and Pitzer [1678] (at T = 100-1500°K), and Sverdlin [359] (at T = 298.2-1000°K). The values of the specific heat C°_p calculated by Vold [4120] are given in a monograph by Justi [2312]. The thermodynamic functions of CH_2Cl_2 obtained from the papers [3858, 3857, 3856, 1772, 2313] have been used in Zeise's Handbook [4384] for compiling tables of the thermodynamic properties of gaseous methylene chloride. The C_p° values calculated by Glockler and Edgell [1772] are rendered in analytical form in the paper [3820]. The thermodynamic functions of the deuterium substitutes of methylene chloride have not been calculated.

In earlier calculations of the thermodynamic functions of methylene chloride [4120, 3856, 2313, 1772], too low values had been used for several fundamental frequencies of the CH_2Cl_2 molecule, which led to somewhat high values of the thermodynamic functions. In later calculations [2450, 1678, 359] the values of the molecular constants of CH_2Cl_2 were not sufficiently reliable. The values of the molecular constants of CH_2Cl_2 closest to the ones used in this Handbook have been used in the paper [1678] by Gelles and Pitzer. This is the reason why the values of the thermodynamic functions of CH_2Cl_2 given in the paper [1678] deviate slightly from the ones of Table 164 (II), the deviation not exceeding 0.1 cal/mole•degree for both Φ_T^* and S_T°. In the calculations of the thermodynamic functions of methylene chloride, Sverdlin [359] used the fundamental frequencies of the CH_2Cl_2 molecule as calculated by Stepanov [392] (see footnote one on page 1048); for the frequency ν_4 the latter had obtained a value which was about 40 cm^{-1} too high. Owing to the discrepancies in the values of the molecular and physical constants, the values of the thermodynamic functions of CH_2Cl_2 calculated by Sverdlin are lower than the values of the corresponding quantities in the paper [1678] and in Table 164 (II). The discrepancies between the values of Φ_T^* and S_T° given in the paper [359] and in Table 164 (II) reach from 0.12 cal/mole•degree at T = 298.15°K up to 0.24 cal/mole•degree at T = 1000°K.

CH_2Br_2. The thermodynamic functions of gaseous methylene bromide have been calculated by Stevenson and Beach [3858, 3857, 3856] ($S^\circ_{298.1}$, Φ^*_T and $H^\circ_T - H^\circ_0$ at T = 291.1-600°K), Edgell and Glockler [1455] ($S^\circ_{298.1}$, C°_p at T = 298.1-600°K), Sverdlin and Godnev [361] (at T = = 298.2-1000°K), Gelles and Pitzer [1678] (at T = 100-1500°K), Dowling and Meister [1397] (at T = 100-1000°K). The values of the thermodynamic functions of CH_2Br_2 given in Zeise's Handbook [4384] are based on the results of the calculations carried out by Stevenson and Beach [3856, 3857, 3858] and by Edgell and Glockler [1455]. On the basis of the calculations of Edgell and Glockler [1455], an empirical analytical formula for C°_p of methylene bromide has been composed in the paper [3820]. The thermodynamic functions of the deuterium substitutes of methylene bromide ($CHDBr_2$ and CD_2Br_2) have been calculated by Dowling and Meister [1397] (at T = 100-1000°K).

In all the earlier calculations for the fundamental frequencies of the CH_2Br_2 molecule, the authors used values that had been determined from the vibrational spectra of liquid methylene bromide, and for the structural parameters they used values found in earlier electron diffraction studies [100, 101, 2600] according to which the C-Br bond length in the CH_2Br_2 molecule is 1.91 A. However in this Handbook, in the calculation of the thermodynamic functions of gaseous methylene bromide, the values determined from the vibrational spectra of gaseous methylene bromide have been used for the sixth and eighth fundamental frequencies of CH_2Br_2; for the C-Br bond length the value of 1.93 A was used which is based on the results of new and more thorough investigations of the molecular structure of the halogen substitutes of methane.

In their publications [3856, 3857, 3858] Stevenson and Beach used the inaccurate value of 478 cm^{-1} for the frequency ν_8 and hence they obtained exceedingly high values of $S^\circ_{298.1}$ and $H^\circ_T - H^\circ_0$. The Φ^*_T values in the papers [3856, 3857, 3858] exceed the corresponding Φ_T^* values in Table 175 (II) by more than 2 cal/mole•degree, which must be attributed to a numerical error committed in the papers [3856, 3857, 3858].

The values of Φ_T^*, S_T° and C_p° given in the papers [1455, 361, 1678, 1397] and in Table 175 (II) agree with each other within 0.2 cal/mole•degree.

The discrepancies between the Φ_T^* and S_T° values in the paper [1397] and in Table 175 (II) do not exceed 0.03 cal/mole•degree because the differences between the values of the molecular constants have been compensated in the calculation of the thermodynamic functions. The difference between the corresponding Φ_T^* and S_T° values in the paper [1678] by Gelles and Pitzer and in Table 175 (II) is about 0.1 cal/mole•degree. This difference is due mainly to the fact that in the calculations of [1678], the product of the principal moments of inertia of CH_2Br_2 was taken too small by mistake.

The Φ_T^* and S_T° values of CH_2Br_2 in the paper of Sverdlin and Godnev [361] are about 0.2 cal/mole•degree lower than the corresponding values of these quantities in Table 175 (II), which must be attributed to the fact that for the fundamental frequencies of CH_2Br_2, the values calculated by Stepanov [392] (see footnote on page 1048),well as $I_AI_BI_C$ values that are slightly lower than the ones used in this Handbook have been used in the calculations in [361]. The major cause of the discrepancy is the high values of the frequencies ν_4 and ν_7, in the paper [361] taken equal to 200 and 825 cm^{-1}, respectively.

$\underline{CH_2I_2}$. The thermodynamic functions of gaseous methylene iodide have been calculated by Glockler and Edgell [1772]* (C_p° at T = 250-600°K), Voelz, Cleveland, Meister, and Bernstein [4117, 4115] (at T =

= 100-1500°K), and by Sverdlin [359] (at T = 298.2-1000°K). The thermodynamic functions of the deuterium substitutes of methylene iodide have not been calculated.

In all the earlier calculations of the thermodynamic functions of gaseous methylene iodide, and likewise in this Handbook, the values found from the vibrational spectrum of liquid methylene iodide had been used for the fundamental frequencies of the CH_2I_2 molecule. The Φ_T^* and S_T° values given in Table 194 (II) are therefore somewhat high. However, the errors in the thermodynamic functions of CH_2I_2 caused by using the fundamental frequencies of CH_2I_2 observed in the spectra of the liquid phase are small as compared to the errors due to inaccurate structural parameters and to neglecting the anharmonicity of the vibrations. The vibrational components of the thermodynamic functions of CH_2I_2 calculated in the Handbook and in the papers [1772, 4117, 1678, 359] obviously should be close to each other since practically the same fundamental frequencies of the CH_2I_2 molecule have been used in all these calculations. The main reason of the discrepancy between the values of the thermodynamic functions of CH_2I_2 is therefore to be sought in the different values used for the principal moments of inertia of the CH_2I_2 molecule and for the physical constants.

In the calculations carried out Voelz et al [4117] and by Sverdlin [359], the principal moments of inertia of CH_2I_2 had been computed with the aid of the structural parameters found by Bastiansen [675] in an electron diffraction study according to which the C-I bond length in the CH_2I_2 molecule was equal to 2.12 A. The principal moments of inertia of CH_2I_2 have been calculated incorrectly in the paper [4117] and, hence, the Φ_T^* and S_T° values given in this paper exceed the corresponding values of these quantities in the papers [1678, 359] and in

Table 194 (II) by about 3 cal/mole·degree. This error has been corrected by the authors of [4117] in the memorandum [4115].

The Φ_T^* and S_T° values of methylene iodide given in the paper [359] are lower than the corresponding values of these quantities in Table 194 (II), viz. by about 0.15 cal/mole·degree. This discrepancy is due chiefly to the different values used for the C-I bond length in the CH_2I_2 molecule. In the paper [359] by Sverdlin, the fundamental frequencies calculated by Maslov [293] have been used for CH_2I_2.* These values agree within ±10- ±20 cm^{-1} with the ones found by experiment. In the calculation of the vibrational components of the thermodynamic functions of CH_2I_2, these deviations compensated each other and had little effect upon the values of the thermodynamic functions of methylene iodide obtained from [359].

The Φ_T^* and S_T° values of methylene iodide calculated by Gelles and Pitzer [1678] are about 0.22 cal/mole·degree lower than the corresponding values of these quantities in Table 194 (II). This discrepancy is due to the fact that in [1678], inaccurate values of the principal moments of inertia of the CH_2I_2 molecule, obtained from the paper [3258], have been used. At T = 500°K the values of the thermodynamic functions of CH_2I_2 obtained from the paper [1678] were abnormally high which obviously is due to an error in the calculation.

$\underline{CF_2Cl_2}$. The thermodynamic functions of dichlorodifluoromethane in a gaseous state have been calculated by Eucken and Bertram [1499] (C_V° at T = 173, 199, and 279°K), Justi and Langer [2313] (C_V° and C_p° at T = 173-473°K), Thompson and Temple [3974] (T = 250-600°K), Masi [2796, 2797] (T = 200-1500°K), Gelles and Pitzer [1678] (T = 100--1500°K) and Albright, Galegar, and Innes [496] (T = 100-1000°K). The values of the thermodynamic functions of CF_2Cl_2 calculated in the papers [3974, 2796, 2797] are rendered in the Handbook [4384], those calculated in the papers [1678] and [496] are rendered in the monograph [119a].

In the papers [2796, 2797, 496], the thermodynamic functions of CF_2Cl_2 have been calculated with the anharmonicity of the vibrations having been taken into consideration, in the remaining papers as well as in this Handbook the thermodynamic functions of CF_2Cl_2 have been calculated in the harmonic-oscillator-rigid-rotator approximation .

Masi [2796, 2797] made precise measurements of the specific heat of gaseous dichlorodifluoromethane at T = 243.15-363.15°K at pressure p from 1.50 to 0.33 atm. By extrapolating these data to p = 0, Masi obtained the C_p° values of an ideal gas, the error having been estimated to be $\pm 0.15\%$. At the same temperatures, Masi calculated C_p° in the harmonic-oscillator-rigid-rotator approximation using the CF_2Cl_2 fundamental frequencies found by Plyler and Benedict [3277]. In this case, the calculated specific heat of dichlorodifluoromethane was 0.6-0.8% below the experimental value. This discrepancy was ascribed to the inaccurate determination of the frequency ν_9 in the paper [3277] ($\nu_9 = 473$ cm^{-1}) and to the fact that the anharmonicity of the vibrations had not been considered when the specific heat of CF_2Cl_2 was calculated from the molecular constants. Therefore, in the final calculation of the thermodynamic functions of CF_2Cl_2 from the molecular constants, Masi took the value of 450 cm^{-1} for the frequency ν_9 and used the method developed by Stockmayer, Kavanagli, and Mickley [3871] for approximately considering the anharmonicity of the vibrations, with the anharmonicity constants x_{ij} found to be $7.5 \cdot 10^{-4} (\nu_i + \nu_j)$, where ν_i and ν_j are the fundamental frequencies (in cm^{-1}) of the CF_2Cl_2 molecule.* It must be said that further investigations of the vibrational spectrum of CF_2Cl_2 [1117, 1921] (see page 1024) have shown that the ν_9 value taken in the calculations of Masi is very close to the real one.

In their calculation of the thermodynamic functions of CF_2Cl_2 Albright, Galegar, and Innes [496] used more accurate values of the fundamental frequencies found by Claassen [1117] from The raman spectrum of gaseous dichlorodifluoromethane. The anharmonic nature of the vibrations was approximately considered in these calculations according to the method used in the paper [2698], together with the results obtained by Masi [2796, 2797] in his measurements of CF_2Cl_2 calculated in this way in [496] practically coincide with the values of the corresponding quantities given in the papers [2796, 2797].

The use of semi-empirical methods of considering approximately the anharmonic nature of the vibrations in the calculations of the thermodynamic functions of CF_2Cl_2 in the papers [496, 2796, 2797] is not justified because the errors that are due to inaccurate structural parameters of the CF_2Cl_2 molecule at temperatures of up to 1000-1500°K are more graver than the errors caused by neglecting the anharmonic nature of the vibrations. Even the methods used in the papers [496, 2796, 2797] for taking the anharmonicity of the vibrations into consideration are not reliable and may lead to considerable errors when they are used in calculating the thermodynamic functions at higher temperatures.

The thermodynamic functions of CF_2Cl_2 given in Table 167 (II) have been calculated in the approximation with the harmonic oscillator and the rigid rotator as a model. The corresponding Φ_T^* and S_T° values, however, given in this table and in the papers [496, 2796, 2797] do not differ much from each other. They coincide at $T = 298.15°K$ and at $T = 1000°K$ the Φ_T^* values diverge by 0.09 cal/mole•degree and the S_T° values by 0.26 cal/mole•degree. This can be explained by the fact that in the papers [496, 2796, 2797] somewhat lower values were used for the principal moments of inertia of the CF_2Cl_2 molecule, which had been calculated from inadequate data on its structure [956] according to which the C-F and C-Cl bond lengths in the CF_2Cl_2 molecule had been taken equal to 1.35 and 1.74 A, respectively. More accurate data [2629] have been used in this Handbook, according to which the C-F and C-Cl bond lengths are equal to 1.335 and 1.775 A, respectively. It must be said that in all the earlier calculations of the thermodynamic functions of CF_2Cl_2 somewhat lower values have been used for the principal moments of inertia, which were based on obsolete structural data.

The Φ_T^* and S_T° values obtained for CF_2Cl_2 in the papers [3974, 1678] are smaller than those of Table 167 (II). The discrepancies are caused by the low values of the principal moments of inertia of the CF_2Cl_2 molecule and the high values of the frequency ν_9 that have been used in the papers [3974, 1678].

Along with Masi [2796, 2797], Eucken and Bertram [1499] and Buffington and Fleischer [1008] also have conducted experiments to determine the specific heat of gaseous dichlorodifluoromethane. In [1499, 1008], the measurements were made only at atmospheric pressure and with an accuracy considerably below that of [2796, 2797].

CF_2Br_2. The thermodynamic functions of gaseous difluorodibromomethane have been calculated by Gelles and Pitzer [1678] (T = 100--1500°K) and by Decker and collaborators [1284] (T = 100-1000°K).

The Φ_T^* and S_T° values for CF_2Br_2 in [1678] and in Table 178 (II) agree with each other within 0.05 cal/mole•degree. Somewhat lower values than in this Handbook have been taken in [1678] for the product of the principal moments of inertia, corresponding to $r_{C-F} = 1.34$ and $r_{C-Br} = 1.91$ A, and for the frequencies ν_1, ν_2, ν_6, and ν_8. For the latter, the values, used in the Handbook, had been determined in the paper [1284] from the infrared spectrum of gaseous difluorodibromomethane, whereas in [1678] the values found from the investigation of the Raman spectrum of liquid difluorodibromomethane have been used for all fundamental frequencies of the CF_2Br_2 molecule.

In the calculations of the thermodynamic functions of CF_2Br_2 which are given in the paper [1284] and in Table 178 (II), the same fundamental frequencies but slightly different structural parameters of the CF_2Br_2 molecule have been used. The values used in [1284] were $r_{C-F} = 1.33$ and $r_{C-Br} = 1.91$ A, the ones used in this Handbook are $r_{C-F} = 1.35$ and 1.93 A. Hence, the values of Φ^*_T and S°_T given in [1284] are by 0.10 cal/mole·degree smaller than the values of the corresponding quantities in Table 178 (II).

CF_2I_2. The thermodynamic functions of gaseous difluorodiiodomethane have never been calculated before.

In this Handbook, the translational and the rotational compounds of the thermodynamic functions of gaseous difluorodiiodomethane have been calculated with the formulas (II.6), (II.7) and (II.183), (II.184) in which the value appearing in Table 148 was used for the product of the principal moments of inertia of the CF_2I_2 molecule. The vibrational components of the thermodynamic functions of CF_2I_2 were calculated from approximate relations of the form

$$\Phi^*_{\text{кол}}(CF_2J_2) = 2\Phi^*_{\text{кол}}(CF_3J) - \Phi^*_{\text{кол}}(CF_4) \qquad \text{(XVII.1)}$$

in terms of the vibrational components of the thermodynamic functions of CF_3I and CF_4, which were calculated for this Handbook with the aid of the fundamental frequencies of the corresponding molecules. The relations of the form of (XVII.1) were chosen out of the row of other possible relations of the same type on the basis of a number of calculations of the vibrational components of the thermodynamic functions of CF_2Br_2 that had been made with similar formulas as well as on the basis of a comparison of the results obtained therein with the values calculated from the fundamental frequencies of the CF_2Br_2 molecule, used in this Handbook. This comparison showed that the best agreement is reached when relations of the form

$$\Phi^{*}_{\text{кол}}(CF_2Br_2) = 2\Phi^{*}_{\text{кол}}(CF_3Br) - \Phi^{*}_{\text{кол}}(CF_4),$$

are used in the calculations; analogous to this, relation of the form (XVII.1) were used for calculating the vibrational components of the thermodynamic functions of CF_2I_2.

CCl_2Br_2. The thermodynamic functions of gaseous dichlorodibromomethane have been calculated by Glockler and Edgell [1772] (C_p° at T = = 250-600°K), Davis, Cleveland, and Meister [1273] (T = 100-1000°K), Gelles and Pitzer [1678] (T = 100-1500°K). The results of Glockler and Edgell have been used in the paper [3820] for establishing the relation for the dependence of C_p° on temperature. The values of the thermodynamic functions of CCl_2Br_2 calculated in [1273] are given in the Handbook [4384], and the ones calculated in [1678] are given in the monograph [119a].

For the specific heat C_p° of dichlorodibromomethane, Glockler and Edgell [1772] obtained higher values than in the calculations of [1273, 1678] which are of a later date. This can be explained by the fact that in the calculations of [1772], for the greater part of the fundamental frequencies of the CCl_2Br_2 molecule, lower values have been used which had been gotten from an investigation of the Raman spectrum of liquid dichlorodibromomethane. The difference between the corresponding C_p° values in the papers [1772, 1273] is 0.10 cal/mole•degree.

In the calculation of the thermodynamic functions of CCl_2Br_2, the same fundamental frequencies have been used in this Handbook and in the paper [1273]. The Φ_T^* and S_T° values of the paper [1273] are below the corresponding values of these quantities in Table 184 (II) by about 0.04 cal/mole·degree. These discrepancies are due mainly to the different values of the principal moments of inertia which have been used. In [1273] they have been calculated for $r_{C-Cl} = 1.75$ and $r_{C-Br} = 1.93$ A whereas $r_{C-Cl} = 1.77$ and $r_{C-Br} = 1.93$ A have been taken for granted in this Handbook.

The values of the thermodynamic functions of CCl_2Br_2 given in the paper [1678] and in Table 184 (II) diverge but slightly although the molecular constants used in [1678] differ from the ones used in this Handbook. This results from the fact that the differences caused by different values of the moments of inertia and fundamental frequencies of the CCl_2Br_2 molecule compensate each other in the calculation of the thermodynamic functions.

§69. CX_2YZ and CXYZV-type halocarbons

The tables 170-172, 180-182, 186-192, and 198-203 in Volume II of the Handbook contain the thermodynamic functions of 19 CX_2YZ and CXYZV-type halocarbons calculated for the corresponding ideal gases in the harmonic-oscillator-rigid-rotator approximation with the molecular constants of Table 149. The constants θ_n, C'_Φ and C'_S used in the calculations are given in Table 154.

The errors in the thermodynamic functions of the CX_2YZ and CXYZV-type halogen substitutes of methane are due mainly to inaccurate values of the molecular constants having been used and to the anharmonicity of the vibrations having been neglected. At temperatures below 1000°K, the errors in the thermodynamic functions are due chiefly to inaccurate molecular constants, amounting to approximately 0.1 cal/mole·degree with $\Phi^*_{298.15}$. At higher temperatures, the errors in the thermodynamic functions are due chiefly to neglecting the anharmonicity of the vibrations, amounting to from 1 to 3 cal/mole·degree with Φ^*_{3000}

TABLE 154

The Constants for the Calculation of the Thermodynamic Functions of CX_2YZ and CXYZV-type Halocarbons in A Gaseous State

Вещество 1	Θ_1	Θ_2	Θ_3	Θ_4	Θ_5	Θ_6	Θ_7	Θ_8	Θ_9	C'_{Φ}	C'_S
	град 2									3 кал/моль·град	
CH_2FCl	4306	2115	1944	1537	1093	554	4385	1778	1445	8,4382	16,3873
CH_2FBr 4	4306	2102	1889	1511	922	452	4393	1765	1351	10,8034	18,7525
CH_2FJ	—	—	—	—	—	—	—	—	—	12,4049	20,3540
CH_2ClBr	4296	2045	1777	1060	889	327	4393	1639	1229	12,6045	20,5536
CH_2ClJ	4286	2003	1620	1033	758	279	4385	1702	1152	14,1675	22,1166
CH_2BrJ	4285	1977	1532	886	744	207	4393	1655	1085	16,1368	24,0859
CHF_2Cl	4349	1886	1695	1164	856	607	1938	1606	525	11,1282	19,0773
CHF_2Br	4335	1842	1633	1033	830	345	1934	1594	465	13,2607	21,2098
CHF_2J	—	—	—	—	—	—	—	—	—	14,7616	22,7107
$CHFCl_2$	4349	1885	1552	1068	659	397	1787	1157	529	12,8235	10,7726
$CHFClBr$	4349	1869	1525	942	613	317	1729	1111	450	14,8169	22,7660
$CHFBr_2$	4339	1862	1529	892	517	247	1683	1013	426	16,6670	24,6161
$CHCl_2Br$	4357	1693	1056	859	475	317	1751	1112	309	16,1374	24,0865
$CHClBr_2$	4349	1714	1088	829	401	242	1653	963	289	17,8498	25,7989
CF_2ClBr	1655	1255	932	576	547	432	1586	633	288	15,9244	23,8735
CF_2ClJ	—	—	—	—	—	—	—	—	—	17,2815	25,2306
CF_2BrJ	—	—	—	—	—	—	—	—	—	18,8710	26,8201
$CFCl_2Br$	1538	1121	721	481	436	309	1187	561	292	17,0013	24,9504
$CFClBr_2$	1529	1137	665	489	384	230	1073	440	281	18,5356	26,4847

1) Substance; 2) deg; 3) cal/mole•degree; 4) J = Iodine.

CH_2FCl. The thermodynamic functions of gaseous fluorochloromethane have already been calculated by Glockler and Edgell [1772] (C_p° at T = 250-600°K) and by Gelles and Pitzer [1678] (T = 100-1500°K). The thermodynamic functions of the deuterium substitutes of fluorochloromethane have not been calculated as yet.

The values of the specific heat of CH_2FCl given in the paper [1772] are by about 0.1 cal/mole•degree greater than the ones calculated in the paper [1678], because several frequencies of CH_2FCl which had been found from the Raman spectrum of liquid fluorochloromethane were somewhat too low. In the calculations by Gelles and Pitzer [1678] as well as in the ones made for this Handbook, identical fundamental frequencies of the CH_2FCl molecule have been used which had been determined in an investigation of the infrared spectrum of gaseous fluorochloromethane. The differences of 0.02 cal/mole·degree among the Φ_T^* and S_T° values of CH_2FCl in the paper [1678] and in Table 170 (II) are due chiefly to the fact that Gelles and Pitzer used slightly smaller values of the principal moments of inertia of the CH_2FCl molecule, which had been calculated in the paper [3258] for a tetrahedral model molecule with the assumption that the C-H, C-F, and C-Cl bond lengths were 1.10, 1.34 and 1.75 A, respectively.

CH_2FBr, CH_2ClI, CH_2BrI, CHFClBr, CF_2ClBr. The thermodynamic functions of CH_2FBr, CH_2ClI, CH_2BrI, CHFClBr, and CF_2ClBr in their gaseous states have been calculated so far only by Gelles and Pitzer [1678]. The thermodynamic functions of the deuterium substitutes of CH_2FBr, CH_2ClI, CH_2BrI and CHFClBr have not been calculated.

The values of Φ_T^* of CH_2FBr, CH_2ClI, CH_2BrI, CHFClBr and CF_2ClBr appearing in the paper [1678] are smaller than the corresponding values of this quantity in the Tables 180, 200, 201, 192 and 189 of Volume II of the Handbook by 0.06, 0.02, 0.07, 0.10, and 0.04 cal/mole·degree, respectively. These differences are caused mainly by the different values taken for the principal moments of inertia because the C-F, C-Cl, C-Br, and C-I bond lengths in the halocarbon molecules were taken somewhat smaller in [1678] than in this Handbook. The product of the principal moments of inertia of CF_2ClBr was taken equal to $60,800 \cdot 10^{-117}$ $g^3 \cdot cm^6$ in the paper [1678] although a value of $62,990 \cdot 10^{-117}$ $g^3 \cdot cm^6$ would correspond to the CF_2ClBr structural parameters used in this paper.

CH_2FI, CHF_2I, CF_2ClI, CF_2BrI. The thermodynamic functions of gaseous CH_2FI, CHF_2I, CF_2ClI, and CF_2BrI have not been calculated so far.

In this Handbook, the translational and the rotational components of thermodynamic functions of CH_2FI, CHF_2I, CF_2ClI, and CF_2BrI have been calculated from the formulas (II.6), (II.7) and (II.183), (II.184) in which the values of Table 149 have been used for the products of the principal moments of inertia of the molecules of these substances. The vibrational components of the thermodynamic functions were calculated by means of the approximate relations

$$\begin{aligned}
\Phi^{*}_{\text{кол}}(CH_2FJ) &= \tfrac{1}{2}\Phi^{*}_{\text{кол}}(CH_2F_2) + \tfrac{1}{2}\Phi^{*}_{\text{кол}}(CH_2J_2), \\
\Phi^{*}_{\text{кол}}(CHF_2J) &= \Phi^{*}_{\text{кол}}(CF_3J) + \Phi^{*}_{\text{кол}}(CHF_3) - \Phi^{*}_{\text{кол}}(CF_4), \\
\Phi^{*}_{\text{кол}}(CF_2ClJ) &= \Phi^{*}_{\text{кол}}(CFCl_3) + \Phi^{*}_{\text{кол}}(CF_3J) - \Phi^{*}_{\text{кол}}(CF_2Cl_2), \\
\Phi^{*}_{\text{кол}}(CF_2BrJ) &= \Phi^{*}_{\text{кол}}(CFBr_3) + \Phi^{*}_{\text{кол}}(CF_3J) - \Phi^{*}_{\text{кол}}(CF_2Br_2)
\end{aligned} \qquad (XVII.2)$$

in terms of the vibrational components of the thermodynamic functions of CF_2Cl_2, $CFBr_3$, CH_2F_2, CH_2I_2, CF_3I, CHF_3, CF_4, $CFCl_3$ and CF_2Br_2 which were calculated for this Handbook from the fundamental frequencies of vibration of the corresponding molecules. The relations (XVII.2) were chosen from the number of other possible relations of the same type because of several calculations of the vibrational components of the thermodynamic functions of CH_2FBr, CHF_2Brm CF_2ClBr, and CF_2Br_2 according to similar formulas and because of a comparison these results with the values used in this Handbook, which were calculated from the fundamental frequencies of the corresponding molecules. This comparison has shown that the best agreement is achieved when the relations

$$\begin{aligned}
\Phi^{*}_{\text{кол}}(CH_2FBr) &= \tfrac{1}{2}\Phi^{*}_{\text{кол}}(CH_2F_2) + \tfrac{1}{2}\Phi^{*}_{\text{кол}}(CH_2Br_2), \\
\Phi^{*}_{\text{кол}}(CHF_2Br) &= \Phi^{*}_{\text{кол}}(CF_3Br) + \Phi^{*}_{\text{кол}}(CHF_3) - \Phi^{*}_{\text{кол}}(CF_4), \\
\Phi^{*}_{\text{кол}}(CF_2ClBr) &= \Phi^{*}_{\text{кол}}(CFCl_3) + \Phi^{*}_{\text{кол}}(CF_3Br) - \Phi^{*}_{\text{кол}}(CF_2Cl_2), \\
\Phi^{*}_{\text{кол}}(CF_2Br_2) &= \Phi^{*}_{\text{кол}}(CFBr_3) + \Phi^{*}_{\text{кол}}(CF_3Br) - \Phi^{*}_{\text{кол}}(CF_2Br_2),
\end{aligned}$$

are used in the calculations; similarly, the relations (XVII.2) have been used for calculating the vibrational components of the thermodynamic functions of CH_2FI, CHF_2I, CF_2ClI, and CF_2BrI.

CH_2ClBr. The thermodynamic functions of gaseous chlorobromomethane have already been calculated by Weber, Meister, Cleveland [4190] (T = 100-1000°K) and by Gelles and Pitzer [1678] (T = 100-1500°K). The thermodynamic functions of the deuterium substitutes of chlorobromomethane have not been calculated.

In the calculation of the thermodynamic functions of CH_2ClBr in the papers [4190, 1678] the products of the principal moments of inertia were taken somewhat smaller.* The differences among the Φ^*_T and S°_T values of CH_2ClBr in the paper [4190] and in Table 186 (II), which amount to 0.03-0.04 cal/mole•degree, are caused by different values of the products of the principal moments of inertia and of the physical constants having been used.

The values of Φ^*_T and S°_T obtained in the paper [1678] at T = = 298.15°K almost coincide precisely with the values of the corresponding quantities in Table 186 (II). At higher temperatures, the Φ^*_T and S°_T values obtained in [1678] slightly exceed the values of the corresponding quantities in Table 186 (II). This discrepancy is due to the fact that in the calculations of [1678] lower values have been taken for the fundamental frequencies of CH_2ClBr, which had been found by Plyler and Benedict [3277] from the infrared spectrum of liquid chlorobromomethane.

CHF_2Cl, $CHFCl_2$. The thermodynamic functions of gaseous difluorochloromethane and dichlorofluoromethane have been calculated by Glockler and Edgell [1771] (C°_p at T = 250-650°K), Gelles and Pitzer [1678] (T = 100-1500°K), and Weissman, Meister, and Cleveland [4200] (T = 100-1000°K). The results of the calculations of Glockler and Edgell are rendered in the Handbook [4384], and the results of Gelles and Pitzer in the monograph [119a]. The thermodynamic functions of CDF_2Cl and $CDFCl_2$ have been calculated by Weissman et al [4200] (T = 100-1000°K).

In their calculations Glockler and Edgell too low values of the fundamental frequencies of the CHF_2Cl and $CHFCl_2$ molecules, which were found from the Raman spectra of the corresponding substances in their liquid states and which were partly evaluated by the authors of [1771] by comparison of the fundamental frequencies of several halogen substitutes of methane. Hence, the specific heats of CHF_2Cl and $CHFCl_2$ obtained in [1771] are by respectively 0.45 and 0.07 cal/mole•degree greater than the corresponding quantities calculated later in the papers [1678, 4200].

In their calculations Gelles and Pitzer [1678] used the same fundamental frequencies of the CHF_2Cl and $CHFCl_2$ molecules as were used in this Handbook. The values of the fundamental frequencies of CHF_2Cl and $CHFCl_2$ used in the calculations of Weissman et al [4200] differ but slightly from the values used in the Handbook. The differences among the Φ^*_T and S°_T values given for CHF_2Cl and $CHFCl_2$ in the papers [1678, 4200] and in the Tables 171 (II) and 172 (II) are therefore caused solely by the different values used for the structural parameters and for the product of the principal moments of inertia calculated from the structural parameters. For CHF_2Cl these differences are 0.04 cal/mole•degree,* for $CHFCl_2$ they are 0.07 cal/mole•degree.

Neilsen and White [3037] have calculated $S^\circ_{232.50}$(CHF_2Cl, gaseous) = 63.92 ± 0.28 cal/mole•degree with the aid of the results of measurements they conducted in order to find the specific heat and the heats of phase conversion of difluorochloromethane. The value of $S^\circ_{232.50}$ (CHF_2Cl, gaseous) obtained in the paper [3037] is in accord with the value of 64.05 cal/mole•degree calculated with the help of the molecular constants of CHF_2Cl used in the Handbook. The specific heats of the vapors of difluorochloromethane and dichlorofluoromethane have been measured by Benning and McHarness [744] at a pressure of 1 atm in the temperature ranges of 322.2-408.3°K in the case of CHF_2Cl and of 288.9-408.3°K in the case of $CHFCl_2$. The results of these measurements agree with the C_p° values of the corresponding gases calculated from the molecular constants in the papers [1678, 4200].

CHF_2Br, $CHFBr_2$. The thermodynamic functions of gaseous difluorobromomethane and dibromofluoromethane have been calculated by Gelles and Pitzer [1678] (T = 100-1500°K) and in publications by Palm, Meister, et [3006, 3169] (T = 100-1000°K). The thermodynamic functions of CDF_2Br have been calculated by Palm, Voelz, and Meister [3169] (T = 100-1000°K).

The values of the thermodynamic functions of CHF_2Br given in the paper [3169] and in Table 181 (II) are practically identical. Any slight deviations are caused by different values used for the structural parameters of the CHF_2Br molecule. The differences between corresponding values of Φ_T^* and S_T° for CHF_2Br given in [1678] and in Table 181 (II) range from 0.5 to 0.9 cal/mole·degree. They are caused mainly by the fact that a value of 380 cm^{-1}, which is much too low and which has been found by estimates (see page 1035), has been used in the calculations of [1678] for the frequency ν_6 of the CHF_2Br molecule. Moreover, a much smaller quantity than in this Handbook has been used in [1678] for the product of the principal moments of inertia.

The Φ_T^* and S_T° values of $CHFBr_2$ in the paper [1678] and in Table 182 (II) differ from each other by about 0.06 cal/mole·degree, mainly due to the difference in the values of the product of the principal moments of inertia. The thermodynamic functions of $CHFBr_2$ are not given in the paper [3006] since they proved to be exactly the same as those calculated earlier by Gelles and Pitzer [1678].

$CHCl_2Br$, $CHClBr_2$. The thermodynamic functions of gaseous dichlorobromomethane and dibromochloromethane have been calculated by Gelles and Pitzer [1678] (T = 100-1500°K) and in publications by Meister, Cleveland et al [3292, 3297] (T = 100-1000°K). The thermodynamic functions of $CDCl_2Br$ and $CDClBr_2$ also have been calculated in the papers [3292, 3297].

The fundamental frequencies of $CHCl_2Br$ and $CHClBr_2$ used in this Handbook and in the papers [3292, 3297] are identical. In their calculations, Gelles and Pitzer [1678] used somewhat lower values of the $CHCl_2Br$ and $CHClBr_2$ fundamental frequencies which had been determined by Pleuler and Benedict [3277] in an investigation of the infrared spectra of the corresponding liquids. The vibrational components of the thermodynamic functions of $CHCl_2Br$ and $CHClBr_2$ calculated in [1678] must therefore be greater than the ones calculated for the Handbook. The rotational components of the thermodynamic functions of $CHCl_2Br$ and $CHClBr_2$ calculated for this Handbook must be somewhaat greater than in the papers [3292, 3297, 1678] because in the above papers rather than in this Handbook smaller values have been used for the product of the principal moments of inertia. Owing to some compensation of the discrepancies between the individual components, the Φ_T^* and S_T° values for $CHCl_2Br$ and $CHClBr_2$ in the paper [1678] differ from the ones in the Tables 187 (II) and 188 (II) by not more than 0.03 cal/mole·degree. The difference between the values of Φ_T^* and S_T° given for $CHCl_2Br$ in the paper [3292] and for $CHClBr_2$ in the paper [3297] and the corresponding values in the Tables 187 (II) and 188 (II) is approximately 0.08 cal/mole·degree.

$CFCl_2Br$, $CFClBr_2$. The thermodynamic functions of gaseous dichlorofluorobromomethane and dibromofluorochloromethane have been calculated by Gelles and Pitzer [1678] (T = 100-1500°K) and by Gilbert, Piotrowski, Dowling, and Cleveland [1744] (T = 100-1000°K).

In the calculation of the thermodynamic functions of $CFCl_2Br$ and $CFClBr_2$ in this Handbook the same fundamental frequencies of the molecules have been used as in the calculations of Gelles and Pitzer [1678]. Hence, the differences between the Φ_T^* and S_T° values given for these substances in the paper [1678] and in the Tables 190 (II) and 191 (II), which amount to 0.06 to 0.10 cal/mole·degree, are due to the different values taken for the principal moments of inertia. In the calculations rendered in the paper [1744] the fundamental frequencies ν_1, ν_2, and ν_7 of the $CFCl_2Br$ and $CFClBr_2$ molecules were taken 15-19 cm^{-1} greater than in this Handbook,* whereas for the C-F, C-Cl, and C-Br bond lengths smaller values were taken equal to 1.35, 1.75, and 1.91 A, respectively. Accordingly, the Φ_T^* and S_T° values given in the paper [1744] for $CFCl_2Br$ and $CFClBr_2$ are smaller than the corresponding values of these quantities in the Tables 190 (II) and 191 (II) by 0.20-0.27 cal/mole·degree (in the case of $CFCl_2Br$) and by 0.10-0.15 cal/mole·degree (in the case of $CFClBr_2$).

SECTION 3. THERMOCHEMICAL QUANTITIES

Out of 69 halogen substitutes of methane, the experimental data of only 19 compounds** are known so that the heats of formation can be determined with their help. An examination of these data conducted by Yudin Khachkuruzov [471] has nevertheless shown that sufficiently reliable values of the heats of formation can be determined by only 16 halogen substitutes of methane.*** It was shown in [471] that the heata of formation of the remaining 53 halocarbons can be determined with an error of about ±5 kcal/mole from the experimental values of the heats of formation of these 16 halogen substitutes of methane. With this end in view, the heats of formation of the halogen substitutes of methane have been calculated in [471] by three independent methods as follows: from the mean energies of bond rupture, from the heats of combustion calculated by the Kharasch method [2392] and by means of interpolation formulas similar to the Bernstein formula [761]. The results of these calculations are very close to one another and they agree well with the experimental values. The final selection of the calculated values of the heats of formation of the halogen substitutes of methane and the estimation of the probable error were accomplished Karapet'yants comparative graphical method (see page 288).

Theoretical values of the heats of formation of the halogen substitutes of methane were obtained also by P. Maslov and Yu. Maslov [293]. Their calculations, however, were done by a simple additive system with initial data that were not grounded well enough; the results of these calculations therefore have not been used in this Handbook.

This part of the Handbook is composed mainly of material from an article by Yudin and Khachkuruzov [471].* A short reasoning of why the particular values of the heats of formation of methane and of 19 of its halogen substitutes have been used in this Handbook is given in §70. For the remaining 26 halocarbons discussed in the Handbook, the calculated heats of formation suggested in the paper [471] have been used. The values used for the heat of formation and for the energy of dissociation of methane and 45 of its halogen substitutes are given in Table 155. The error in the calculated heats of formation of the halocarbons listed in Table 155 amounts to ±5 kcal/mole, the error with CH_2FCl, CH_2FBr, CH_2ClBr, $CHFBr_2$, and $CClBr_3$ is about ±8 kcal/mole.

§70. The Head of Formation and the Energy of Dissociation of Methane and Its Halogen Substitutes

CH_4 (gaseous). The heat of combustion of methane has been determined by several investigators. A large part of this work, however, was carried out in the last century when the accuracy of calorimetric measurement was not very great. A survey on the results of these investigations is given in a paper by Rossini [3492].

In 1931, Rossini [3492, 3490] determined the heat of combustion of methane using a calorimetric compensation method. Rossini's experimental technique eliminated the usual calorimetric errors related to the direct measurements of heat effects. The thorough technique of measurement and a careful examination of the reagents and combustion products permitted Rossini to determine the heat of formation of methane with great accuracy. The results of the first investigations [3492] were later determined with greater accuracy in Rossini's papers [3500, 3340] in which he obtained $\Delta H^\circ c_{298.15} = -212.798 \pm 0.072$ kcal/ /mole and $\Delta H^\circ f_{298.15} = -17.889 \pm 0.075$ kcalmole. At almost the same time as Rossini, Roth and Banse also [3517] determined the heat of combustion of methane ($\Delta H^\circ c_{298.15} = -213.27 \pm 0.64$ kcal/mole); within the limits of error measurement, their result agrees with Rossini's data.

The value of

$$\Delta H^\circ f_{298.15}(\mathrm{CH_4,\ gas}) = -17.88 \pm 0.08 \text{ kcal/mole}$$

is used in this Handbook for the heat of formation of methane on the basis of Rossini's experimental data [3492, 3490, 3500, 3340] with the slight change in the atomic weights of carbon and hydrogen taken into consideration. To the value of the heat of formation used for CH_4 corresponds a value of

$$D_0(\mathrm{CH_4}) = 392.118 \pm 0.45 \text{ kcal/mole}$$

<u>CH_3F (gaseous)</u>. Calorimetric data that could be used in determining the heat of formation of monomethyl fluoride are not available. This quantity, however, can be determined approximately with the help

of the results of measurements obtained from [2661, 2559, 1328] in the investigation of the dissociative ionization of CH_3F under the influence of electron impacts.

The calculations based on using the appearance potential of the CH_3^+ ion and of the ionization potential of the CH_3 radical obtained from the papers [2661, 2559], as well as of the heats of formation of F and CH_3 used in the Handbook, lead to the value $\Delta H^\circ f_{298}$ (CH_3F, gaseous) = -59 kcal/mole.* The data by Dibeler and Reese [1328] lead to a heat of formation, $\Delta H^\circ f_{298}$(CH_3F, gaseous), equal to -62 and -79 kcal/mole, respectively, with an error of ± 15 kcal/mole.

More reliable values of the heat of formation of monomethyl fluoride have been determined by Yudin and Khachkuruzov [471] by calculating this quantity from three different methods** and comparing the resulting $\Delta H^\circ f_{298}$(CH_3F, gaseous) values according to the Karapet'yants method with the experimental values of the heats of formation of the other halogen substitutes of methane.***. The value

$$\Delta H^\circ f_{298.15}(\mathrm{CH_3F,\ gas}) = -68 \pm 5 \text{ kcal/mole}$$

was obtained from the paper [471]; it is used also in this Handbook. The dissociation energy corresponding to this value is

$$D_0(\mathrm{CH_3F}) = 409{,}084 \pm 5{,}0 \text{ kcal/mole}$$

CH_3Cl (gaseous). The heat of combustion of gaseous methyl chloride was determined by Berthelot [786] and Thomsen [3983]. A more reliable value of the heat of combustion of methyl chloride, found by Thomsen (ΔHc_{291} = -176.95 kcal/mole) was used also in the thermochemical Handbooks [3508, 813, 98] in the calculation of the heat of formation of CH_3Cl. The value $\Delta H^\circ f_{298.15}$ (CH_3Cl, gaseous) = -19.6 kcal/mole corresponds to this heat of combustion.

Lacher and collaborators [2508] determined the heat of hydrogenation of methyl chloride at 521°K with great accuracy (ΔH°_{521} = -19.665

± 0.045 kcal/mole). The calculations which were based on the results obtained from the paper [2508], and the data in this Handbook concerning the thermodynamic properties of the reaction components in the hydrogenation of methyl chloride lead to the value

$$\Delta H^\circ f_{298,15}(CH_3Cl,\ \text{газ}) \doteq -20{,}62 \pm 0{,}10 \text{ kcal/mole}$$

which was used also in this Handbook. It corresponds to

$$D_0(CH_3Cl) = 371{,}782 \pm 0{,}45 \text{ kcal/mole}$$

CH$_3$Br (gaseous). The heat of com ustion of methyl bromide was measured by Thomsen [3983] and Berthelot [786]. The $\Delta H^\circ f_{298}$ (CH$_3$Br, gaseous) values calculated from the data of [3983, 786] are equal to -8.2 and -11.8 kcal/mole, respectively. The former value is used in the thermochemical handbooks [3508, 813, 98].

The results of thermochemical investigations conducted by Hartley, Pritchard, and Skinner [1961, 1962] and by A. Carson, E. Carson, and Wilmshurst [1067] make it possible to determine the heat of formation of CH$_3$Br with much greater accuracy. In the papers [1961, 1962], measurements were made of the heat of solution of Hg(CH$_3$)$_2$, Br$_2$, CH$_3$Br and HgBr$_2$ as well as of the heat of bromination of mercury dimethyl in ethyl alcohol. In the paper [1067], the heat of combustion of liquid mercury dimethyl was determined. The calculations performed with the thermochemical quantities as found in the papers [1961, 1962, 1067] lead to the value

$$\Delta H^\circ f_{298,15}(CH_3Br,\ \text{газ}) = -8{,}6 \pm 0{,}5 \text{ kcal/mole}$$

which has been used in this Handbook, and to which corresponds

$$D_0(CH_3Br) = 357{,}603 \pm 0{,}7 \text{ kcal/mole}$$

CH$_3$I (gaseous). The heat of combustion of gaseous methyl iodide has been measured by Thomsen [3983], that of liquid methyl iodide by Berthelot [792]. The results of Thomsen's measurements lead to the value $\Delta H^\circ f_{298.15}$ (CH$_3$I, gaseous) = -0.45 kcal/mole, which corresponds to $\Delta H^\circ f_{298.15}$ (CH_3I, liquid) = -7.4 kcal/mole, whereas Berthelot found $\Delta H^\circ f_{298.15}$ *CH_3I, liquid) = -1.8 kcal/mole. The latter value of the heat of formation of CH_3I (liquid) was used in the thermochemical Handbooks [3508, 813, 98].

The thermochemical investigations carried out in the papers [1961, 1962, 1067, 1067a] make it possible to find the heat of formation of methyl iodide with much greater accuracy.

Hartley, Pritchard, and Skinner [1961, 1962] have measured the reaction heat of iodination of mercury dimethyl in methyl alcohol and the heats of solution of the components of this reaction in methyl alcohol. A. Carson, E. Carson, and Wilmshurst [1067] have measured the heat of combustion of mercury dimethyl. The results of the measurements obtained in the papers [1961, 1962, and 1067] lead to the value $\Delta H^\circ f_{298.15}$($CH_3I$, liquid) = -2.3 ± 0.5 kcal/mole.

In an adiabatic calorimeter, Carson, Carter, and Pedley [1067a] measured the heat of reduction of liquid methyl iodide in an $LiAlH_4$ solution in ether and the heat of the reaction between lithium hydride and iodine in a solution of $LiAlH_4$ in ether. The results of these measurements lead to the value $\Delta H^\circ f_{298.15}$($CH_3I$, liquid) = -2.9 ± ±0.5 kcal/mole.

The values of the heat of formation of liquid methyl iodide based on data of the papers [1961, 1962, 1067, 1067a] are equivalent with regard to their accuracy. The value $\Delta H^\circ f_{298.15}$ (CH_3I, liquid) = = -2.6 ± 0.7 kcal/mole has therefore been taken in the Handbook. In as much as the heat of vaporization of methyl iodide under standard conditions is 6.7 kcal/mole [3508], the value

$$\Delta H^\circ f_{298.15}(CH_3J,\ \text{газ}) = 4,1 \pm 0,7 \quad \text{kcal/mole}$$

has been used for the heat of formation of gaseous methyl iodide, corresponding to

$$D_0(CH_3J) = 343{,}704 \pm 0{,}8 \text{ kcal/mole}$$

CH_2F_2 (gaseous). The heat of combustion of gaseous methylene fluoride has been determined in a calorimetric bomb by Neugebauer and Margrave [3049, 3052]. From the results of the measurements the value $\Delta H^\circ f_{298.15}(CH_2F_2$, gaseous) = -105.5 kcal/mole was calculated in the paper [3052]. However, the heat of formation of methylene fluoride found in the paper [3052] is not reliable because the experimental technique used in this study was imperfect. The inaccuracy of this value found by theoretical methods from reliably established heats of formation of halogen substitutes of methane.

In the paper [2677], the value $\Delta H^\circ f_{298}(CH_2F_2$, gaseous) = -110 kcal/mole is given, which was calculated by Luft from his estimates of the energy of disruption of the C-H and C-F bonds in the CH_2F_2 molecule. It is, however, not stated in the paper [2677] what method had been used to estimate these quantities.

Yudin and Khachkuruzov [471] have calculated the heat of formation of methylene fluoride by three independent,* and they obtained the values -118, -121 and -121 kcal/mole. The first of these values agrees best with the experimental heat of formation of the other halogen substitutes of methane, if the values are compared to each other according to the Karapet'yants graphical method. Therefore, the heat of formation of methylene fluoride is taken equal to

$$\Delta H^\circ f_{298,15}(CH_2F_2, \text{ gas}) = -118 \text{ kcal/mole}$$

in this Handbook; the error is about ±5 kcal/mole. To this heat of formation corresponds a

$$D_0(CH_2F_2) = 426{,}040 \pm 5{,}2 \text{ kcal/mole}$$

CH_2Cl_2 (gaseous). The heat of combustion of liquid methylene chloride has been measured by Berthelot and Ogier [798]; their data correspond to the value $\Delta H^\circ f_{298.15}(CH_2Cl_2$, liquid) = -31.3 kcal/mole.

Much more accurate are the results obtained by Smith and collaborators [3786] in measurements of the heat of combustion of liquid methylene chloride: $\Delta Hc_{298.15} = -144.517 \pm 0.400$ kcal/mole. This value refers to the following composition of the combustion products: HCl (1:600 H_2O) and CO_2 (gaseous). These data, together with the data from [3508] on the heat of solution of HCl and the heat of vaporization of CH_2Cl_2, made it possible to find $\Delta H°f_{298.15}(CH_2Cl_2$, liquid) = $-29.3 \pm$ $\pm$ 0.4 kcal/mole and

$$\Delta H°f_{298,15}(CH_2Cl_2,\ \text{gas}) = -22,5 \pm 0,5\ \text{kcal/mole}$$

This value of the heat of formation of gaseous methylene chloride also has been used in this Handbook. The energy of dissociation corresponding to this value is

$$D_0(CH_2Cl_2) = 350,837 \pm 0,7\ \text{kcal/mole}$$

CH_2I_2 (gaseous). A calorimetric measurement of the heat of combustion of liquid methylene iodide was carried out by Berthelot [792] who found ΔHc_{298} (CH_2I_2, liquid) = -178.4 kcal/mole for the composition of the combustion products CO_2 (gaseous), H_2O (liquid), I_2 (solid). The calculations based on these data and the thermochemical quantities used in this Handbook lead to the value $\Delta H°f_{298.15}(CH_2I_2$, liquid) = 16 kcal/mole. Together with the heat of vaporization of methylene iodide at 298.15°K, which is equal to 11.5 ± 0.5 kcal/mole, * the above result makes it possible to determine the heat of formation of gaseous methylene iodide:

$$\Delta H°f_{298,15}(CH_2J_2,\ \text{gas}) = 27\ \text{kcal/mole}^{**}$$

this value has been used in this Handbook. The error in this value of the heat of formation of CH_2I_2 is estimated to be ±4 kcal/mole. The energy of dissociation corresponding to this value is

$$D_0(CH_2J_2) = 294,772 \pm 4\ \text{kcal/mole}$$

CHF_3 (gaseous). The heat of combustion of gaseous trifluoromethane has been measured in a calorimetric bomb by Neugebauer and Margrave [3052] whence these authors found $\Delta H^\circ f_{298.15}(CHF_3$, gaseous) = -162.6 kcal/mole. However, this result is not in agreement with the values of $\Delta H^\circ f_{298.15}(CHF_3$, gaseous) calculated by various methods that make use of the well established values of the heat of formation of the halogenated methane compounds (see [471]). Besides, the reliability of the method used in [3052] for measuring the heat values of gas reactions in a calorimetric bomb is questionable. In the determination of the heat of formation of trifluoromethane it is therefore of interest to use the results of experimental measurements obtained from the investigation of the dissociative ionization of CHF_3 under the influence of electron impacts.

Farmer and collaborators [1530] measured the appearance potential of CF_3^+ ions during the dissociative ionization of CHF_3 under the effect of electron impacts as well as the ionization potential of the CF_3 radical. The calculations performed in [471] with the above data lead to the value $D_{298}(F_3C - H) = 102 \pm 2$ kcal/mole. Exactly the same value of $D_{298}(F_3 C - H)$ was obtained in the paper [471] from the results of an experimental investigation of the photolysis in CHF_3, rendered in the paper [3359]. The calculation which was based on the value of $D_{298}(F_3C - H)$ from [471] and on the heats of formation of CF_3 and H, used in this Handbook, leads to the following value of the heat of formation of trifluoromethane:

$$\Delta H^\circ f_{298.15}(CHF_3, \text{gas.}) = -170 \pm 2 \quad \text{kcal/mole}$$

This value agrees satisfactorily with the heats of formation of other halogenated methane compounds found experimentally. A similar value, $\Delta H^\circ f_{298.15}(CHF_3$, gaseous) = -168 kcal/mole, was calculated by Luft, [2677] who used the dissociation energy of the C-F bond in the CHF_3 molecule as found by extrapolation from the dissociation energies of the carbon-halogen bonds in the other trisubstituted halogenated-methane compounds.

The above value of the heat of formation of trifluoromethane is much better established than the value found by Neugebauer and Margrave [3052] in their calorimetric measurements. It was therefore used also in this Handbook. The dissociation energy corresponding to this value is

$$D_0(CHF_3) = 445{,}071 \pm 2{,}5 \quad \text{kcal/mole}$$

$CHCl_3$ (gaseous). The heat of combustion of trichloromethane has been determined by Berthelot [789], Thomsen [3983], Kablukov and Perel'man [200], and by Smith and collaborators [3786]. However, only the results found by these researchers can be used in determining the heat of formation of trichloromethane since the values of the heat of combustion of trichloromethane given in the papers [789, 200] do not refer to a definite composition of the combustion products. Also the values of the heat of combustion, found by Thomsen [3983], imply a great error whose magnitude is difficult to estimate.*

Smith and collaborators [3786] measured the heat of combustion of liquid trichloromethane with the aid of a quartz spiral and found the value $\Delta Hc_{298.15} = -113.146$ kcal/mole which corresponds to the following final composition of the combustion products: CO_2 (gaseous), HCl (1:600 H_2O). The calculation based upon these data, the data of the Handbook [3508] for the heat of solution of HCl, and the data from this Handbook for the other thermochemical quantities leads to the value $\Delta H^\circ f_{298.15}(CHCl_3, \text{liquid}) = -32.351$ kcal/mole.** Further calculations being based on this result and on the data from the Handbook [3508] for the heat of vaporization of trichloromethane lead to the value

$$\Delta H^\circ f_{298,15}(CHCl_3, \text{gas}) = -24{,}9 \pm 0{,}5 \quad \text{kcal/mole}$$

which has also been used in this Handbook. The dissociation energy corresponding to this value is

$$D_0(CHCl_3) = 330{,}629 \pm 0{,}7 \quad \text{kcal/mole}$$

The value $\Delta H°f_{298.15}(CHCl_3$, gaseous) = -24 kcal/mole, estimated by Bichowsky and Rossini [813] has been used in the thermochemical Handbook [3508].

$CHBr_3$ (gaseous). A calorimetric measurement of the heat of combustion of liquid tribromomethane was conducted by Kablukov and Perel'man [200] (ΔHc_{293} = -90.11 kcal/mole), but the composition of the combustion products was not established. The calorimetric data obtained in [200] therefore cannot be used in the calculation of the heat of formation of tribromomethane.

The value $\Delta H°f_{298.15}(CHBr_3$, gaseous) = +6 kcal/mole, estimated by Bichowsky and Rossini has been used in the thermochemical Handbook [3508].

The calculations of Yudin and Khachkuruzov [471] which were made with the help of the mean energy of bond disruption, the heat of combustion calculated with the Kharasch method [2392], and the Bernstein interpolation formula [761], led to $\Delta H°f_{298.15}(CHBr_3$, gaseous) values equal to +10.0, +7.9, and +10.9 kcal/mole, respectively, which are in agreement with the value found according to the Karapet'yants graphical method.

$$\Delta H°f_{298,15}(CHBr_3,\ \text{газ}) = 10 \quad \text{kcal/mole}$$

which has been used in this Handbook. The error in this value of the heat of formation of tribromomethane has been estimated to be about +3 kcal/mole. The corresponding dissociation energy is

$$D_0(CHBr_3) = 289{,}532 \pm 3 \quad \text{kcal/mole}$$

CHI_3 (gaseous). A calorimetric measurement of the heat of combustion of solid triiodomethane was carried out by Berthelot [792]. His value of ΔHc_{291} = -161.9 kcal/mole corresponds to the following composition of the combustion products: CO_2 (gaseous), H_2O (liquid), I_2 (solid). The calculations based on these data and on the thermochemical quantities used in this Handbook lead to $\Delta H°f_{298.15}$ (CHI_3, solid) = = 33.7 kcal/mole. This result, together with the heat of fusion $\Delta Hm_{298.15}$ = 3.9 kcal/mole [3508] and the heat of vaporization $\Delta Hv_{298.15}$ = 13.2 ± 0.5 kcal/mole* of triiodomethane, leads to

$$\Delta H°f_{298,15}(CHJ_3, \text{gas}) = 51 \text{ kcal/mole**}$$

which has been used also in this Handbook. The error in this value of the heat of formation of gaseous triiodomethane is about ±5 kcal/mole. The corresponding dissociation energy is

$$D_0(CHJ_3) = 245{,}083 \pm 5 \text{ kcal/mole}$$

CF_4 (gaseous). The heat of formation of carbon tetrafluoride was first determined by Wartenberg and Schutte [4171] from the results of their calorimetric measurements of the heat of fluorination of carbon. The value $\Delta H°f_{298}(CF_4$, gaseous) = -162.5 kcal/mole, which was found in the paper [4171] and used in the thermochemical Handbooks [3508, 813, 98], has been calculated on the assumption that only carbon tetrafluoride is formed in the fluorination of carbon. Ruff and Bretschneider [3552] examined the products of carbon fluorination and found that, apart from CF_4, they also contain other carbon fluorides. As it was not possible to analyze quantitatively the products of carbon fluorination with a sufficient accuracy, the thermochemical investigation of this reaction has not been continued.

For determining the heat of formation of CF_4, Wartenberg [4157] proposed to measure the heat of combustion of alkali metals in carbon tetrafluoride. With this aim, the author of [4157] measured the heat of combustion of potassium in carbon tetrafluoride and from the results of the measurements found the value $\Delta H°f_{298}(CF_4$, gaseous) = -231 kcal/mole. This result, however, cannot be regarded reliable because a thorough analysis of the initial substances and end products of the reaction was not made in the work of [4157]. This shortcoming was eliminated in the thermochemical investigations conducted by Kirkbride and Davidson [2408] and by Vorob'yev and Skuratov [129, 130] who, apart from this, used also a more perfect calorimetric measuring technique.

Kirkbride and Davison [2408], as well as Wartenberg [4157], measured the heat of combustion of potassium in CF_4. Vorob'yev and Skuratov [129, 130] measured the heat of combustion of sodium in CF_4. According to Kirkbride and Davidson [2408], the heat value of the reaction 4K (solid) + CF_4 (gaseous = C (graphite) + 4KF (solid) at 298.15°K is -319.8 kcal/mole which corresponds to a value of $\Delta H°f_{298.15}$ (CF_4, gaseous) = -219.4 ± 2.0 kcal/mole.* According to the measurements of Vorob'yev and Skuratov [129, 130], the heat value of the reaction 4Na (solid) + CF_4 (gaseous) = C (graphite) + 4NaF (solid) at 298.15°K is -325.5 ± 2.2 kcal/mole, which corresponds to $\Delta H°f_{298.15}$(CF_4, gaseous) = -220.9 ± 2.3 kcal/mole.**

Along with the measurements of the heat of combustion of alkali metals in carbon tetrafluoride, calorimetric measurements were taken of the heat values of other reactions*** in order to determine the heat of formation of CF_4. Scott, Good, and Waddington [3666] measured the heat of combustion of mixtures of teflon and paraffin in a revolving bomb and from the resulting data found the value $\Delta H°f_{298.15}$(CF_4, gaseous) = -218.3 ± 1.0 kcal/mole. Jessup, McCoskey, and Nelson [2244] measured the heat of combustion of methane in fluorine from which they were able to calculate $\Delta H°f_{298.15}$(CF_4, gaseous) = -220.3 ± 3.0 kcal//mole. In order to determine the heat of formation of CF_4, Duns [1430] and Neugebauer and Margrave [3050] measured the heat values of the thermal decomposition and of the hydrogenation of tetrafluoroethylene. Duus [1430] obtained the value $\Delta H^\circ f_{298.15}(CF_4, \text{gaseous}) = -212.7$ kcal//mole. Neugebauer and Margrave [3050], however, pointed out the possible systematic errors in the measurements of Duus which might arise because the heat values of the side reactions had not been fully considered and because the final reaction products had not been analyzed with sufficient care. Neugebauer and Margrave [3050] have therefore again measured the heat values of the thermal decomposition and of the hydrogenation of tetrafluoroethylene using better techniques of examining the final products. From the resulting data, Neugebauer and Margrave [3050] found $\Delta H^\circ f_{298.15}(CF_4, \text{gaseous}) = -217.1$ kcal/mole.

The most reliable values of the heat of formation of CF_4 have been obtained by Kirkbride and Davidson [2408] and by Vorob'yev and Skuratov [129, 130]. Their results are confirmed by data which were obtained by completely different ways [3666, 2244]. The method chosen in the investigations of [1430, 3050] is less reliable because it is difficult to consider all factors that have an effect upon the final result. Not fully considering these factors resulted in Duus' value of $\Delta H^\circ f_{298.15}(CF_4, \text{gaseous})$ which is clearly too low [1430]. Neugebauer and Margrave [3050] carried out a more thorough investigation than Duus. But also they were obviously not able to consider some side reactions completely, and so the value of $\Delta H^\circ f_{298.15}(CF_4, \text{gaseous})$ obtained in the paper [3050] must also be regarded as too low.

On the basis of the above results of the experimental determinations of the heat of formation of carbon tetrafluoride the value

$$\Delta H^\circ f_{298,15}(CF_4, \text{газ}) = -220 \pm 2 \text{ kcal/mole}$$

has been used in this Handbook*; it corresponds to

$$D_0(CF_4) = 462,173 \pm 3,0 \quad \text{kcal/mole}$$

CF_3Cl (gaseous). The heat of formation of trifluorochloromethane has been determined by Kirkbride and Davidson [2408] and by Wartenberg and Schiffer [4169] from their results of thermochemical investigations of the combustion of potassium in gaseous trifluorochloromethane. In the papers [2408, 4169], the values of -171 and -162 kcal/mole, respectively, were found for $\Delta H°f_{298.15}(CF_3Cl$, gaseous). The most reliable value of the heat of formation of CF_3Cl was found by Kirkbride and Davidson [2408]. Nevertheless, the authors of [2408] admit that the error in their value of the heat of formation of CF_3Cl may reach ±5 kcal/mole.

The value used in this Handbook for the heat of formation of CF_3Cl is based on data given by Mears and Stahl [2825] who measured the heat values of the complex substitution and of the disproportionation for CCl_4, $CFCl_3$, CF_2Cl_2, and CF_3Cl*:

$$\Delta H°f_{298,15}(CF_3Cl,\ \text{газ}) = -171,3 \pm 5,0 \text{ kcal/mole}^{**}$$

which corresponds to

$$D_0(CF_3Cl) = 423,732 \pm 5,0 \text{ kcal/mole}$$

<u>CF_3Br (gaseous)</u>. The dissociation energy of the C-Br bond in the CF_3Br molecule can be found from data on the pyrolysis of trifluorobromomethane as were obtained from the paper [3913], and from the results of an investigation of the dissociative ionization of CF_3Br by the electron impact method [1530, 1330, 2200]. Szwarc and Sehon [3913] found the value $D_{298}(F_3C - Br) = 64.5$ kcal/mole from data on the pyrolisis of CF_3Br. Yudin and Khachkuruzov [471] have calculated this quantity from the appearance potential of the CF_3^+ ion during an electron bombardment of CF_3Br and from the ionization potential of the CF_3 radical as obtained from the papers [1530, 1330, 2200]. The most accurate values of these quantitites were found in the papers [1530, 1330]. They correspond to a value of $D_{298}(F_3C - Br) = 64.6$ kcal/mole which is in excellent agreement with the value of this quantity found by Szwarc

and Sehon [3913]. The data of the latter paper led to $D_{298}(F_3C - Br) = 65 \pm 2$ kcal/mole. The calculations which were based on this value $D_{298}(CF_3 - Br)$ and on the heats of formation of CF_3 and Br used in this Handbook lead to the value

$$\Delta H^\circ f_{298,15}(CF_3Br, \text{gas}) = -158 \pm 2 \quad \text{kcal/mole}$$

which corresponds to

$$D_0(CF_3Br) = 408{,}383 \pm 3{,}6 \quad \text{kcal/mole}$$

<u>CF_3I (gaseous).</u> The dissociation energy of the C-I bond in the CF_3I molecule can be calculated from the data found by the electron impact method the papers [1330, 2782, 1530]. The $D_{298}(F_3C - I)$ values calculated by Yudin and Khachkuruzov [471] from data of the papers [1330, 2782, 1530] are equal to 49, 46, and 57 kcal/mole, respectively. The last value is less reliable than the first two since the data of [1530] are interpreted with certainty than those of the papers [1330, 2782]. According to [471], the value of $D_{298}(F_3C - I) = 49$ kcal/mole is the one that agrees best with the calculated values of the heat of formation and with the experimental values of the heats of formation other halogen substitutes of methane. Using this value of the dissociation energy of the $F_3C - I$ bond and the heats of formation of the CF_3 radical and of monatomic iodine, taken in this Handbook, results in the value

$$\Delta H^\circ f_{298,15}(CF_3J, \text{gas}) = -144 \pm 5 \quad \text{kcal/mole.}$$

which was used in this Handbook. It corresponds to

$$D_0(CF_3J) = 393{,}263 \pm 5{,}3 \quad \text{kcal/mole}$$

<u>CF_2Cl_2 (gaseous).</u> The heat of formation of CF_2Cl_2 has been determined by Kirkbride and Davidson [2408] and by Wartenberg and Schiffer [4169] with the aid of the results of thermochemical investigations of the combustion of potassium in gaseous dichlorodifluoromethane. Very similar values of $\Delta H^\circ f_{298.15}(CF_2Cl_2$, gaseous), equal to respectively

-112 and -111 kcal/mole have been obtained from the papers [2408, 4169].* However, this agreement does not mean that the heat of formation of CF_2Cl_2 is actually near -112 kcal/mole but rather indicates that the same thermochemical methods have been used in the measurements of [2408, 4169], and that the same errors have been made when the results of these measurements were used in the calculation of the heat of formation of CF_2Cl_2. In the paper of Kirkbride and Davidson [2408] the error in the heat of formation of CF_2Cl_2 is estimated to be ±5 kcal/mole. At the same time, for the heats of formation of CF_3Cl and $CFCl_3$ using the results of an investigation of the combustion of potassium in the respective gases, Wartenberg and Schiffer [4169] found values that were lower than the more reliable results of Kirkbride and Davidson [2408] and Mears and Stahl [2825]. This fact points to systematical errors in the paper of Wartenberg and Schiffer [4169] which led to low values of the heats of formation of the fluorochloromethanes.

The value used in this Handbook for the heat of formation of CF_2Cl_2 is based on the results found by Mears and Stahl [2825] (see footnote one on page 1105) in measuring the heat values of complex substitution and of disproportionation of several chlorofluoro substitutes of methane. The calculations carried out with these data and the values of the thermochemical quantities used in this Handbook lead to the value

$$\Delta H^\circ f_{298,15}(CF_2Cl_2,\ \text{gas}) = -119{,}1 \pm 5 \quad \text{kcal/mole}$$

which corresponds to

$$D_0(CF_2Cl_2) = 381{,}801 \pm 5 \ \text{kcal/mole}$$

<u>$CFCl_3$ (gaseous)</u>. On the basis of results of thermochemical investigations of the combustion of potassium in gaseous trichlorofluoromethane, Kirkbride and Davidson [2408], Wartenberg and Schiffer [4169],

and Neugebauer [3049] determined the heat of formation of $CFCl_3$. The $\Delta H^\circ f_{298.15}(CFCl_3$, gaseous) values found in the papers [2408, 4169, 3049] are -70, -63, and -66.2 kcal/mole.* The most careful thermochemical investigation of the combustion of potassium in trichlorofluoromethane was conducted by Kirkbride and Davison [2408]. Nevertheless, the possible error in the obtained value of the heat of formation of $CFCl_3$ is estimated in the paper [2408] to ±4 kcal/mole.

The heat of formation of $CFCl_3$ found by Kirkbride and Davidson [2408] agrees with the value based on the results of a measurement of the heat values of the reactions of complex substitution and disproportionation of several chloro-fluoro substitutes of methane, obtained by Mears and Stahl [2825] (see footnote one on page 1105)**

$$\Delta H^\circ f_{298,15}(CFCl_3, \text{gas}) = -70{,}9 \pm 5 \quad \text{kcal/mole}$$

This value of the heat of formation of $CFCl_3$ has been used in this Handbook. It corresponds to

$$D_0(CFCl_3) = 343{,}893 \pm 5 \quad \text{kcal/mole}$$

CCl_4 (gaseous). The heat of combustion of gaseous carbon tetrachloride has been measured by Thomsen [3983] and Berthelot [791], that of liquid carbon tetrachloride by Berthelot [791] and by Smith and collaborators [3786]. Thomsen [3983] obtained an evidently too high value of the heat of combustion of CCl_4 owing to fundamental shortcoming in the experimental technique that he used (cf. [471]). Berthelot [791] and Smith and collaborators [3786] burned CCl_4 in a calorimetric bomb; in these investigations, a mixture of carbon tetrachloride and paraffin was combusted, in which the amount of CCl_4 was 4% of the weight of the paraffin. As Berthelot has not brought the combustion products of such a mixture to a definite final composition, the data on the heats of combustion obtained by him cannot be used in the calculation of the heat of formation of CCl_4. More reliable results were found by Smith and collaborators [3786]. However, the actual inaccuracy in their value of the heat of formation of liquid carbon tetrachloride ($\Delta H^\circ f_{298.15}$ = -29.8 ± 0.4 kcal/mole) is more greater than the one given in the paper [3786].

In the thermochemical Handbooks [3508, 813, 98] the value $\Delta H^\circ f_{298.15}(CCl_4$, gaseous) = -25.5 kcal/mole has been used, which is based on the data given for the heat of hydrogenation of CCl_4 by Bodenstein, Gunther, and Hoffmeister [849]. Yudin and Khachkuruzov [471] have again calculated the heat of hydrogenation of CCl_4 with the aid of data of measurements given in the paper [849] and considering the value used in the Handbook [3508] for the heat of formation of silver azide which was used in the work [849], to initiate the hydrogenation of CCl_4. With the heat of hydrogenation of CCl_4 obtained by this way (ΔH°_{293} = -62.09 kcal/mole of CCl_4), with the heat of formation of HCl used in this Handbook, and with the heat of formation of amorphous carbon [3050] taken into consideration the value

$$\Delta H^\circ f_{298.15}(CCl_4, \text{gas}) = -24.7 \pm 0.8 \quad \text{kcal/mole}$$

was obtained in the paper [471]; this value has been used also in this Handbook.

Neugebauer [3049] determined the heat of formation of CCl_4 with the aid of results of a measurement of the heat of combustion of magnesium in carbon tetrachloride. The value $\Delta H^\circ f_{298.15}(CCl_4$, liquid) = = -32.3 kcal/mole, obtained by him, corresponds to $\Delta H^\circ f_{298.15}(CCl_4$, gaseous) = -24.5 ± 1.5 kcal/mole which is in agreement with the value used here.* The heat of formation of CCl_4 used in this Handbook corresponds to

$$D_0(CCl_4) = 307{,}993 \pm 1{,}0 \quad \text{kcal/mole}$$

CCl_3Br (gaseous). The heat of formation of trichlorobromomethane has been calculated by Yudin and Khachkuruzov [471] by means of data given by Sullivan and Davidson [3900] on the kinetics of the reaction (XVII.3), and with the aid of results of an investigation of CCl_3Br by the electron impact method found by Farmer and collaborators [1530].

Sullivan and Davidson [3900] examined the kinetics of the reversible reaction

$$CHCl_3(gas) + Br_2(gas) \rightleftarrows CCl_3Br(gas) + HBr(gas) \qquad (XVII.3)$$

in the temperature range of 420-455°K and with the resulting data calculated the mean heat value of the reaction in this temperature range, $\Delta H = -0.9$ kcal. The calculations based on the experimental data of Sullivan and Davidson [3900] and on the thermodynamic functions of the components of the reaction (XVII.3) used in this Handbook made it possible to find the heat value at 0°K, which is equal to -2.21 kcal/mole of CCl_3Br, and which corresponds to the value*

$$\Delta H^\circ f_0(CCl_3Br, gas) = -8,18 \pm 0,50 \text{ kcal/mole}$$

which is confirmed by calculation based on the data of Farmer and collaborators [1530].

TABLE 155

The Values (in cal/mole) of the Thermochemical Quantities of Methane and of Its Halogen Substitutes in Their Gaseous State.

Вещество 1	D_0	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{293.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
CH_4	392 118	−16 005	−17 845	−17 880	2353	2397
CH_3F	409 084	−66 103	−67 965	−68 000^a	2376	2421
CH_3Cl	371 782	−18 751	−20 586	−20 620	2442	2490
CH_3Br	357 603	−4 944	−8 543	−8 600	2486	2536
CH_3J b	343 704	6 364	4 143	4 100	2532	2584
CH_2F_2	426 040	−116 191	−117 969	−118 000^a	2504	2555
CH_2FCl	390 183	−70 284	−71 973	−72 000^a	2633	2689
CH_2FBr	376 067	−56 540	−59 950	−60 000^a	2720	2778
CH_2FJ	362 400	−45 464	−46 984	−47 000^a	3278	3358
CH_2Cl_2	350 837	−20 888	−22 476	−22 500	2774	2835
CH_2ClBr	338 217	−8 640	−11 954	−12 000^a	2856	2919
CH_2ClJ	323 052	3 934	2 033	2 000^a	2937	3002
CH_2Br_2	323 109	6 096	1 070	1 000^a	2951	3016
CH_2BrJ	310 948	15 666	12 056	12 000^a	3035	3102
CH_2J_2	294 772	29 251	27 041	27 000	3104	3173
CHF_3	445 071	−168 354	−169 977	−170 000	2704	2764
CHF_2Cl	406 272	−119 505	−120 982	−121 000^a	2890	2956
CHF_2Br	393 259	−106 864	−109 961	−110 000^a	3077	2148
CHF_2J	378 162	−94 358	−95 976	−96 000^a	3225	3298
$CHFCl_2$	368 495	−71 678	−72 987	−73 000^a	3098	3171
$CHFClBr$	355 428	−58 983	−61 964	−62 000^a	3233	3308
$CHFBr_2$	341 353	−45 280	−49 941	−50 000^a	3361	3438
$CHCl_3$	330 629	−23 762	−24 891	−24 900	3318	3396
$CHCl_2Br$	316 648	−10 153	−12 966	−13 000^a	3441	3520
$CHClBr_2$	303 578	2 545	−1 944	−2 000^a	3573	3655
$CHBr_3$	289 532	16 219	10 079	10 000	3729	3813
CHJ_3	245 083	52 895	51 037	51 000	4016	4105
CF_4	462 173	−218 588	−219 987	−220 000	2972	3044
CF_3Cl	423 732	−170 097	−171 294	−171 300	3214	3294
CF_3Br	408 383	−155 120	−157 972	−158 000	3367	3450
CF_3J	393 263	−142 591	−143 985	−144 000	3493	3577
CF_2Cl_2	381 801	−118 116	−119 098	−119 100	3469	3555
CF_2ClBr	371 650	−108 337	−110 976	−111 000^a	3619	3708
CF_2ClJ	357 555	−96 833	−97 991	−98 000^a	3769	3860
CF_2Br_2	357 628	−94 687	−98 953	−99 000^a	3800	3891
CF_2BrJ	344 539	−84 189	−86 968	−87 000^a	3956	4049
CF_2J_2	329 353	−71 594	−72 983	−73 000^a	4014	4110
$CFCl_3$	343 893	−70 158	−70 904	−70 900	3745	3838
$CFCl_2Br$	333 962	−60 599	−62 982	−63 000^a	3916	4012
$CFClBr_2$	320 937	−47 946	−51 960	−52 000^a	4092	4191
$CFBr_3$	307 905	−35 286	−40 937	−41 000^a	4263	4364
CCl_4	307 993	−24 208	−24 709	−24 700	4030	4130
CCl_3Br	291 593	−8 180	−10 333	−10 448	4186	4287

Вещество 1	D_0	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{293.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
CCl_2Br_2	280 221	2 820	—963	—1 000[a]	4363	4467
$CClBr_3$	267 229	15 440	10 060	10 000[a]	4573	4680
CBr_4	255 219	27 078	20 082	20 000[a]	4765	4874

1) Substance; a) estimated value, according to [471]; b) J = Iodine.

The above value of the heat of formation of CCl_3Br at 0°K has been used in this Handbook. It corresponds to

$$D_0(CCl_3Br) = 291{,}593 \pm 0{,}7 \text{ kcal/mole}$$

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[Footnotes]

971* If one does not take into account the different isotope modifications, the number of compounds corresponding to this formula is 70. The possible number of compounds of type CX_4 is 5, of type CX_3Y 20, of type CX_2Y_2 10, type CX_2YZ 30 and type CXYZV 5.

971** The molecules of halogen-substituted methane of the type CX_4 belong to the point symmetry group T_d, those of type CX_3Y to the symmetry group C_{3v}, those of type CX_2Y_2 to the symmetry group C'_{2v}, of type CX_2YZ to the symmetry group C_1 and those of type CXYZV to the symmetry group C_s. The molecules of the halogen derivatives of methane of the type CX_4 are spherical rotators, those of type CX_3Y are symmetrical rotators and those of types CX_2Y_2, CX_2YZ, CXYZV, asymmetrical rotators.

971*** Numerous investigations of the infrared spectra and Raman spectra of methane and its halogen derivatives are known. The present Handbook examines the results of the most important investigations which are suitable for the determination of the molecular constants of these compounds. Special attention in this connection was given to the results of the investigations of the spectra of the corresponding gases. The spectra of the liquids and solutions are examined in the cases where the gas spectra were not obtained or insufficiently studied.

973* The maximum deviations do not exceed ±4°.

973** CH_3F, CH_3Cl, CH_3Br, CH_3I, CH_2F_2, CH_2FCl, CH_2Cl_2, CH_2ClBr, CH_2Br_2, CH_2I_2, CHF_3, CHF_2Cl, $CHFCl_2$, $CHCl_3$, $CHBr_3$, CHI_3, CF_4, CF_3Cl, CF_3Br, CF_3I, CF_2Cl_2, $CFCl_3$, $CFBr_3$, CCl_4, CCl_3Br, CCl_2Br_2, CBr_4, CI_4.

978 Thomas and Welsh [3963c], as a result of an analysis of the rotational structure of the bands ν_1, ν_2 and ν_3 in the Raman spectrum of CH_4, obtained for the beginning of these bands values, practically coinciding with those given in Table 146 ($\nu_1 = 2916.7$, $\nu_2 = 1533.6$, $\nu_3 = 3018.9$ cm^{-1}).

979 For the determination of B_0, Childs used the relation $\xi_3 + \xi_4 = 1/2$ which applies only to harmonic vibrations.

982* The results of a study of the Raman spectrum of gaseous CF_4, obtained by Monostori and Weber [2939a] on an apparatus with larger dispersion than in the earlier studies (5 A/mm at 4358 A) were published in 1960. The following values were found in the work [2939a] for the fundamental frequencies of the molecule CF_4: $\nu_1 = 908.5$, $\nu_2 = 435.0$, $\nu_3 = 1283.0$, $\nu_4 = 631.2$ cm^{-1}.

982** The correspondence between the partially resolved rotational structure of the bands in the Raman spectrum of CF_4 and the value of r_{C-F} found by Hofman and Livingston [2094] was verified by Monostori and Weber [2939a]. It was found in the work [2939a] that the distance between the maxima of the rotational branches of the band ν_2 is 33 cm^{-1} while the value calculated on the basis of the Plazcek and Teller relation [3263a], using $r_{C-F} = 1.327$ A, is 29.6 cm^{-1}.

983 The vibration frequencies of the molecule CCl_4 vary slightly upon transition from liquid to gas. Special investigations on this problem were carried out by Lisitsa and Malinko [274].

984* The adopted value for the interatomic distance C-Cl agrees with the value of the inertial moment of the molecule CCl_4 ($I = 490 \cdot 10^{-40}$ g$\cdot$cm^2), obtained by Simova [3739, 3740] on the basis of the measurements of the distance between the maxima in the unresolved band ν_1, observed by her in the Raman spectrum of liquid CCl_4.

984** Later electron diffraction investigations of the structure of the molecule CCl_4 [3664, 2953a] led to values of r_{C-Cl} which agree with those found in the work [666]: $r_{C-Cl} = 1.768 \pm 0.003$ A, [3664], $r_{C-Cl} = 1.765 \pm 0.002$ A [2953a].

989 Approximate values for the frequencies of the normal vibrations of the molecules CH_3Cl and CD_3Cl (and also the molecules CH_3Br, CD_3Br, CH_3I and CD_3I) were calculated by King, Mills and Crawford [2406] on the basis of equations for the potential functions of the molecules of these compounds, found by Chang and Dennison [1088, 1087]. The calculation of the frequencies of the normal vibrations of the molecules CH_3Cl and CD_3Cl has also been carried out in the work of Tanaka [3921].

991 The theoretical calculation of the centrifugal stretching constants of the molecule CH_3Cl was carried out by Chang and Dennison [1088].

992 An isotope splitting of the frequency ν_3 was observed in the work [638] for the molecules CH_3Br^{79} and CH_3Br^{81}, of 1 cm^{-1}.

997* In 1959, a report on the results of studies on the infrared spectrum of CH_3I in the range from 3333-5000 cm^{-1} was published [990a]. In this range, the rotational structure of the $\nu_2 + \nu_4$ band obtained in the case of high resolution ($\cong 0.07$ cm^{-1}) could be analyzed, and the values (in cm^{-1}) of the constants: $B'' = 0.25018$, $B' = 0.24898$, $D_k = 5.6 \cdot 10^{-5}$, $A' = 5.095$, $\xi_4 = 0.052$, $\nu_0 = 4302.15$ could be determined, assuming that $A'' = 5.104$ cm^{-1}.

997** The results of the study on the infrared spectrum of CHF_3 carried out by Price were published in the work by Bernstein and Herzberg [762].

1001 Wolfe [4309] also determined the values of the constants A_0 and C_0 for the asymmetric molecule $CHCl_2^{35}Cl^{37}$.

1008 The frequency ν_3 was observed in the infrared spectrum of CF_3Br only by Plyler and Acquista [3271], who found it equal to 348 cm^{-1}.

1015 These frequencies are related to fully-symmetric and double-degenerate oscillations.

1032 In Table 149 values determined from the infrared spectrum of gaseous bromo-chloro methane were adopted for the frequencies ν_2, ν_3, ν_4, ν_5, ν_8, ν_9, whereas for the frequencies ν_1, ν_6, ν_7 values determined from the Raman spectrum of liquid bromo-chloro methane were adopted.

1034 In 1960, the results of a study on the microwave spectrum of CHF_2Cl [717a] in the range from 14-38 Gc were published. In the work [717a] the wave numbers of the purely rotational transitions in the vibrational ground states of CHF_2Cl^{35} and CHF_2Cl^{37} molecules, corresponding to $I = 0_0 \rightarrow 1_1$, $1_0 \rightarrow 2_1$, $1_{-1} \rightarrow 2_0$, $2_{-2} \rightarrow 3_{-1}$ and $3_1 \rightarrow 3_2$, were determined with high accuracy, and the following values of the rotational constants were found: $A_0 = 10234.7$, $B_0 = 4861.2$, $C_0 = 3507.7$ Mc for CHF_2Cl^{35} and $A_0 = 10233.8$, $B_0 = 4717.1$ and $C_0 = 3432.4$ Mc for CHF_2Cl^{37}. The values $I_AI_BI_C = 3385.3 \cdot 10^{-117}$ $(g \cdot cm^2)^3$ for CHF_2Cl^{35} and $I_AI_BI_C = 3565.4 \cdot 10^{-117}$ $(g \cdot cm^2)^3$ for CHF_2Cl^{37} correspond to the values of the rotational constants obtained in the work [717a].

1035 The values of the force constants of CHF_2Br adopted in the work [3169] were also used to calculate the fundamental frequencies of the CDF_2Br molecule.

1041 The values of the frequencies ν_2, ν_3, ν_7, ν_8 of the $CHCl_2Br$ molecule obtained in the work [3292] practically coincide with the values of these quantities as calculated from data given in the work [3277].

1045 After this text had been compiled and the thermodynamic functions of $CFCl_2Br$ and $CFClBr_2$ had been calculated, a work by Gilbert, Piotrowski, Dowling and Cleveland [1744] (see also [1744a]) appeared, in which the Raman spectra of liquid fluoro-dichloro-bromo methane and fluoro-chloro-dibromo methane was reinvestigated and for the first time their infrared soectra were obtained (in the range from 400-3000 cm^{-1} for the liquids and from 630-3000 cm^{-1} for the gases). On the basis of an analysis of the vibrational spectra of liquid $CFCl_2Br$ and $CFClBr_2$ the values of all fundamental frequencies of the corresponding molecules which are in good agreement with the values of these quantities determined earlier by Delwaulle and Francois [1303], were redetermined in the work [1744]. The most considerable difference was obtained only for the value of the frequency ν_2 of the $CFClBr_2$ molecule. This frequency was identified in the work [1303] with a band at 790 cm^{-1}, observed in the Raman spectrum. Gilbert and collaborators [1744] found that in the vibrational spectra of $CFClBr_2$ two bands, weak in the Raman spectrum, by very intense in the infrared spectrum with centers at about 790 and 815 cm^{-1}, correspond to the frequency ν_2. They assume that vibration frequencies ν_2 and $\nu_3 + \nu_4$ between which a Fermi resonance takes place, correspond to these bands. A certain assignment of the frequency ν_2 to one of these bands in the work [1744] did not seem to be possible, and for the frequency ν_2 a mean value was adopted (803 cm^{-1} for liquid $CFClBr_2$ and 806 cm^{-1} for the gas). The values of the fundamental frequencies of the $CFCl_2Br$ and $CFClBr_2$ molecules determined in the work [1744] (in cm^{-1}) are given in the Table below (in parentheses, the values of the frequencies as found from the infrared spectra of the corresponding gases are given).

1 Молекула	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
$CFCl_2Br$	1069 (1080)	782 (796)	502	336	305	217	828 (838)	391	204
$CFClBr_2$	1061 (1075)	803 (806)	462	340	268	161	741 (754)	307	196

1) Molecule

1046 CCl_3I, CFI_3, $CClI_3$, $CBrI_3$, CBr_3I, CCl_2I_2, CBr_2I_2, $CHFI_2$,

$CHClI_2$, $CHBrI_2$, $CFCl_2I$, CCl_2BrI, $CFBr_2I$, $CClBr_2I$, $CHCl_2I$, $CHBr_2I$, $CFClI_2$, $CFBrI_2$, $CClBrI_2$, CHFClI, CHClBrI, CHFBrI, CFClBrI, CI_4.

1047 Tables of the thermodynamic functions of methane and its halogen substitution products calculated by Gelles and Pitzer [1678] and in several other works are given in Vvedenskiy's book [119a].

1048* The work of Stepanov [392] aimed at determining a self-consistent system of values of the force constants of the halogen substitution products of methane, starting from the most general analytic expression for the quadratic part of the potential energy and from the experimental data on the values of the fundamental frequencies of the molecules of the halogen substitution products of methane that are available to it. Varying the values of the force constants Stepanov [392] succeeded in obtaining values of the fundamental frequencies that are most similar to those found experimentally and given in the summary by Wu [4343]. The data given in the summary by Wu [4343] were, however, in the following subject to very important modifications (even the calculations carried out by Stepanov [392] had revealed several obvious inaccuracies in the frequency assignments of the halogen substitution products of methane). Consequently, for some halogen substitution products of methane the values of the individual frequencies as calculated by Stepanov in the work [392] differed considerably from the values obtained in the following from an analysis of the infrared and Raman spectra.

1048** Using the force constants of the fluorine, chlorine and bromine substitution products of methane found by Stepanov [392] Maslov [293] calculated the corresponding values of the influence coefficients of the molecules of these compounds. Considering the variation of these quantities in compounds of the type of CH_4, CH_3X, CH_2X_2, CHX_3, CX_4, where X = F, Cl, Br, Maslov carried out a rough estimate of the influence coefficients of CH_3I, CH_2I_2, CHI_3 and CI_4 and with their help calculated the values of the fundamental frequencies. In doing so, rather considerable discrepancies between the calculated and the experimentally found values of the frequencies were obtained. Besides, the frequencies of CHI_3 and CI_4 were miscalculated in the work [293]; in the following, the calculations were corrected by Sverdlin [360].

1049* The tables of the thermodynamic functions of CCl_4, $CFCl_3$, CF_2Cl_2, CF_3Cl and CF_4, calculated by Albright, Galegar and Innes [496] were supplemented by K. Kobe and D. Kobe [2449b] by means of values corresponding to T = 273.15; 291.15 and 298.15°K, and converted to values of temperature in the Celsius, Fahrenheit and Rankine scales.

1049** CHF_3, CHF_2Cl, CF_2Cl_2, CH_3Cl, $CHFCl_2$, $CFCl_3$, CH_2Cl_2, CF_3CI, CF_4.

1051* CD_4, CT_4, CH_3D, CH_2D_2, CHD_3, CH_3T, CH_2T_2, CHT_3, CD_3T, CD_2T_2, CDT_3.

1051** Wilson [4287] calculated the constant $\rho = 1.72 \cdot 10^{-5}$ deg^{-1} for CH_4, which makes it possible to estimate the centrifugal expansion of the molecule for the calculation of the thermodynamic functions of gaseous methane. However, such calculations have not been made.

1053 Furthermore, on the basis of the results of calorimetric measurements carried out by Eucken and Schroder [1505], the value $S^{\circ}_{298.15}(CF_4$, gaseous$) = 62.8 \pm 0.5$ cal/mole·degree was obtained in the Handbooks [2363, 98].

1054 The r_{C-F} value of CF_4 used in the papers [1678, 496] is not mentioned.

1056 $\nu_1 = 450$, $\nu_2 = 214$, $\nu_3 = 762$, $\nu_4 = 350$ cm^{-1}.

1062 The values of the thermodynamic functions of CH_3Br calculated by Stevenson and Beach are rendered in the Handbook by Zeise [4384]. They were used also by Spencer and Flannagan [3280] to represent the temperature dependence of the specific heat of methyl bromide in analytical form.

1063* The results of the calculations made by Edgell and Glockler have been used in the paper [3820] to represent the temperature dependence of the specific heat of methyl iodide in analytical form.

1063** In the paper [1549], the thermodynamic functions of CD_3I are calculated, too. The values of the thermodynamic functions of CH_3I and CD_3I calculated in [1549] are rendered in the Handbook by Zeise [4384] and in a monograph by Vvedenskiy [119a].

1063*** The calculation of $I_A I_B I_C$ for a tetrahedral model of the CH_3I molecule with the C-H and C-I bond lengths taken from [1678] leads to the value $I_A I_B I_C = 63.8 \cdot 10^{-117}$ $(g \cdot cm^2)^3$.

1064* The values of the thermodynamic functions of CHF_3 and CDF_3 calculated in the paper [1283] are rendered in the Handbook by Zeise [4384] and in the monograph by Vvedenskiy [119a].

1064** The results of the calculations are given in the monograph [2312] and have been used in the paper [3820] to represent the temperature dependence of the specific heat of trichloromethane in an analytical form.

1064*** The values of the thermodynamic functions of $CHCl_3$ and $CDCl_3$ calculated in the papers [2726, 2728] are rendered in the Handbook by Zeise [4384].

1065* The values of the thermodynamic functions of $CHBr_3$ calculated by Stevenson and Beach are rendered in the Handbook by Zeise [4384]. They have been used in the paper [3820] to represent the dependence of the specific heat C_p of tribromomethane on temperature in an analytical form.

1065** These data are given in the Handbook [4384] and in the monograph [119a].

1068 One might take notice of the fact that a great part of the values of the thermodynamic functions of $CFCl_3$ from the paper [1678] coincide almost precisely with the values of the corresponding quantities in the paper [769] whereas the value of S°_{1500} obtained from the paper [1678] is clearly too low.

1069* The specific heat of gaseous trichlorofluoromethane at a pressure of 1 atm was measured by Benning and McHarness [744] in the temperature range of 311-408°C.

1069** The difference between corresponding values of Φ^*_T does not exceed 0.08 cal/mole•degree.

1075 The C°_p values of methylene iodide calculated by Glockler and Edgell [1772] are given in the Handbook by Zeise [4384] and have been used by Spencer and Flannagan [3820] to represent the dependence of C°_p of methylene iodide on temperature in an analytical form.

1077 See footnote two on page1048).

1078 For the remaining fundamental frequencies of CF_2Cl_2 the values suggested by Plyler and Benedict [3277] have been used.

1087 The values used in the paper [4190] were $r_{C-Cl} = 1.76$, $r_{C-Br} = 1.91$ A, those used in the paper [1678] were $r_{C-Cl} = 1.75$, $r_{C-Br} = 1.91$ A.

1088 The same discrepancies are obtained when the thermodynamic functions of CHF_2Cl are calculated from the experimental data of the rotational constants of the CHF_2Cl^{35} and CHF_2Cl^{37} molecules obtained from the paper [717a] (see footnote one to page 1034).

1091* See footnote one to page 1045.

1091** CH_3F, CH_3Cl, CH_3Br, CH_3I, CH_2F_2, CH_2Cl_2, CH_2I_2, CHF_3, $CHCl_3$, $CHBr_3$, CHI_3, CF_4, CF_3Cl, CF_3Br, CF_3I, CF_2Cl, $CFCl_3$, CCl_4, CCl_3Br.

1091*** The experimental data available for CH_3F, CH_2F_2, and $CHBr_3$ are not enough for determining the heats of formation of these compounds with sufficient accuracy.

1092 In 1961, Skuratov and Kolesov [381a] published critical remarks on the paper [471] in which it was shown accurately that it is not possible to carry out further experimental thermochemical investigations of the halogen substitutes of methane. However, the authors of the remarks [381a] are of the opinion that such investigations should be made only by calorimetric methods. Meanwhile, for this purpose Baybuz [80b] succeeded in employing a method of the explosion of gas mixtures in a spherical bomb (see footnotes to pages 1103-1110). Valuable information may be obtained from measurements of the equilibrium, from kinetic investigations, and by means of the electron impact method. A discussion is made in [471] of all existing experimental data that can be used in calculating the heat of formation of the halogen substitutes of methane without regarding the methods by which these data have been obtained. One may agree with the authors of the remarks [381a] that in the paper [471] the error in the suggested values of the heats of formation of the halogen substitutes of methane has been estimated too low in several cases. On the other hand, the authors of this Handbook cannot share the negative opinion of the authors of the remarks [381a] concerning the methods used in [471] in the calculation of the heat of formation of the halogen substitutes of methane and concerning the values of the heat of formation of several compounds of this kind, suggested in the paper [471].

1094* The same result was found by Margrave [2771] and Luft [2677].

1094** From the mean bond-breaking energy, from the heat of combustion of methylfluoride as calculated by the Kharasch method [2392], and by means of the Bernstein interpolation formula [761].

1094*** The following series of compounds have been discussed: CH_3F, CH_3Cl, CH_3Br, CH_3I and CCl_3F, CCl_4, CCl_3Br, CCl_3I; CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4 and CF_4, CHF_3, CH_2F_2, CH_3F, CH_4.

1097 See footnote two to page 1094.

1098* An estimate, which is based on the results of several semi-empirical methods of calculating heats of vaporization explained in the papers [468, 469].

1098** The thermochemical Handbook of the U. S. National Bureau of Standards [3508] uses the value $\Delta H°f_{298.15}(CH_2I_2$, gaseous) = = 25 kcal/mole which was found by Bichowsky and Rossini [813] from data of Berthelot [792] and their estimates of the heat of vaporization of methylene iodide.

1100* The reasons why this error exists are discussed in the paper [471].

1100** In the paper [3786], the value -32.4 ± 0.4 kcal/mole is given for this quantity.

1102* The heat of vaporization, being equal to 13.2 ± 0.5 kcal/mole, has been determined by the authors of the Handbook on the basis of calculations according to Forcrand's formula [1583, 468] with Tm = 398°K [3508], and as the result of a calculation according to the Mendeleyev rule with a correction term [469] (with the heats of vaporization of $CHCl_3$ and $CHBr_3$).

1102** Bichowski and Rossini [813] estimated $\Delta H^\circ f_{291}(CHI_3$, gaseous) = = +44 kcal/mole, using the results of the calorimetric measurements carried out by Berthelot [792].

1103* As a $\Delta H^\circ f_{298.15}$(KF, solid) value different from the one taken in this Handbook has been used in the paper [2408], the value found therein is $\Delta H^\circ f_{298.15}(CF_4$, gaseous) = -218 ± 2 kcal/ /mole.

1103** As a $\Delta H^\circ f_{298.15}$(NaF, solid) value different from the one taken in this Handbook has been used in the papers [129, 130], the value found in these is $\Delta H^\circ f_{298.15}(CF_4$, gaseous = -219.2 ± ± 2.3 kcal/mole.

1103*** A more detailed discussion of the results of the investigations [3666, 2244, 1430, 3050] is made in the paper [471].

1104 The value of the heat of formation used in this Handbook was confirmed by Baybuz [80b] who found the value $\Delta H^\circ f_{298.15}$ (CF_4, gaseous) = -220.1 ± 1.4 kcal/mole by evaluating the results of measurements of the explosion of the mixtures of CF_4 with H_2, O_2, CO and H_2O.

1105* Mears and Stahl [2825] carried out measurements at T = = 573.15°K and at p = 1 atm. They obtained the following heat values of the gas reactions:

$$HF + CCl_4 = CFCl_3 + HCl, \quad \Delta H^\circ_{573} = 4{,}37 \pm 0{,}20 \text{ kcal.}$$

$$HF + CFCl_3 = CF_2Cl_2 + HCl, \quad \Delta H^\circ_{573} = -6{,}60 \pm 0{,}50 \text{ kcal,}$$

$$HF + CF_2Cl_2 = CF_3Cl + HCl, \quad \Delta H^\circ_{573} = -9{,}88 \pm 0{,}40 \text{ kcal,}$$

$$2CFCl_3 = CCl_4 + CF_2Cl_2, \quad \Delta H^\circ_{573} = -2{,}62 \pm 0{,}10 \text{ kcal,}$$

$$2CF_2Cl_2 = CFCl_3 + CF_3Cl, \quad \Delta H^\circ_{573} = -3{,}73 \pm 0{,}20 \text{ kcal.}$$

1105** In 1961, after the information in this Handbook had been compiled, Baybuz [80b] determined the heats of formation of CF_4, CF_3Cl, $CFCl_3$, and CCl_4 by means of a better method of evaluating the results of the measurements of gas mixture explosions in a spherical bomb. Baybuz's paper questioned the reliability of the data of Mears and Stahl [2825]. The value $\Delta H^\circ f_{298.15}(CF_3Cl$, gaseous) = -166.2 ± 2.2 kcal/mole was found for CF_3Cl in the paper [80b]. However, preliminary results of the heat of combustion of Na in CF_3Cl, found in 1961 at the Moscow State University [41a] lead to the value $\Delta H°f_{298.15}$ (CF_3Cl, gaseous) = -172.3 ± 3 kcal/mole.

1107 With the values of the heats of formation of KF and KCl of this Handbook, the data of the papers [2408, 4169] lead to $\Delta H°f_{298.15}$(CF_2Cl_2, gaseous) values equal to -113 and -112 kcal/mole, respectively.

1108* With the values of the heats of formation of KF and KCl of this Handbook, the data of the papers [2408, 4169] lead to $\Delta H°f_{298.15}$($CFCl_3$, gaseous) values equal to -71 and -64 kcal/mole, respectively.

1108** In 1961, Baybuz [80b] found the value $\Delta H°f_{298.15}$($CFCl_3$, gaseous) = -66.4 ± 2.1 kcal/mole by means of a better method of evaluating the results of measurements of the explosion pressure of mixtures of H_2, O_2, and $CFCl_3$ in a spherical bomb (see also footnote two on original page 1105**).

1109 The value of the heat of formation used in the Handbook also was confirmed by experiments carried out by Baybuz [80b] in order to measure the explosion pressure of mixtures of H_2, O_2, CO, and CCl_4 in a spherical bomb. With these data, the value $\Delta H°f_{298.15}$(CCl_4, gaseous) = -24.6 ± 1.9 kcal/mole was obtained in [80b].

1110 On this basis of the data from [3900], the value $\Delta H°f_{298.15}$ (CCl_3Br, gaseous) = -10.3 ± 0.5 kcal/mole, corresponding to $\Delta H°f_0$(CCl_3Br, gaseous) = -8.13 kcal/mole, was found in the paper [471].

Chapter 18

ETHYLENE AND ITS FLUORINE-CHLORINE DERIVATES

(C_2H_4, C_2F_4, C_2Cl_4, $C_2H_2F_2$, $C_2H_2Cl_2$, C_2H_3F, C_2H_3Cl, C_2HF_3, C_2HCl_3, C_2F_3Cl, C_2FCl_3, C_2H_2FCl, C_2HF_2Cl, C_2HFCl_2)

The molecules of ethylene and of its halogen derivates are very similar in their structure so that it is advisable to examine the compounds of this class in common. In the present Handbook the bromine and iodine derivates of ethylene will not be considered, because of the thermal instability of these compounds at high temperatures.

The halogen derivates of ethylene can be divided into three groups according to the general formulas C_2X_4, $C_2X_2Y_2$ and C_2X_3Y, C_2X_2YZ, C_2XYZV, where X, Y, Z, V, are either a halogen or hydrogen. The molecules of the halogen derivates of ethylene of the type C_2X_4 possess the highest symmetry (point group of symmetry V_h); the molecules $C_2X_2Y_2$ have a lower symmetry (point group of symmetry C_{2v}, C_{2h} and C_2); and the symmetry of the molecules C_2X_3Y, C_2X_2YZ and C_2XYZV is lowest (point group of symmetry C_s). The molecular constants and the thermodynamic functions of ethylene and its fluorine and chlorine derivates are considered in the present chapter in accordance with the belonging of these compounds to the three groups mentioned.

Three isomeric forms are known of the halogen derivates of ethylene of the types $C_2X_2Y_2$ and C_2X_2YZ: the cis-, the trans- and the asymmetric form. The numerical differences in thermodynamic properties between the various isomeric forms of the halogen derivates of ethylene are small. The calculations carried out have shown that they are of the same order, as the errors in the determination of the thermodynamic properties of these compounds from the experimental data available. Therefore, the present Handbook does not contain any tables of the thermodynamic properties of the various isomeric forms of fluorine-chlorine derivates of ethylene of the types $C_2X_2Y_2$ and C_2X_2YZ. In the present Handbook the polymeric forms of ethylene and its halogen derivates will not be considered either.

Division 1. MOLECULAR CONSTANTS

Analyses of the spectra of ethylene and its halogen derivates as well as the electron-diffraction analysis have shown that the molecules of all these compounds are plane, with a characteristic double bond linking the atoms of carbon.

Of the compounds considered in this chapter, the vibrational spectra have not been examined for the type C_2HFCl_2 and for the types $C_2F_2Cl_2$, C_2HF_3, C_2HF_2Cl and C_2HFCl_2 the structure parameters have not been experimentally determined. In the present Handbook the lacking data have been replaced by estimates which are based on the results of the experimental analysis of the spectra and the molecular structure of the other halogen derivates of ethylene.

The information on the molecular constants of ethylene and its halogen derivates is in the main limited to data concerning the values of the fundamental frequencies and the structure of the corresponding molecules. The constants of anharmonicity of the oscillations, the interaction between oscillation and rotation, and the constants of the centrifugal distorsion have not been determined for the molecules of ethylene and some of its halogen derivates. As regards ethylene and some of its halogen derivates, the excited electron states were also studied.

§71 Molecules of the Type C_2X_4

The molecules of ethylene and of its halogen derivates of the type

C_2X_4 belong to the point group of symmetry V_h ($\sigma = 4$) and have 12 normal vibrations. The completely symmetrical vibrations with the frequencies ν_1, ν_2, ν_3, ν_4 correspond to an extension of the bonds C-X, C = C a change of the valence angle in X-C-X and a torsion of the groups CX_2 around the bond C = C. The remaining eight frequencies correspond to the antisymmetrical vibrations in the plane (ν_5, ν_6, ν_9, ν_{10}, ν_{11}, ν_{12}) and outside the plane of the molecule (ν_7, ν_8).

In the infrared spectra of the molecules C_2X_4 vibrations with the frequencies ν_7, ν_9, ν_{10}, ν_{11}, ν_{12} are active, and vibrations with the frequencies ν_1, ν_2, ν_3, ν_5, ν_6 and ν_8 are active in the Raman spectra. The torsion oscillation (ν_4) are neither active in the infrared spectra nor in the Raman spectra.

The molecules C_2X_4 possess no own dipole moment, since they belong to the point group of symmetry V_h. Therefore their rotation spectra can only be observed as a Raman spectrum and not in the infrared.

C_2H_4 . The analysis of the vibration spectra of ethylene began in 1905 [1139] and was dealt with in the publications of many investigators, but only in 1950 they succeeded in obtaining a reliable interpretation of these spectra and in finding the exact values of the fundamental frequencies of C_2H_4.

The infrared spectrum of gaseous ethylene in the range of 700-4800 cm^{-1} was analyzed by Coblentz [1139], Levin and Meyer [2597], Smith [3790], Gelloui and Barker [1646], Tompson and Garris [3973], Rasmussen and Brattain [3401], Arnett and Crawford [568], Plyler [3270], Allen and Plyler [510], and Ozawa [3160]. The infrared spectrum of ethylene in the photographic range (8500-14,300 cm^{-1}) was analyzed by Badger and Binder [600], Schieb and Lueg [3615], Lewis and Houston [2602], Bonner [864], Gaenswein and Mecke [1649], and Tompson [3968]. The rotational structure of the vibration-rotation bands of C_2H_4 was resolved in the papers [2597, 3790, 1646, 3973, 568, 510, 3968].

In paper [3160] infrared spectra of ethylene under high pressure and in presence of impurities of other gases were obtained, which permitted the observation of the bands of C_2H_4, active only in tye Raman spectrum under normal conditions.

The vibration Raman spectrum of gaseous ethylene in low dispersion was investigated by Daure [1269], Dickinson, Dillon, Rasetti [1335], Lewis and Houston [2602], Bhagavantam [810], Hemptinne and Charette [1987], Stoicheff [3872], and in high dispersion ba Feldmann, Romanko and Welsh [1547]. The vibration Raman spectrum of liquid ethylene was investigated by Bonner [864], Hemptinne Jungers, Delfosse [1988], Glockler and Renfrew [1781], Rank, Shull and Axford [3382], Hemptinne and Charette [1987], using devices with low dispersion.

The vibration spectra of the deuterosubstituted ethylene have also been thoroughly studied: C_2D_4 [1160, 1646, 1988, 1987, 568, 510], C_2HD_3 [1988, 1987, 1090], $C_2H_2D_2$ [1988, 1987, 1090, 2553, 1089, 1213] and C_2H_3D [1988, 1987, 1203, 1213, 1202]. At the examination of the vibration Raman spectrum of C_2H_4 in paper [1547] some vibrational frequencies of the molecule of $C^{12}H_2C^{13}H_2$ were discovered.

The first interpretations of vibration spectra of ethylene were proposed by Mecke [2830] in 1932. Later on, however, as the knowledge on the vibration spectra became more profound and extended, this had to be corrected, which resulted in new attributions of the fundamental frequencies of the C_2H_4 molecule.

Table 156 gives the attributions of the fundamental frequencies of the C_2H_4 molecule adopted by the various investigators together with those accepted in the present Handbook.* The most important divergences in the attribution of the fundamental frequencies of the C_2H_4 molecule occur with the frequencies ν_4, ν_5, ν_6, ν_8 and ν_{10}. There were no divergencies in the attribution of the fundamental frequencies ν_1, ν_2, ν_3

and ν_7, ν_9, ν_{11}, ν_{12}, since the most intense bands in the Raman spectrum correspond to the first set and the most intense bands in the infrared spectrum to the second set.

Up to 1956 the frequencies ν_1, ν_2, ν_3 were taken as the values of the maxima of the Q-branches of the corresponding bands, measured by Dickinson, Dillon and Rasetti [1335] in the Raman spectrum of gaseous ethylene. Similar values of the frequencies ν_1, ν_2, ν_3 were obtained by Bhagavantam [810] and are adopted by Conn and Sutherland [1160] and by Wu [4340] (for ν_1 and ν_3). In 1956 Feldman, Romanko and Welsh [1547]* resolved the rotational structure in the Raman spectrum of gaseous ethylene, determined the beginning of the bands ν_1 and ν_3, and measured more precisely than before the position of the maximum of the Q-branch of the band ν_2. The values found in [1547] for ν_1, ν_2 and ν_3 were adopted in the present Handbook. Their errors obviously do not exceed ±0.5 cm^{-1}.

TABLE 156

Attributions of the Fundamental Frequencies of the C_2H_4 Molecule, Proposed by Various Investigators
(The values of the frequencies are given in cm^{-1})[a]

1 Частота	2 Тип колебания	3 Мекке [2530], 1932 г.	4 Боннер [951], 1936 г.	5 Конн, Сезерленд [1160], 1939 г.	6 Ву [4340], 1939 г.	7 Галлоуэй, Баркер [1646] 1942 г.	8 Герцберг [152], 1945 г.	9 Расмуссен, Браттен [3401], 1947 г.	10 Арнетт, Крауфорд [568], Ранк и др. [3382], 1950 г.	11 Свердлов, Пахомова [366], 1953 г.	12 Фельдман, Романко, Уэлш [1547], 1956 г.	13 Настоящий Справочник
ν_1	A_{1g}	3019	3019,3	3020	3020	3019,3	3019,3	3019,3	3019,3	3019	3026,4	3026,4
ν_2	A_{1g}	1623	1623,3	1626	1623	1623,3	1623,3	1623,3	1623,3	1623	1622,6	1622,6
ν_3	A_{1g}	1342	1342,4	1343	1343	1342,4	1342,4	1342,4	1342,4	1342	1342,2	1342,2
ν_4	A_{1u}	—	825	700	828	825	825	950	1027	—	—	1027
ν_5	B_{1g}	3240	3069	3075	3272	3069	3272,3	3075	3272,3	3075	3102,5	3102,5
ν_6	B_{1g}	1097	950	1030	950	1055	1050	1250	1236	1236	1236	1236
ν_7	B_{1u}	940	940	950	950	949,2	949,2	949,2	949,2	949	—	949,2
ν_8	B_{2g}	940	1100	943	1100	950	943	943	943	943	950	943
ν_9	B_{2u}	3107	3107,4	3107	3107	3105,5	3105,5	3105,5	3105,5	3105	—	3105,5
ν_{10}	B_{2u}	950	950	1020	950	995	995	800	810,3	810	—	810,3
ν_{11}	B_{3u}	2998	2988,2	2988	2988	2989,5	2989,5	2989,5	2989,5	2990	—	2989,5
ν_{12}	B_{3u}	1444	1443,9	1444	1444	1443,9	1443,5	1443,9	1443,5	1444	—	1443,5

a) In the present Handbook the same designations are adopted for the fundamental frequencies of the C_2H_4 molecule as in Herzberg's book

[152] and in the papers [568, 3382, 366, 1547]. In the papers [1160, 4340, 1646, 3401] the designations were different.

1. Frequency;
2) type of vibration;
3) Mecke [2830] 1932;
4) Bonner [864] 1936;
5) Conn, Sutherland [1160] 1939;
6) Wu [4340] 1939;
7) Gallaway, Barker [1646] 1942;
8) Herzberg [152] 1945;
9) Rasmussen, Brattain [3401] 1947;
10) Arnett, Crawford [568] Rank et al. [3382] 1950;
11) Sverdlov, Pakhomova [366] 1953;
12) Feldman, Romanko, Welsh [1547] 1956;
13) Present Handbook.

For the vibrational frequencies ν_7, ν_9, ν_{11}, ν_{12} Conn and Sutherland [1160] and Wu [4340] chose the values of the centers of the corresponding bands, measured by Levin and Meyer [2597] in the infrared spectrum of gaseous ethlene, obtained on a spectrometer with high dispersion. Later on, Gallaway and Barker [1646] determined and analyzed the rotational structure of the bands ν_7, ν_9 and ν_{11} and found the beginning of these bands. For the frequencies ν_{12} they accepted in their paper [1646] the value found by Levin and Meyer. Herzberg [152] referred this value to the vacuum. In the present Handbook we adopted for the frequencies ν_7, ν_9, ν_{11}, ν_{12} the values recommended by Herzberg [152] based on the data of Gallaway and Barker [1646] and Levin and Meyer [2597].* The errors of determination with the adopted values of the frequencies ν_7, ν_9, ν_{11} and ν_{12} seem not to exceed ± 2 cm^{-1}.

For the frequency ν_{10} Conn and Sutherland [1160] chose a value equal to 1020 cm^{-1}. This value of ν_{10} was calculated by them with the help of the isotope relation Teller-Redlich, attributing the frequency ν_{10} = 727 cm^{-1} to the C_2D_4 molecule; this choice was based on their interpretation of the infrared vibration spectrum of deuteroethylene. Wu [4340] interpreted the most intense band in the infrared spectrum of ethylene with the center at about 950 cm^{-1} as due to the superposition of the bands ν_7 and ν_{10} and chose for the corresponding frequency of C_2H_4 the same value, equal to 950 cm^{-1}. Gallaway and Barker [1646] observed in the infrared spectrum of C_2H_4 a very weak band with the center at about 995 cm^{-1}, which they attributed to the frequency ν_{10}. This attribution was also accepted by Herzberg [152]. Rasmussen and Brattain [3401] observed in the infrared spectrum of ethylene a weak band with its center at about 807.1 cm^{-1}; they attributed it to the frequency ν_{10} with a value of 800 cm^{-1}. A very weak band was observed by Gallaway and Barker [1646] at about 995 cm^{-1} attributed in paper [3401] to the frequency ν_7 of the $C^{12}H_2 \cdot C^{13}H_2$ molecule. A band at about 800 cm^{-1} was also observed in the infrared spectrum of ethylene by Tompson and Harris [3973], who attributed it to one of the fundamental frequencies of the C_2H_4 molecule. Coblentz [1139] too observed a weak absorption band in this part of the spectrum of ethylene. The next investigators of the vibration spectrum of ethylene, however, ignored this observation, supposing that in the spectrum obtained by Coblentz this band did not pertain to ethylene but to some impurities. Arnett and Crawford [568] investigated especially the infrared spectrum of ethylene in the range of the band with its center at about 800 cm^{-1}, resolved and analyzed its rotational structure and determined the beginning of the band at 810.3 cm^{-1}. Arnett and Crawford [568] ascribed this value to the frequency ν_{10} since one then obtained the more satisfactory attribution of the bands with centers at 2046.5 and 1656 cm^{-1}, respectively to the frequencies $\nu_6 + \nu_{10}$ and $2\nu_{10}$.* The final proof of the correctness of the attribution of the frequency ν_{10} proposed by Arnett and Crawford [568], was given as a result of the calculations of the fundamental frequencies of ethylene molecules and its deuteroderivates by Sverdlov and Pakhomova [366]. In the present Handbook a value of ν_{10} = 810.3 cm^{-1} was accepted.

Conn and Sutherland [1160] identified the frequency ν_8 with the weak band at 943 cm^{-1}, observed by Glockler and Renfrew [1781] in the Raman spectrum of liquid ethylene. The same attribution was chosen by Herzberg [152] for the frequency ν_8 as well as in the papers [3401, 568, 3882, 366]. In [864, 4340] the frequency ν_8 was erroneously assumed as equal to 1100 cm^{-1}. In the Raman spectrum of liquid ethylene Bonner [864] observed a band with its center at 950 cm^{-1} which encouraged Gallaway and Barker [1646] to assume ν_8 = 950 cm^{-1}. The correctness of the attribution of the frequency ν_8 chosen by Herzberg [152] was confirmed by Stoicheff [3872], who observed in the Raman spectrum of gaseous ethylene a weak and broad band with two maxima in the range of 950 cm^{-1}. In connection with this, Feldman, Romanko and Welsh [1547]* chose ν_8 = 950 cm^{-1}. However, the value ν_8 = 943 cm^{-1}, accepted in the papers [152, 3401, 568, 3382, 366] is better than the value ν_8 = 950 cm^{-1}, as it agrees with the attribution of the band at 1889.6 cm^{-1}, observed in the infrared spectrum [1139, 2597, 1646] to the frequency $\nu_7 + \nu_8$, The value ν_8 = 943 cm^{-1} has therefore been accepted in the present Handbook.

Conn and Sutherland [1160] estimated the frequency ν_6 to 1030 cm^{-1}, proceeding from the attribution of the infrared band at 2046.5 cm^{-1} [2597] to the frequencies $\nu_6 + \nu_{10}$ and from the estimate ν_{10} = 1020 cm^{-1}. Wu [4340] accepted the value ν_6 = 950 cm^{-1} proposed by Bonner [864], concluding from his attribution of the bands of C_2H_4 situated in the photographic range. Gallaway and Barker [1646] and Herzberg [152] assuming ν_{10} = 995 cm^{-1}, estimated the frequency ν_6 equal to 1055 or 1050 cm^{-1} from the complex frequency $\nu_6 + \nu_{10}$ = 2046.5 cm^{-1}. Later on, analogous calculations led Rasmussen and Brattain [3401] to the value of ν_6 = 1250 cm^{-1}, and Arnett and Crawford [568] to the value of ν_6 = 1236 cm^{-1}, the first authors assuming ν_{10} = 800 cm^{-1} and the second ones ν_{10} = = 810.3 cm^{-1}. The value of ν_6 = 1236 cm^{-1} was verified by Rank, Shull and Axford [3382] who discovered in the Raman spectrum of liquid ethylene a band with its center at 1236 cm^{-1}. The accuracy of the attribution proposed in the papers [568, 3382] for the frequency ν_6 was verified by the calculations of Sverdlov and Pakhomova [366]. In the present Handbook we accept a value of $\nu_6 = 1236 \pm 3$ cm^{-1}, the error is determined by the inaccuracy of measuring the center of the corresponding band in the Raman spectrum of liquid ethylene [3382]. The attempts undertaken in [3872, 1547] to detect the band ν_6 in the Raman spectrum of the gaseous ethylene remained without success.

Up to the present days the frequency ν_5 was usually given a value of either 3075 or 3272 cm^{-1}, in connection with the fact that the corresponding lines were repeatedly observed in the Raman spectrum of ehtylene * (see Table 156). Playler [3270] showed that the value of $\nu_5 =$ $= 3272$ cm^{-1}, adopted by Herzberg [152] and the papers [568, 3382], is not satisfactory, as it leads to an anomalously high value of the correction for the anharmonicity of oscillation. The measurements of the degree of depolarization of the line at 3075 cm^{-1} [3382] and the calculations of Sverdlov and Pakhomova [366] also spoke in favor of the low value of ν_5. Stoicheff [3872] applied a more precise method to obtain the Raman spectrum of gaseous ethylene as in the previous investigations, and detected a band with its maximum at 3108 ± 5 cm^{-1} not observed before. He showed that this band corresponded to the frequency ν_5 of the C_2H_4 molecule in the gas, while the band previously observed in the Raman spectrum of liquid ethylene at 3075 cm^{-1} corresponds to the ν_5 frequency of the C_2H_4 molecule in liquid ethylene. The band at 3272 cm^{-1}, observed in the Raman spectrum of gaseous ethylene, is attributed by Stoicheff [3872] to the complex frequency $\nu_2 + 2\nu_{10}$. Feldman, Romanko and Welsh [1547] investigated in high dispersion the Raman spectrum of gaseous ethylene in the range from 2800 to 3300 cm^{-1}. In this range they recorded a series of lines of the band ν_5 and based on their attributions, they calculated the beginning of the band ν_5, equal to

3102.5 cm^{-1}.

In the papers [1160, 4340, 1646, 152] the value of the frequency ν_4 of the torsion oscillation was estimated to approximately 800 cm^{-1}, either from an erroneous interpretation of the band with the center at 1656 cm^{-1}, observed in the Raman spectrum, or from calculations, using the results of experimental measurements of the specific heat of gaseous ethylene and the values of the remaining frequencies* observed in the spectra.

The true value of the frequency ν_4 was established by Arnett and Crawford [568] as a result of an analysis of the infrared spectra of the molecule of ethylene and of the molecules of all deuteroderivates of ethylene in the range of the frequencies ν_4, ν_7, ν_8 of the nonplanar oscillations and of a subsequent theoretical processing of the data obtained. The fact is that the frequency of the torsion oscillation is active in the infrared spectra of the molecules of C_2H_3D, trans-$C_2H_2D_2$ and C_2HD_3. This made is possible to determine with sufficient reliability the force constant of the torsion oscillation and to calculate the value of ν_4 of the molecules of C_2H_4, cis-$C_2H_2D_2$, CH_2CD_2 and C_2D_4, where the frequency is not active in the vibration spectra. Thus the frequecy ν_4 of the C_2H_4 molecule was determined in paper [568] as equal to 1027 cm^{-1}. This result was subsequently verified by calculations carried out in the papers [366, 1213]. A value of ν_4 = 1027 cm^{-1} has been accepted in the present Handbook.

The values of the fundamental frequencies of the C_2H_4 molecule adopted in the present Handbook are compiled in Table 157. The errors of the adopted values of frequencies are estimated as to ±0.5 cm^{-1} for ν_1, ν_2, ν_3, ν_5 and ν_{10}, ± 1 cm^{-1} for ν_7, ν_9, ν_{11} and ν_{12}, ± 3 cm^{-1} for ν_4 and ν_6 and ±10 cm^{-1} for ν_8. The values of the fundamental frequencies of the C_2H_4 molecule adopted in the present Handbook are similar to the values adopted in the first edition,* and to the values recommended by Sverdlov and Pakhomova [366] from own calculations of the vibrational frequencies of the molecules of the deuteroderivates of ethylene.** The most essential differences in the values concern the frequencies ν_1 and ν_5, which is due to their improvement achieved by Feldman, Romanko and Welsh [1547].

The rotational constants and the moments of inertia of the C_2H_4 molecule were determined by many investigators by way of fine structure analyses of the bands in the infrared spectrum [600, 3615, 597, 3968, 3790, 1646, 510] and in the Raman spectrum [1547] of ethylene, and also from an analysis of the structure of the rotational Raman spectrum [2602, 3477, 1398]. The most precise values of the rotational constants of the vibrational ground state of the molecules of C_2H_4 and C_2D_4 were obtained by Allen and Plyler [510] and by Dowling and Stoicheff [1398].

TABLE 157

Adopted Values of the Molecular Constants of C_2H_4, C_2F_4 and C_2Cl_4 ($\sigma = 4$)

Постоянная 1	C_2H_4	C_2F_4	C_2Cl_4	1 Постоянная	C_2H_4	C_2F_4	C_2Cl_4
ν_1, см$^{-1}$ 2	3026,4	778	447	ν_8, см$^{-1}$	943	508	512
ν_2, см$^{-1}$	1622,6	1872	1571	ν_9, см$^{-1}$	3105,5	1 337	908
ν_3, см$^{-1}$	1342,2	394	235	ν_{10}, см$^{-1}$	810,3	218	176
ν_4, см$^{-1}$	1027	190	110	ν_{11}, см$^{-1}$	2989,5	1 186	777
ν_5, см$^{-1}$	3102,5	1340	1000	ν_{12}, см$^{-1}$	1443,5	558	310
ν_6, см$^{-1}$	1236	551	347	$I_A I_B I_C \cdot 10^{-117}$, (г·см^2)^3 3	5,477	15 875	336 800
ν_7, см$^{-1}$	949,2	406	288				

1) Constant; 2) cm^{-1}; 3) (g·cm^2)^3.

Allen and Plyler [510] resolved the rotational structure of the band ν_{11} in the infrared spectrum of C_2H_4 and C_2D_4, working with a spectrometer with a diffraction grating of high resolution. The analysis of the data obtained for C_2H_4 permitted them to determine the values

$B_0 = 0.9998$ and $C_0 = 0.8294$ cm^{-1}, where the errors are estimated by the authors of the paper [510] as ±0.0002 cm^{-1}. A more realistic estimate of the errors of the values of these quantities is ±0.001 cm^{-1}, if we take into consideration that the mean deviation of the calculated values from the observed values of the lines of the P- and R- branches with $J \leq 10$ is 0.04 cm^{-1}, as this is pointed out in paper [510].

Dowling and Stoicheff [1398] photographed the purely rotational Raman spectra of C_2H_4 and C_2D_4 with an average linear inverse dispersion of 6.75 cm^{-1}/mm in second order of a concave diffraction grating with a radius of curvature of 0.4 m. The analysis of the data obtained enabled the authors of paper [1398] to determine the following values of the rotational constants of C_2H_4: $A_0 = 4.828 \pm 0.009$, $B_0 = 1.0012 \pm 0.0009$, $C_0 = 0.8282 \pm 0.0004$ cm^{-1}. Dowling and Stoicheff were the first to determine the value of the constant A_0 immediately by way of analyzing the spectroscopic data, instead of using the approximate relation $1/A_0 = 1/C_0 + 1/B_0$, as this was done in earlier investigations. The values of the rotational constants B_0 and C_0 found in paper [1398] agree with the values of these quantities obtained in the papers [510, 3477], within the limits of error of determination of the latter. It must be noted that, if in earlier determinations of the rotational constants of C_2H_4 by analyzing the rotational structure of the vibrational-rotational bands and of the pure rotational spectrum the relations of the theory of the energy levels of symmetric rotators* was applied, in the papers [1398, 510, 3477] the resolution obtained was high enough to make it possible to apply the relations of the energy levels of asymmetric rotators.

In the present Handbook we chose for the vibrational ground state of the molecule of C_2H_4 the above values of the rotational constants, determined by Dowling and Stoicheff [1398]. The corresponding values of the product of the principal moments of inertia are compiled in Table 157.

The structure parameters of the molecules of ethylene (in the electron ground state) were determined by analyzing the rotational structure of the bands of the vibrational-rotational [597, 3217, 3968, 1646, 510] and of the rotational [1398] spectra, and also by analyzing electron-diffraction data [4264, 3204, 663, 664].* The most precise values of the structure parameters of the C_2H_4 molecule were given by Bartell and Bonham [663, 664], Allen and Plyler [510] and Dowling and Stoicheff [1398]. Bartell and Bonham [664] carried out a very accurate electronographic investigation into the structure of C_2H_4, working with a sector-microphotometric method, and obtained $r_{C-H} = 1.084 \pm 0.003$, $r_{C=C} = 1.3227 \pm$ $\pm\ 0.002$ A, $\angle H - C - H = 115°30' \pm 36'$. The values based on the investigation of the rotational structure of the band ν_{11} in the infrared spectra of C_2H_4 and C_2D_4 [510] and of the pure rotational Raman spectra of C_2H_4 and C_2D_4 [1398] agree with the values of the structure parameters of C_2H_4 found in paper [664]: $r_0(C - H) = 1.086 \pm 0.003$, $r_0(C = C)$ $= 1.337 \pm 0.003$ A, $\angle H - C - H = 117°22' \pm 1°$ [510] and $r_0(C - H) = 1.086$ $\pm\ 0.003$, $r_0(C = C) = 1.339 \pm 0.002$ A, $\angle H - C - H = 117°34' \pm 30'$ [1398]. In the present Handbook the values obtained by Dowling and Plyler [1398] were adopted for the structure parameters of the C_2H_4 molecule.

The information on excited electron states of the C_2H_4 molecule is based on examinations of the electron spectra of ethylene in the ultraviolet and the visible range and on a series of theoretical studies. The results of the investigation of the spectrum of C_2H_4 in the ultraviolet range, published till 1941, are considered in the surveys by Sponer [3825, 3827]. In the following years the ultraviolet spectra of C_2H_4 and C_2D_4 were analyzed by Wilkinson [4278, 4279, 4272, 4276b]. The emission spectrum of C_2H_4 in the visible range was studied by Goldfard and Pimentel [1792b]. A detailed interpretation of the excited electron states of C_2H_4 was made by Mulliken [2984a, 3003a] and Walsh [4145a]. Later on the theory of the electron states of the C_2H_4 molecule was developed in the papers [3005, 3119, 3826, 3193, 2613, 2461]. As a result of the investigations made, it became known that in the excited electron states of the C_2H_4 molecule, the groups CH_2 are turned through 90° with respect to each other. The first excited electron state of the C_2H_4 molecule is a triplet with an excitation energy of about 45,000 cm^{-1}.

C_2F_4. The infrared spectrum of gaseous tetrafluorethylene was analyzed by Torkington and Tompson [4005] (500-3200 cm^{-1}), Matutano [2813] (250-5000 cm^{-1}), Nielsen, Claassen, Smith [3090] (370-3500 cm^{-1}), Mann, Acquista, Plyler [2753] (190-455 cm^{-1}) and Kiyama, Minomura and Ozawa [2429] (500-3200 cm^{-1}). The Raman spectra of gaseous tetrafluorethylene were studied by Nielsen, Claassen Smith [3090] and those of liquid tetrafluorethylene by Monfils and Duchesne [2938]. The numerous investigations of the vibrational spectra of C_2F_4 were carried out with prism spectrometers with a dispersion insufficient to resolve the rotational structure of the bands. In paper [3090] the Raman spectrum of gaseous tetrafluorethylene was obtained with the help of an instrument with a dispersion of 15A/mm, which permitted a sufficiently accurate determination of the position of the maxima of the different bands.

The vibrational spectra of C_2F_4 were first interpreted by Nielsen, Claassen and Smith [3090] using data on the infrared spectrum and the Raman spectrum of gaseous tetrafluorethylene they had obtained. The results of later studies confirmed the correctness of this interpretation and permitted an improvement of the values of the fundamental frequencies ν_4, ν_6, ν_7, ν_8 and ν_{10}.

The investigation of the Raman spectrum of liquid tetrafluorethylene [2938] showed that the vibrational frequencies of the C_2F_4 molecule do not considerably vary at the transition from gas to liquid.

Mann, Acquista and Plyler [2753] analyzed the infrared spectrum in the longwave range, not studied by Nielsen, Claassen and Smith [3090]. This enabled the authors of paper [2753] to determined the value of the frequency of ν_{10} = 218 cm^{-1}, estimated in paper [3090] to 245 cm^{-1}, and also the value of the frequency of ν_7 = 406 cm^{-1} in paper [3090], considered as equal to 407 cm^{-1} from non-published data of Plyler. For the frequencies ν_6 and ν_8 the authors of [2753] chose values equal to 551 and 508 cm^{-1}, respectively, based on data obtained by Monfils and Duchesne [2938]. Nielsen, Claassen and Smith [3090] accepted for these frequencies values equal to 544 and 510 cm^{-1} respectively. The value of ν_6 = 544 cm^{-1} in paper [3090] was calculated from the complex frequencies, and the value ν_8 = 510 cm^{-1}, adopted according to an analysis of the Raman spectrum of the gas, where the authors of paper [3090] observed a doublet band with maxima at 503 and 517 cm^{-1}. The frequency ν_4 of the torsion oscillation was considered as equal to 190 cm^{-1} by Mann, Acquista and Plyler [2753] concluding from a comparison of entropy of C_2F_4 [1634] calculated from calorimetric data and from molecular constants, and also from the results of the calculations of the value of ν_4 from the complex frequencies of C_2F_4 and from the force constant of the torsion oscillation of the molecule of C_2H_4, found by Arnett and Crawford [568].* For the remaining fundamental frequencies of C_2F_4 (ν_1, ν_2, ν_3, ν_5, ν_9, ν_{11}, ν_{12}) Mann, Acquista and Plyler [2753] adopted the values found by Nielsen, Claassen and Smith [3090].

The values of the fundamental frequencies of the C_2F_4 molecule recommended by Mann, Acquista and Plyler are adopted in the present Handbook and compiled in Table 157. The accuracy of these values is verified by calculations of the fundamental frequencies of the fluorchlorethylene by Mann, Fano, Meal and Simanouchi [2758]. The errors of the adopted values of the fundamental frequencies of C_2F_4 are estimated as amounting to ±3 to ±5 cm^{-1} and to ±10 cm^{-1} for the value of the frequency ν_4 of the torsion oscillation.

The structure parameters of the C_2F_4 were determined in electron-diffraction studies [960, 2327, 981, 2204]. The most reliable values of the structure parameters of C_2F_4 were obtained by I. Karle and G. Karle [2327]: $r_{C=C} = 1.313 \pm 0.010$, $r_{C-F} = 1.313 \pm 0.035$ A, $\angle F - C - F = 114 \pm 2°$. Similar values of the corresponding structure parameters for $C_2H_2F_2$ were also obtained in paper [2327], which agree with the results of an analysis of the microwave spectrum of the difluorethylene [3448, 1457]. The values of the structure parameters of C_2F_4 obtained in paper [2327] were later on confirmed by the results of the electron-diffraction studies of Braun and Livingston [981]: $r_{C=C} = 1.33 \pm 0.06$, $r_{C-F} = 1.30 \pm 0.02$, A, $\angle F - C - F = 114 \pm 3°$. Somewhat different values of structure parameters of C_2F_4 were obtained by Brockway and Livingston [960] ($r_{C=C} = 1.27$, $r_{C-F} = 1.32$A, $\angle F - C - F = 110°$) and James and Livingston [2204] ($r_{C=C} = 1.27 \pm 0.04$, $r_{C-F} = 1.33 \pm 0.02$A, $\angle F - C - F = 110 \pm 2°$). The results of these investigations are, however, less reliable than the results obtained in paper [2327]. The product of the principal moments of inertia of C_2F_4, compiled in Table 157, is calculated from the structure parameters found by I. Karle and G. Karle in paper [2327].

The electron spectrum of C_2F_4 has not been studied.

$\underline{C_2Cl_4}$. The infrared vibrational spectrum of liquid tetrachlorethylene was studied in the papers [1139, 862, 3818, 1610, 1410, 3268, 760, 2753] (190-4000 cm^{-1})* and of gaseous tetrachlorethylene in paper [4336] (400-5000 cm^{-1}). All these studies were carried out with prism spectrometers of low dispersion. The Raman spectrum of liquid tetrachlorethylene was investigated in the papers[3327, 1239, 1240, 3960, 2954, 2738, 1982, 4337, 2470, 4303, 3381, 3580]. The raman spectrum of gaseous tetrachlorethylene has not been analyzed.

Many investigators* tried to interpret the vibrational spectrum of C_2Cl_4. The greatest difficulties consist in the attribution of the fundamental frequencies active in the infrared spectrum (ν_7, ν_9, ν_{10}, ν_{11}, ν_{12}).

In the present Handbook we adopt for C_2Cl_4 the attribution of the fundamental frequencies recommended by Mann et al. [2759, 2758]. For the fundamental frequencies of C_2Cl_4 active in the Raman spectrum (ν_1, ν_2, ν_3, ν_5, ν_8), we chose in Table 157 the values found by Wittek [4303] for the centers of the corresponding bands in the Raman spectrum of the liquid tetrachlorethylene. In Table 157 we adopted for the frequency ν_4 of the torsion oscillation (not active in the vibrational spectra of C_2Cl_4) the value found by Mann, Acquista and Plyler [2753] as a result of the calculation of ν_4 from the force constant of the corresponding vibration of C_2F_4 ($0.245 \cdot 10^{-11}$erg/rad^2) and the attribution of a very weak line in the Raman spectrum of liquid tetrachlorethylene at 218 cm^{-1} to the frequency $2\nu_4$. In Table 157 the vibrational frequencies ν_7, ν_9, ν_{11}, ν_{12} were given the values of the centers of the bands measured in the infrared of liquid tetrachlorethylene by Mann, Acquista and Plyler [2753] and the value of the center of the intense absorption band found by Pitzer in the infrared spectrum of liquid tetrachlorethylene was attributed to the frequency ν_{10}.

The fundamental frequencies given in Table 157 have thus been obtained for liquid tetrachlorethylene. The corresponding values of the fundamental frequencies of the free C_2Cl_4 molecule in gaseous form must be slightly higher,** since the inter molecular interactions in the liquid occur at the expense of a weakening of the intramolecular field. In the case of the tetrachlorethylene this difference, however, amounts to about 5 cm^{-1}, as far as one can judge from a comparison of the values of the frequencies observed in the infrared spectra of liquid and gaseous tetrachlorethylene.* In view of this fact, the errors of the values of the fundamental frequencies of the C_2Cl_4 molecule compiled in Table 157 are estimated as ±5 cm^{-1} and of the frequency ν_4 as ±10 cm^{-1}.

The structure parameters of the C_2Cl_4 molecule were determined from the results of electron-diffraction studies by Brockway, Pauling, Beach [959], Lipscomb,** I. Karle and G. Karle [2328] and Rao and Livingston [3387]. In these studies similar values were obtained for the length of the bond C – Cl(≅ 1.72 A) and of the angle C – C – Cl(≅ 123°), but different values of the length of the bond C = C. In the papers by Brockway, Pauling and Beach [959] it was proposed $r_{C=C}$ = 1.38 A, while, according to [517], Lipscomb obtained a value of $r_{C=C} = 1.34 \pm 0.05$ A. The following electron-diffraction studies with C_2Cl_4 [2328, 3387] were based on more effective methods.*** I. Karle and G. Karle [2328] obtained $r_{C-Cl} = 1.72 \pm 0.01$, $r_{C=C} = 1.30 \pm 0.03$ A and $\angle C - C - Cl = 123°.25 \pm 0°.75$, and Rao and Livingston [3387] found $r_{C-Cl} = 1.724$, $r_{C=C}$=1.327A, $\angle C - C - Cl = 123°.35$. The value $r_{C=C}$ = 1.30 A, found by I. Karle and G. Karle, is smaller than the value of the length of the bond C = C, obtained by these investigators for the C_2F_4 molecule (see page 1136). Meanwhile, from a comparison of the structure parameters of ethylene and its halogen derivates and of general theoretical notions it follows that, as in the C_2H_4 molecule hydrogen is substituted by halogen atoms, the length of the bond C = C is reduced and this quantity must attain its minimum in the C_2F_4 molecule. According to the data of the papers [2327, 1457] the lengths of the bonds C = C in the molecules of C_2F_4 and $C_2H_2F_2$ (asymm.) coincide within the limits of errors of their determination. It is natural to assume an analogous accordance for the molecules C_2Cl_4 and $C_2H_2Cl_2$ (asymm.). Based on an investigation of the microwave spectrum of the dichlorethylene in paper [3679] $r_{C=C} = 1.32 \pm 0.02$ A was found for the molecule of $C_2H_2Cl_2$ (asymm.), in accordance with the value of this quantity for the C_2Cl_4 molecule obtained by Rao and Livingston [3387]. In the present Handbook the following values of the structure parameters are therefore adopted according to the results of the electron-diffraction studies on the molecular structure of C_2Cl_4 $r_{C-Cl} = 1.72 \pm 0.01$, $r_{C=C} = 1.32 \pm 0.02$ A $\angle C - C - Cl = 123°.3 \pm 0°.7$ which were used in calculating the product of the principal moments of inertia given in Table 157.

The ultraviolet spectrum of tetrachlorethylene was investigated by Lacher, Hummel, Bohmfalk and Park [2509].

§72. MOLECULES OF THE TYPE $C_2X_2Y_2$

The molecules of halogen-substituted ethylene of the type $C_2X_2Y_2$ exist in three isomeric forms (cis, trans and asymmetric); as regards the structure, they differ from one another by the order of bonds linking the X and Y atoms with the carbon atom (cf. Fig. 19). The molecules of halogen-substituted ethylene of the type $C_2X_2Y_2$, apart from being a member of one or another isomeric form, are characterized by one and the same symmetry parameter $\sigma = 2$, possessing 12 nondegenerate fundamental frequencies, nine of which corresponding to plane vibrations $(\nu_1, \nu_2, \ldots, \nu_9)$ and three to nonplanar vibrations $(\nu_{10}, \nu_{11}, \nu_{12})$.

The various isomers of the molecules of halogen-substituted ethylene of the type $C_2X_2Y_2$ pertain to different point groups of symmetry, owing to which their vibrational spectra are different (cf. Table 158).

Table 159 contains the values of the molecular constants of fluorine and chlorine derivatives of ethylene of the type $C_2X_2Y_2$, accepted in the present Handbook.

$C_2H_2F_2$. The asymmetric modification of difluorethylene, CH_2CF_2,* is the only one that has been investigated experimentally.

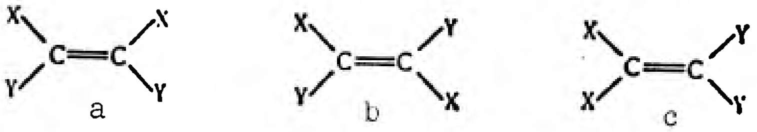

Fig. 19. Isomeric forms of molecules of halogen derivatives of ethylene of the type $C_2X_2Y_2$; a) cis form; b) trans form; c) asymmetric form.

TABLE 158

Characteristics of the Fundamental Frequencies of the Isomeric Molecules of Halogen-substituted Ethylene of the Type $C_2X_2Y_2$

1 Изомеры $C_2X_2Y_2$	2 Точечная группа симметрии	3 Типы колебаний	4 Основные частоты	5 Активность в колебательных спектрах	
				6 инфракр. спектр	7 спектр комб. рассеяния
CX_2CY_2	C_2	A_1, плоск. 8 A_2, неплоск. 9 B_1, плоск. B_2, неплоск.	$\nu_1, \nu_3, \nu_4, \nu_7, \nu_9$ ν_{12} $\nu_2, \nu_5, \nu_6, \nu_8$ ν_{10}, ν_{11}	Акт. 10 Неакт. 11 Акт. »	Акт. » » »
12 Цис-$C_2X_2Y_2$	C_{2v}	A_1, плоск. A_2, неплоск. B_1, плоск. B_2, неплоск.	$\nu_1, \nu_3, \nu_5, \nu_7, \nu_9$ ν_{10}, ν_{11} $\nu_2, \nu_4, \nu_6, \nu_8$ ν_{12}	» Неакт. Акт. »	» » » »
13 Транс-$C_2X_2Y_2$	C_{2h}	A_g, плоск. A_u, неплоск. B_g, неплоск. B_u, плоск.	$\nu_1, \nu_3, \nu_4, \nu_6, \nu_8$ ν_{10}, ν_{11} ν_{12} $\nu_2, \nu_5, \nu_7, \nu_9$	Неакт. Акт. Неакт. Акт.	» Неакт. Акт. Неакт.

1) Isomers
2) point group of symmetry
3) types of vibrations
4) fundamental frequencies
5) activity in the vibrational spectra
6) infrared spectrum
7) Raman spectrum
8) plane
9) nonplanar
10) active
11) inactive
12) cis
13) trans

The infrared spectrum of gaseous difluorethylene was investigated by Torkington and Thompson [4005] (500-3200 cm^{-1}), Maturano [2813] (250-5000 cm^{-1}), Cole and Thompson [1147] (the bands at 803, 926, and 955 cm^{-1}) and Smith, Nielsen and Claassen [3773] (445-5000 cm^{-1}). The Raman spectrum of liquid difluorethylene was studied by Edgell and Byrd [1453] and that of gaseous difluorethylene by Smith, Nielsen and Claassen [3773]. The vibrational spectra of the deutero-derivatives of difluorethylene ($CHDCF_2$ and CD_2CF_2) were examined by Edgell and Ultee [1462].

TABLE 159

Accepted Values of the Molecular Constants of the Fluorine and Chlorine Derivatives of Ethylene, of the type $C_2X_2Y_2$ ($\sigma = 2$)

Молекула 1	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}	$I_AI_BI_C$
	2 см$^{-1}$											3	10^{-117} г^3·см^6
CH_2CF_2	3060	3103	1728	1380	1302	955	926	550	438	803	611	714	963,2
CH_2CCl_2	3035	3135	1616	1391	1088	788	601	375	299	874	458	686	10167
Цис-$C_2H_2Cl_2$ 4	3077	3072	1587	1294	1179	848	711	571	173	876	406	697	9841
Транс-$C_2H_2Cl_2$ 5	3073	3080	1578	1274	1200	846	817	350	250	895	227	763	4822
CF_2CCl_2	1327	1032	1749	993	622	459	434	258	192	564	323	167	88450
Цис-$C_2F_2Cl_2$	1260	1139	1733	972	565	437	412	334	184	518	349	150	84970
Транс-$C_2F_2Cl_2$	1190	1186	1707	892	632	426	425	288	175	529	333	140	82170

1) Molecule; 2) cm^{-1}; 3) g^3•cm^3; 4) cis; 5) trans

According to Table 158 all the fundamental frequencies of the CH_2CF_2 molecule are active in the Raman spectrum and, with the exception of the frequency ν_{12} of torsional oscillations, also in the infrared spectrum.

Torkington and Thompson [4005] Matutano [2813] analyzed parts of the infrared spectrum of CH_2CF_2 they had observed, but they did not interpret the fundamental frequencies. Cole and Thompson [1147] investigated the contours of the most intense bands in the infrared spectrum of CH_2CF_2.

The vibrational spectra of CH_2CF_2 were interpreted and all fundamental frequencies of the molecule were determined for the first time in the papers [1453, 3773]. Edgell and Byrd [1453] interpreted the Raman spectra of liquid CH_2CF_2 they had obtained, taking into account the results of measurements of Torkington and Thompson [4005] in the infrared spectrum of the gas. Smith, Nielsen and Claassen [3773] interpreted the infrared spectrum and the Raman spectrum of gaseous CH_2CF_2 obtained by them. The values obtained in papers [3773, 1453] are similar for all fundamental frequencies of the CH_2CF_2 molecule, except for ν_4 and ν_{12}. Edgell and Byrd [1453] determined the frequency ν_4 of deformation oscillations from the Raman spectrum of liquid difluorethylene and obtained 1359 cm^{-1}, while Smith, Nielsen and Claassen [3773] obtained for it a value of 1414 cm^{-1} from the infrared spectrum of the gas and 1405 cm^{-1} from the Raman spectrum of the gas. The frequency ν_{12} of torsion oscillations was determined in the papers [1453, 3773] on the basis of investigations of the Raman spectrum of liquid difluorethylene where values of 712 cm^{-1} [1453] and 590 cm^{-1} [3773] were obtained.

This inconsistency was eliminated by Edgell and Ultee [1462] who showed that in the infrared spectrum of CH_2CF_2 Smith, Nielsen and Claassen [3773] had actually recorded the peaks of two branches of the ν_4 band at 1414 and 1361 cm^{-1}. The second branch of this band was observed by Edgell and Byrd [1453] in the Raman spectrum of the fluid at 1359 cm^{-1} and Smith, Nielsen and Claassen [3773] in the Raman spectrum of the gas at 1358.7 cm^{-1}.

Using these data and the values of the peaks of the corresponding bands of the $CHDCF_2$ and CD_2CF_2 molecules, Edgell and Ultee [1462] showed with the help of the Teller-Redlich product rule that the center of the ν_4 band of the CH_2CF_2 molecule must be close to 1380 cm^{-1}.

For the frequency of the torsional oscillation of CH_2CF_2 Edgell and Ultee [1462] used the value determined by Edgell and Byrd [1453] from the Raman spectrum of liquid difluorethylene since it has been verified by calculations in which the dynamic constants of the torsional oscillations of C_2H_4 and C_2F_4, found in papers [568, 2753], were used. For the remaining fundamental frequencies of the CH_2CF_2 molecule Edgell and Ultee [1462] used the same values as in paper [3773]. The values of the fundamental frequencies of the molecules of CH_2CF_2, $CHDCF_2$ and CD_2CF_2, determined in paper [1462], were verified by calculations of Sverdlox, Klochkovskiy and Kukina [365].

The values of the fundamental frequencies of the CH_2CF_2 molecule, recommended by Edgell and Ultee [1462] are adopted in the present Handbook and given in Table 159. The errors of the adopted values of the fundamental frequencies of the CH_2CF_2 molecule may be estimated as being within the limits of ± 3 to ± 5 cm^{-1}.

The structural parameters of the CH_2CF_2 molecule were determined on the basis of electron-diffraction studies [2327] and investigations of the microwave spectra of asymmetric difluorethylene [3449] and its deuterium derivatives [1457]. The results of all these investigations agree with one another.

Electron-diffraction studies of the structure of the CH_2CF_2 molecule, carried out by I. Karle and J. Karle [2327] with the help of the sector-microphotometrical method and a method of electron-diffraction analysis, improved by him, yielded the same values of the structural parameters as were obtained in earlier investigations of the microwave spectrum of CH_2CF_2 [3449]: $r_{C=C} = 1{,}311 \pm 0{,}035$, $r_{C-F} = 1{,}321 \pm 0{,}015$, $r_{C-H} = 1{,}07 \pm 0{,}02$ Å, $\angle F{-}C{-}F = 110 \pm 3^\circ$ $\angle H{-}C{-}H = 117 \pm 7^\circ$.

Edgell, Kinsey and Amy [1457] measured the microwave spectrum of CH_2CF_2 more accurately than in paper [3449] and measured also the microwave spectrum of $CHDCF_2$ and CD_2CF_2. As a result of the spectrum analysis the authors of paper [1457] determined very accurately the values of the rotational constants and the moments of inertia of the vibrational ground state of the molecules of CH_2CF_2, $CHDCF_2$ and CD_2CF_2. Under the assumption that $\angle H{-}C{-}H = \angle D{-}C{-}D = 120°$, $r_0(C{-}H) - r_0(C{-}D) = 0{,}009$ Å, Edgell, Kinsey and Amy [1457] calculated the following values of the structural parameters of CH_2CF_2: $r_0(C{=}C) = 1{,}311 \pm 0{,}005$, $r_0(C{-}F) = 1{,}321 \pm 0{,}005$, $r_0(C{-}H) = 1{,}10 \pm 0{,}05$ Å, $\angle F{-}C{-}F = 109°15' \pm 25'$, $\angle H{-}C{-}H = 120°$ (adopted).*

The principal moments of inertia of the vibrational ground state of the CH_2CF_2 molecule are, according to data [1457], equal to (in 10^{-40} g·cm^2): $I_A = 76{,}2750$, $I_B = 80{,}4586$, $I_C = 156{,}968$; the values of $I_AI_BI_C$, given in Table 159, correspond to them.

The ultraviolet spectrum of difluorethylene has not been investigated.

<u>$C_2H_2Cl_2$.</u> A series of investigators studied the vibrational spectra of all three isomeric forms of dichlorethylene, which made it possible to determine the fundamental frequencies of the corresponding molecules in a sufficiently reliable way.

The results of investigating the vibrational spectra of cis- and trans-dichlorethylene, published until 1945, are considered in Herzberg's monograph [152] where these spectra are also interpreted.

The results of investigations of the Raman spectra, obtained until 1942, are considered by Kohlrausch [236] and Hibben [2065]. Thorough investigations of the vibrational spectra of cis- and trans-$C_2H_2Cl_2$ were also carried out by Bernstein and Ramsay [766] and Pitzer and Hollenberg [3260].

The vibrational spectra of deuterosubstituted cis- and trans-$C_2H_2Cl_2$ were studied by Bernstein and Ramsay [766] ($C_2D_2Cl_2$) and

Bernstein and Pullin [765] (C_2HDCl_2).

Bernstein and Ramsay [766] obtained the infrared spectra of gaseous and liquid cis- and trans-$C_2H_2Cl_2$ and $C_2D_2Cl_2$ in the range of 400-3500 cm^{-1} and reinterpreted them, taking into account all the spectroscopic investigations carried out previously, the investigations of the equilibrium between cis- and trans-$C_2H_2Cl_2$ [4320] and using the theoretical relationship between the frequencies of the isotopic molecules. These investigations enabled Bernstein and Ramsay [766] to verify the correctness of the interpretation of the vibrational bands of cis-$C_2H_2Cl_2$, given by Herzberg [152], improving the values of the frequencies $\nu_2, \nu_4, \nu_6, \nu_8$ and ν_{12}. The interpretation of the vibrational frequencies of cis-$C_2H_2Cl_2$, given by Herzberg [152] and Bernstein and Ramsay [766] were verified by Pitzer and Hollenberg [3260], who studied the infrared spectrum of gaseous cis-$C_2H_2Cl_2$ in the range of 130-400 cm^{-1}.

The values of the fundamental frequencies of the molecule of cis-$C_2H_2Cl_2$, given in Table 159, are based on recommendations by Pitzer and Hollenberg [3260], verified by calculations of Sverdlov, Klochkovskiy and Kukina [365]. The values of the fundamental frequency of cis-$C_2H_2Cl_2$, recommended by Pitzer and Hollenberg, differ from the corresponding values recommended by Bernstein and Ramsay [766] only as regards the frequency ν_{12} of torsional oscillation. Bernstein and Ramsay obtained a value of $\nu_{12} = 691\ cm^{-1}$, while according to Pitzer and Hollinger $\nu_{12} = 697\ cm^{-1}$. Note that Herzberg [152], on the basis of Wu's data [4336], adopted a value of $\nu_{12} = 694\ cm^{-1}$.

Great difficulties are connected with the interpretation of the vibrational spectrum of trans-$C_2H_2Cl_2$. Hertzberg [152], on the basis of the data on the spectra of trans-$C_2H_2Cl_2$ he had at his disposal, could only determine the values of nine frequencies from the 12 fundamental frequencies of the molecule of trans-$C_2H_2Cl_2$. The first values of all fundamental frequencies of the molecule of trans-$C_2H_2Cl_2$ were determined by Bernstein and Ramsay [766]. It must be noted that in paper [766] the rotational structure of the ν_{10} band was studied in particular and its center was determined. Furthermore, essential corrections were allowed for by Pitzer and Hollenberg [3260] in the interpretation of the vibrational spectra of trans-$C_2H_2Cl_2$, given by Bernstein and Ramsay.

With the help of a spectrometer with diffraction grating Pitzer and Hollenberg [3260] investigated the infrared spectrum of gaseous trans-$C_2H_2Cl_2$ in the range of from 130 to 400 cm^{-1} and arrived at the result that the values attributed by Bernstein and Ramsay [766] to the frequencies ν_9 and ν_{11} (192 and 265 cm^{-1}) and verified by O'Loan [3132] were incorrect. This fact prompted Pitzer and Hoolenberg to reinterpret the vibrational spectra of trans-$C_2H_2Cl_2$, taking into account both their own spectroscopic data and the data of Bernstein and Ramsay, as well as the results of studies of the Raman spectrum of liquid trans-$C_2H_2Cl_2$, obtained by Kreusch, Ziomek and Cleveland [2483].

The values of the fundamental frequencies of the molecule of trans-$C_2H_2Cl_2$, given in Table 159, are based on an interpretation of the vibrational spectra of trans-$C_2H_2Cl_2$, given by Pitzer and Hollenberg [3260] and verified by calculations of Sverdlov, Klochkovskiy and Kukina [365]. The values given for the frequencies $\nu_1, \nu_3, \nu_4, \nu_6, \nu_8, \nu_{12}$ are based on measurements of the Raman spectrum of the liquid [2483], the values of the frequencies ν_2, ν_5, ν_7 and ν_{10} on measurements of the infrared spectrum of the liquid [766] and the values of the frequencies ν_9 and ν_{11} on measurements of the infrared spectrum of the gas [3260] and data of Wood and Stevenson [4320] on the equilibrium between cis- and trans-$C_2H_2Cl_2$.

The infrared spectrum of vapor of asymmetric dichlorethylene (CH_2CCl_2) was investigated by Emschwiller and Lecomte [1483] (525--1450 cm^{-1}), Thompson and Torkington [3975] (500-2000 cm^{-1}) and Evans [1509] (320-700 cm^{-1}). The Raman spectrum of the liquid asymmetric dichlorethylene was studied by Cabann [1039], Thompson and Torkington [3975], Shorygin (according to [415]), Joyner and Glockler [2310] and Evans [1509].

The first vibrational spectra of CH_2CCl_2 were interpreted by Thompson and Torkington [3975] and then reinterpreted by Joyner and Glockler [2310] on the basis of the more complete data on the Raman spectrum they had obtained. The interpretations of the vibrational spectra of CH_2CCl_2 differ mainly in the attribution of the frequencies ν_{11} and ν_{12}.

Joyner and Glockler [2310] did not discover the faint line at 540 cm^{-1} in the Raman spectrum of CH_2CCl_2, observed by Thompson and Torkington [3975] and attributed by them to the frequency ν_{11}. Also other investigators [1039, 415, 1509] did not observe this line in the Raman spectrum of CH_2CCl_2 so that one may consider it as pertaining to an impurity in the dichlorethylene sample investigated by Thompson and Torkington [3975]. The fundamental frequency ν_{11} of the CH_2CCl_2 molecule was identified by Joyner and Glockler with the 458 cm^{-1} line in the Raman spectrum. Thompson and Torkington observed the corresponding line in the Raman spectrum at 450 cm^{-1} and attributed it to the frequency ν_{12} of the torsional oscillation. This inconsistency in the attributions of the fundamental frequencies of CH_2CCl_2 was eliminated by Evans [1509] who again investigated the Raman spectrum of liquid asymmetric dichlorethylene with a spectrometer with photoelectric recording and a dispersion of 7 A/mm at 4358 A and obtained the first infrared spectrum of vapor in the range 320-700 cm^{-1}. In this spectral range

Evans registered three bands of CH_2CCl_2 with the centers at 375, 458 and 601 cm^{-1}, corresponding to the frequencies ν_8, ν_{11} and ν_7. The frequency ν_{12} does not appear in the infrared spectrum and is only observed in the Raman spectrum.

Table 159 gives the values of the fundamental frequencies of the CH_2CCl_2 molecule, determined by Joyner and Glockler [2310] on the basis of an interpretation of the vibrational spectra suggested by them, which was verified by additional investigations of Evans [1509] and the agreement between the experimental value of $S^\circ_{298,15}(CH_2CCl_2$, gas) and the value calculated from the fundamental frequencies of the CH_2CCl_2 molecule* found in paper [2310], which was established by Hildenbrandt et al [2027].

Electron diffraction studies of the molecular structure of all three isomers of dichlorethane were carried out by Brockway, Beach and Pauling [959] who, assuming the C = C bond length as equal to 1.38 A obtained the following values for the length of the C – Cl bond and the angle between C – C – Cl in the molecules of cis-$C_2H_2Cl_2$, trans-$C_2H_2Cl_2$ and CH_2CCl_2, respectively: $1,67 \pm 0,03$ Å, $123,5 \pm 1°$, $1,69 \pm 0,02$ Å, $122,5 \pm 1°$ и $1,69 \pm 0,02$ Å, $122 \pm 1°$. Further investigations of the molecular structure of ethylene and its halogen derivatives, however, showed that the value adopted in paper [959] for the C = C bond length was much too high so that incorrect values were obtained for the C – Cl bond lengths.

Sekino and Nishikawa [3679] investigated the microwave spectrum of $CH_2CCl_2^{35}$ and $CH_2CCl^{35}Cl^{37}$ determined the values of the rotational constants of the corresponding molecules in the vibrational ground state with high accuracy. These results and the supposition that the C – H bond length and the angle in C – C – H in the molecule of CH_2CCl_2 are the same as in the molecule of C_2H_4 ($r_{C-H} = 1,07$ Å, $\angle C-C-H = 120°$, according to [1646]), enabled Sekino and Nikishawa to determine the values of the simple structural parameters of CH_2CCl_2: $r_{C=C} = 1{,}32 \pm 0{,}02$, $r_{C-Cl} = 1{,}727 \pm 0{,}01$ Å, $\angle C-C-Cl = 123°10' \pm 30'$.

The values of the structural parameters of the CH_2CCl_2 molecule, obtained from the microwave spectra in paper [3679] agree with the values of the corresponding quantities obtained in later electron-diffraction studies [2631, 2093]. Livingston, Rao, Kaplan and Rocks [2631] made electron-diffraction studies of the molecular structure of CH_2CCl_2, using a visual method, with and without a sector, and a microphotometrical method, applying a sector. The results of investigations carried out with these three methods are in good agreement with one another. The most accurate values of the structural parameters of CH_2CCl_2 were obtained in paper [2631] with the help of the sector-microphotometrical method: $r_{C=C} = 1{,}324 \pm 0{,}020$, $r_{C-Cl} = 1{,}710 \pm 0{,}010$ Å, $\angle Cl-C-Cl = 114{,}5 \pm 1°$. Electron-diffraction studies of the molecular structure of cis-$C_2H_2Cl_2$, carried out by Hoffman [2093], yielded the following results: $r_{C=C} = 1{,}336 \pm 0{,}016$, $r_{C-Cl} = 1{,}722 \pm 0{,}010$ Å, $\angle C-C-Cl = 123° \pm 1°{,}5$.

The values of the products of the principal moments of inertia of cis-, trans and asymmetric $C_2H_2Cl_2$, given in Table 159, were calculated from the structural parameters adopted in the paper of Sekino and Nishikawa [3679].*

The ultraviolet spectrum of dichlorethylene was studied by Lacher et al [2509].

$C_2F_2Cl_2$. The infrared spectrum of gaseous asymmetric difluordichlorethylene was investigated by Torkington and Thompson [4005] (500-3200 cm^{-1}), Nielsen, Claassen and Smith [3089] (442-5000 cm^{-1}) and Mann and Plyler [2760] (188-400 cm^{-1}) with the help of prism spectrometers of low dispersion. The Raman spectrum of liquid CF_2CCl_2 was in-

investigated by Hatcher and Yost [1973] and Nielsen, Claassen and Smith [3089]. The most accurate measurements of the band peaks in the vibrational spectra of difluor-dichlorethylene were carried out by Nielsen, Claassen and Smith.

The first attempts of interpreting the vibrational spectra of CF_2CCl_2 were undertaken by Torkington and Thompson [4005]. These attempts, however, were very incomplete since the authors of paper [4005] had insufficiently complete data on the vibrational spectra of CF_2CCl_2 at their disposal. A more satisfactory interpretation of the vibrational spectra of CF_2CCl_2 was suggested by Nielsen, Claassen and Smith [3089], on the basis of their own careful investigation of the infrared spectrum and the Raman spectrum of difluor-dichlorethane.* But owing to the fact that in paper [3089] the infrared spectrum of CF_2CCl_2 had only been investigated up to 442 cm^{-1}, serious errors in the attributions of the frequencies ν_5, ν_7, ν_8 and ν_{11} were admitted in the interpretation of the vibrational spectra of CF_2CCl_2, suggested by Nielsen, Claassen and Smith. They were first discovered by Mann, Fano, Meal and Shimanouchi (cf. [2760, 2758]), who calculated the fundamental frequencies of the molecule of CF_2CCl_2 on the basis of the dynamic constants of the molecules of C_2F_4 and C_2Cl_4.

To verify the changes in the interpretation of the fundamental frequencies of CF_2CCl_2, suggested by Mann, Fano, Meal and Shimanouchi, the infrared spectrum of CF_2CCl_2 was investigated in paper [2760] in the range of from 188 to 400 cm^{-1}. In this range of the spectrum Mann and Plyler [2760] discovered two bands of CF_2CCl_2 with centers at 258 and 323 cm^{-1}. The band at 258 cm^{-1} had previously been observed only in the Raman spectrum [3089, 1973], the weak band at 323 cm^{-1}, however, had not been observed previously. On the basis of an analysis of the profile of the band at 258 cm^{-1}, Mann and Plyler [2760] showed that the frequency ν_8 belongs to this band and not the frequency ν_{11} erroneously suggested by Nielsen, Claassen and Smith [3089]: this latter frequency ν_{11} corresponds to the band at [illegible] cm^{-1}. In paper [3089] the frequency ν_8 was incorrectly identified with the center of the band at 434 cm^{-1} observed in the Raman spectrum. In the papers [2760, 2758] it was shown that this band must agree with the frequency ν_7 which in paper [3089] was incorrectly identified with the center of the band at [illegible] cm^{-1}, observed in the infrared spectrum and in the Raman spectrum. According to [2760, 2758] the latter corresponds to the frequency ν_5. In paper [3089] the frequency ν_5 had falsely been identified with the center of the band at 640 cm^{-1} which actually corresponds to the harmonic frequency $2\nu_{11}$.

The values of the fundamental frequencies of the molecule of CF_2CCl_2, recommended in the papers [2760, 2758], are given in Table 159.

A thorough investigation of the vibrational spectrum of trans-$C_2F_2Cl_2$ was carried out by Mann and Plyler [2761]. In paper [2761] the infrared spectrum of gaseous trans-$C_2F_2Cl_2$ was obtained in the range 150-5000 cm^{-1}, by means of spectrometer with a set of prisms and a diffraction grating (low dispersion), as well as the Raman spectrum of liquid trans-$C_2F_2Cl_2$. On the basis of the results of measurements of the degree of polarization of the lines in the Raman spectrum, of an investigation of the intensity distribution in the infrared spectrum, and also on the basis of results of calculating the values of the fundamental frequencies of the molecule of trans-$C_2F_2Cl_2$ from the dynamic constants of C_2F_4 and C_2Cl_4 [2758], Mann and Plyler succeeded in completely interpreting the vibrational spectra of trans-$C_2F_2Cl_2$. The values of the fundamental frequencies of the molecule of trans-$C_2F_2Cl_2$, recommended in paper [2761], are given in Table 160.

The values of the frequencies $\nu_2, \nu_3, \nu_5, \nu_7, \nu_8$ and ν_{10}, given in Table 159, are based on measurements of the Raman spectrum of liquid trans-$C_2F_2Cl_2$, the values of $\nu_1, \nu_4, \nu_6, \nu_9, \nu_{11}$ – are based on measurements of the infrared spectrum of the gas, and the frequency ν_{12} of torsional oscillations are determined by means of calculations(cf. [2758]). The value of the frequency ν_1 given in Table 159 is the nonperturbed value recommended by Mann and Plyler. In paper [2761], on the basis of an analysis of the infrared spectrum of trans-$C_2F_2Cl_2$, it was shown that between the vibrations with the frequencies $\nu_4 + \nu_8$ and ν_1 Fermi resonance must occur.* The observed value of the frequency $\nu_1 = 1214$ cm^{-1}.

When investigating the infrared spectrum of gaseous trans-$C_2F_2Cl_2$, Mann and Plyler [2761] discovered a series of weak lines of cis-$C_2F_2Cl_2$ which enabled them to approximately determine the values of several fundamental frequencies of the molecule of cis-$C_2F_2Cl_2$. Mann, Fano, Meal and Shimanouchi [2758] used the dynamic constants of C_2F_4 and C_2Cl_4 to calculate the values of all fundamental frequencies of the molecule of cis-$C_2F_2Cl_2$, in agreement with experimental data [2761]. The values of the fundamental frequencies of the molecule of cis-$C_2F_2Cl_2$, calculated in paper [2758], are given in Table 159.

The values of the structural parameters of the isomeric molecules of difluor-dichlorethylene have not been determined experimentally. In paper [3089] the following values are adopted for the structural parameters of CF_2CCl_2: $r_{C=C} = 1{,}27$, $r_{C-F} = 1{,}32$, $r_{C-Cl} = 1{,}7$ Å, $\angle F-C-F = \angle Cl-C-Cl = 110°$. Mann and Plyler [2761], on the basis of data on the structure of the molecules of C_2F_4, C_2Cl_4, CH_2CF_2 which were at their disposal, estimated the following values of the structural parameters of the molecule of trans-$C_2F_2Cl_2$: $r_{C=C} = 1{,}31$, $r_{C-F} = 1{,}31$, $r_{C-Cl} = 1{,}72$ Å, $\angle C-C-F = \angle C-C-Cl = 123°$. The errors of the values of structural parameters of the molecule of trans-$C_2F_2Cl_2$, suggested in paper [2761], may be estimated as amounting to ±0.02 A for the interatomic distances and ±3° for the angles between the bonds. Within the limits of the above errors the values of the corresponding structural parameters may be viewed as identical for all three isomers of the $C_2F_2Cl_2$ molecules.

The values adopted in the present Handbook for the structural parameters of the isomeric molecules of $C_2F_2Cl_2$ have been suggested by Mann and Plyler [2761]. Table 159 gives the values of the products of the principal moments of inertia of the molecules of CF_2CCl_2, trans-$C_2F_2Cl_2$ and cis-$C_2F_2Cl_2$, in accordance with the values of structural parameters adopted.

The ultraviolet spectra of trans-$C_2F_2Cl_2$ and CF_2CCl_2 were investigated by Lacher, Hummel, Bohmfalk and Park [2509].

§73. MOLECULES OF THE TYPES OF C_2X_3Y AND C_2X_2YZ

The molecules of halogen-substituted ethylen of the types C_2X_3Y and C_2X_2YZ belong to the point group of symmetry $C_s(\sigma = 1)$ and have 12 fundamental frequencies, appearing in the infrared spectrum and in the Raman spectrum. The nine fundamental frequencies of the molecules of C_2X_3Y and **C_2X_2YZ ($\nu_1, \nu_2, \ldots, \nu_9$)** correspond to plane vibrations and three frequencies (ν_{10}, ν_{11}, ν_{12}) to nonplanar vibrations. In the Raman spectrum the lines corresponding to ν_1, ν_2, ..., ν_9 are polarized while the lines corresponding to the frequencies ν_{10}, ν_{11} and ν_{12} are depolarized.

The halogen derivatives of ethylen of the type C_2X_2YZ, just as the halogen derivatives of ethylen of the type $C_2X_2Y_2$, may exist in three isomeric forms: cis-, trans- and asymmetric forms (cf. Fig.20).

Table 160 contains the values of the molecular constants of fluorine and chlorine derivatives of ethylene of the types C_2X_3Y and C_2X_2YZ, adopted in the present Handbook.

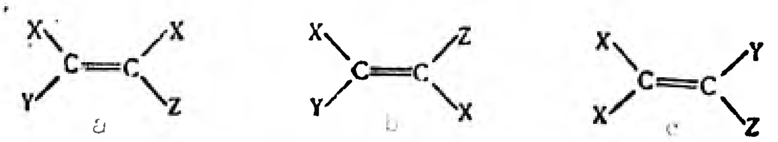

Fig. 20. Isomeric forms of the molecules of halogen derivatives of ethylene of the type C_2X_2YZ. a) cis-form, b) trans-form, c) asymmetric form.

TABLE 160

Accepted Values of the Molecular Constants of Fluorine and Chlorine Derivatives of Ethylene of the types C_2X_3Y and C_2X_2YZ ($\sigma = 1$)

1 Молекула	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}	$I_AI_BI_C$
	2 см$^{-1}$												3 10^{-117} г^3·см^6
CH_2CHF	1654	3080	3115	3150	1306	1380	928	1156	483	931	863	712	95,177
CH_2CHCl	1610	3030	3080	3130	724	1370	395	1280	1030	942,5	896,8	620	323,700
CH_2CFCl	1656	3016	3069	1383	1186	947	699	432	371	836	607	515	3182,5
CF_2CHF	1788	3150	1362	1264	929	1171	485	623	232	750	555	305	5160
CF_2CHCl	1745	3130	1333	1199	845	970	433	579	201	751	572	243	12871
CF_2CFCl	1792	1336	1215	1058	689	517	338	463	188	538	369	166	39100
CCl_2CHF	—	—	—	—	—	—	—	—	—	—	—	—	40900
CCl_2CHCl	1589	3080	1242	932	840	628	274	381	172	780	450	211	92800
CCl_2CFCl	1645	1181	988	857	520	407	250	358	174	537	313	130	180400

1) Molecule; 2) cm^{-1}; 3) g^3·cm^6.

C_2H_3F. The infrared spectrum of gaseous fluorethylene was investigated by Torkington and Thompson [4005] (500-3200 cm^{-1}), Cole and Thompson [1147] (665-1250 cm^{-1}) and Bak and Christensen [625] (400--3500 cm^{-1}). The Raman spectrum of fluorethylene has not been studied. The infrared spectra of the deutero-derivatives of fluorethylene were investigated by Bak and Christensen [625].

The vibrational bands in the infrared spectrum of fluorethylene were first interpreted by Torkington and Thompson [4005], later on the attributions of the frequencies ν_{10} and ν_{11} of nonplanar deformation vibrations were altered according to a suggestion in paper [4005] and the values of the other frequencies were improved (cf. Table 161).

Pitzer and Freeman [3257], on the basis of a consideration of the correspondence between the values of the dynamic constants of the molecules of the halogen derivatives of ethylene of the type C_2H_3X, cast doubt upon the correctness of the interpretations of the frequencies ν_{10} and ν_{11} in paper [4005], and suggested to adopt the values of $\nu_{10} = 924$ and $\nu_{11} = 860$ cm^{-1}. Cole and Thompson [1147], however, used an analysis of the rotational structure of the band at 924 cm^{-1} to show that this band corresponds to a plane vibration, thus verifying its attribution to the frequency ν_7. Moreover, in paper [1147] the center of the band of ν_7 was defined more precisely and it was shown that the bands at 730 and 860 cm^{-1} in the infrared spectrum pertain to frequencies of nonplanar vibrations. In contrast to paper [4005], however, their attribution to the frequencies ν_{10} and ν_{11} was changed (cf. Table 161).

TABLE 161

Interpretations of the Fundamental Frequencies of the C_2H_3F Molecule by Various Investigators (frequency values given in cm^{-1})

1 Частота	2 Тип колебания	3 Торкингтон и Томпсон [4005], 1945 г.	4 Питцер и Фриман [3257], 1946 г.	5 Кол и Томпсон [1147], 1949 г.	6 Бак и Кристенсен [625], 1958 г.	7 Шерер и Потс [3622], 1959 г.	8 Настоящий Справочник
ν_1	A'	1650	—	—	1654	—	1654
ν_2	A'	3080	—	—	3080	—	3080
ν_3	A'	3110	—	—	3115	—	3115
ν_4	A'	3135	—	—	3150	—	3150
ν_5	A'	1306	—	—	1306	—	1306
ν_6	A'	1393	—	—	1380	—	1380
ν_7	A'	924	—	928	929	—	928
ν_8	A'	1153	—	1156	1156	—	1156
ν_9	A'	500	—	—	483	—	483
ν_{10}	A''	860	924	729,6	940	931	931
ν_{11}	A''	732	860	862,7	863	864	863
ν_{12}	A''	715	715	711,7	711	714	712

1) Frequency;
2) type of vibration
3) Torkington and Thompson [4005], 1945

4) Pitzer and Freeman [3257], 1946
5) Cole and Thompson [1147], 1949
6) Bak and Christensen [625], 1958
7) Scherer and Potts [3622], 1959
8) Present Handbook.

Later on Bak and Christensen [625] investigated the infrared spectra of fluorethylene and its deuterium derivatives in a somewhat higher resolution than Torkington and Thompson [4005] which enable them to improve the values of a series of frequencies. The interpretation of the fundamental frequencies of C_2H_3F suggested by Bak and Christensen [625] differ essentially from the interpretation given by Torkington and Thompson [4005], corrected by Cole and Thompson [1147], only as regards the frequency ν_{10}. The value suggested by Bak and Christensen for the frequency ν_{10} is equal to 940 cm^{-1}, though they did not succeed in observing such a band in the infrared spectrum of C_2H_3F. Bak and Christensen substantiated the choice of ν_{10} = 940 cm^{-1} on the one hand by analogy with C_2H_3Cl and C_2H_3Br, for which the corresponding frequencies amount to about 940 cm^{-1}, and, on the other hand, by applying the sum and product rules to the vibrational frequencies of C_2H_3F and its deuterium derivatives. The fact that a band with the center at 940 cm^{-1} was not observed in the infrared spectrum of C_2H_3F was explained by Bak and Christensen by assuming it masked by the R-branch of the ν_7 band. The band centered at 730 cm^{-1} was not attributed in paper [625] to a definite vibrational frequency of the molecule of C_2H_3F, but it is indicated indirectly that it might pertain to the frequency of a vibrational transition between vibrational states of C_2H_3F.

Scherer and Potts [3622], based on values of the fundamental frequencies of the molecules of C_2H_3F and its deuterium derivatives obtained in paper [625], calculated the frequencies of nonplanar vibrations of all these molecules. The differences between the experimental and the calculated values here do not exceed ±1 cm^{-1}. A value of [illegible] cm^{-1} was obtained by Scherer and Potts for the frequency ν_{10} of the C_2H_3F molecule, its error may amount to ±2 cm^{-1}. It should be noted that the difficulties arising in the interpretation of the vibrational frequencies of C_2H_3F are chiefly caused by the absence of data on the Raman spectrum of this compound.

The values of the fundamental frequencies of fluorethylene adopted in the present Handbook, are contained in Tables 160 and 161. The value chosen for the frequency ν_{10} was calculated by Scherer and Potts [3622]. The values given for the other fundamental frequencies of C_2H_3F were chosen on the basis of results of the papers [625, 1147] (cf. Table 161). The errors of the values given for ν_2, ν_3 and ν_4 were estimated to amount to ±10 cm^{-1}, as the corresponding bands in the infrared spectrum overlap so that it was difficult to determine their centers accurately. The errors of the values of the remaining fundamental frequencies of the C_2H_3F molecule, given in Table 160, may amount to ±2, up to ±5 cm^{-1}.

The structural parameters of the C_2H_3F molecule were determined by Bak and co-workers [626] and also by Morgan and Goldstein [2949], on the basis of results of an analysis of the microwave spectra of fluorethylene and its isotopic modifications. An electron-diffraction study of the molecular structure of C_2H_3F has not been made. When investigating the rotational structure of the ν_{10} band in the infrared spectrum of C_2H_3F, Cole and Thompson [1147] determined only the values of the differences between the rotational constants, A-B, for the ground state and the excited vibrational states.

Bak and co-workers [626] investigated the microwave spectra of 10 isotope modifications of the CH_2CHF molecule, corresponding to the rotational transitions $0_0 \rightarrow 1_{-1}$, $1_0 \rightarrow 2_{-1}$, $1_{-1} \rightarrow 2_{-2}$, $1_1 \rightarrow 2_0$, $4_{-3} \rightarrow 4_{-2}$, $5_{-4} \rightarrow 5_{-3}$ and $6_6 \rightarrow 6_{-4}$ in the vibrational ground state. For six isotope modifications of the molecule of CH_2CHF the values of the rotational constants A_0, B_0, C_0, were determined in paper [626]. The corresponding values of the moments of inertia were used to find the structural parameters of the CH_2CHF molecule. The structural parameters of CH_2CHF were calculated under the assumption that the molecules of the isotope modifications of CH_2CHF were plane and that the bond lengths of C-H in the CH_2 group were identical. The first of the above assumptions was justified as the inertial defect $(I_C - I_B - I_A)$ is insignificant compared to the values of the moments of inertia and has different signs for the different isotope modifications of the CH_2CHF molecule. The second assumption is justified since in the calculations with fixed values of the C-H bond lengths in the CHF group the differences in the values of the C-H bond lengths in the CH_2 group did not exceed 0.01 A. The following values of the structural parameters of CH_2CHF were obtained as a result of calculations carried out in [626]: $r_{C=C} = 1{,}333$, $r_{C-F} = 1{,}348$, r_{C-H} (group CHF) $= 1{,}073$, r_{C-H} (group CH_2) $= 1{,}080$ Å, $\angle F-C-H = 115°{,}4$, $\angle C-C-H$ (group CHF) $= 123°{,}7$, $\angle C-C-H$ (CH_2 group) = 121°1 and 118°5. The errors of the structural parameters of CH_2CHF are not given in paper [626], however, to judge from the different variants of calculations of these quantities, carried out in paper [626], they may be estimated for the interatomic distances as amounting to about ±0.005 A.

Morgan and Goldstein [2949] investigated the microwave spectra of the molecules of $C^{12}H_2C^{12}HF$, $C^{13}H_2C^{12}HF$ and $C^{13}H_2C^{13}HF$, corresponding to the pure rotational transitions $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ in the vibrational ground state.* These data were used in paper [2949] to determine the values of the rotational constants B_0 and C_0 of the above molecules with errors not exceeding 0.0005%. Assuming that the C_2H_3F molecule is plane and that $\angle$ H—C—H = $\angle$C—C—H=120°, the authors of paper [2949] calculated the moments of inertia for 1134 variants of possible values of the other structural parameters. A comparison of the calculated values of the moments of inertia of the molecules of $C^{12}H_2C^{12}HF$, $C^{13}H_2C^{12}HF$ and $C^{12}H_2C^{13}HF$ with experimental data and an application of calculations according to the method of least squares, using the derivatives of the moments of inertia with respect to the structural parameters enabled the authors of paper [2949] to determine the following values of these quantities: $r_{C=C} = 1{,}337 \pm 0{,}002$, $r_{C-F} = 1{,}344 \pm 0{,}002$, r_{C-H} (group CHF) = $1{,}080 \pm 0{,}005$, r_{C-H} (group CH_2) = $1{,}075 \pm 0{,}005$ Å, $\angle$ C—C—F = = $121{,}0 \pm 0{,}2$; $\angle$ C—C—H = 120° (accepted), which agree with the values obtained by Bak et al [626].*

The value of the product of the principal moments of inertia of the C_2H_3F molecule given in Table 160 corresponds to the values of the rotational constants of the vibrational ground state** obtained in papers [626, 2949]:** $A_0 = 2{,}13471$, $B_0 = 0{,}35480$, $C_0 = 0{,}30415$ см$^{-1}$.

The ultraviolet spectrum of C_2H_3F has not been investigated.

C_2H_3Cl. The infrared spectrum of gaseous chlorethylene was investigated by Wu [4336] (400-5000 cm^{-1}), Thompson and Torkington [3975] (500-3330 cm^{-1}),Cole and Thompson [1147] (830-1110 cm^{-1}) and Gullikson and Nielsen [1885] (295-5000 cm^{-1}). Cole and Thompson [1147] obtained the infrared spectrum of C_2H_3Cl with resolved rotational structure of the bands with a spectrometer with diffraction grating. In the other papers the infrared spectrum of C_2H_3Cl was obtained in prism spectrometers with nonresolved rotational structure of the bands.

The Raman spectrum of chlorethylene was investigated by Gullikson and Nielsen [1885]. The Raman spectrum of liquid chlorethylene was studied by Evans and Bernstein [1510]. Earlier investigations of the

Raman spectrum of liquid chlorethylene were considered in Kohlrausch's monograph [236]. The vibrational spectra of the deuterium derivatives of chlorethylene were only investigated for CH_2CDCl [1510].

Thompson and Torkington [3975] were the first who determined the values of all fundamental frequencies of the chlorethylene molecule on the basis of an interpretation of the infrared spectrum of dichlorethylene, suggested by these authors. Further investigations of the vibrational spectra of C_2H_3Cl [1147, 1510, 1885] verified the correctness of the interpretation given by Thompson and Torkington.

The values of the fundamental frequencies of the chooorethylene molecule adopted in the present book are given in Table 160. For the frequencies (ν_1, ν_2, ..., ν_9) of the plane vibrations, we chose the values obtained by Thompson and Torkington [3975] for the Q-branch of the corresponding band in the infrared spectrum. For the frequencies of nonplanar deformation vibrations (ν_{10}, ν_{11}) we chose the values of the centers of the corresponding bands, found by Cole and Thompson [1147]. The frequency ν_{12} of torsional oscillations was given the mean value of the values of ν_{12} obtained in papers [4336, 3975], which agrees with the value found by Gullikson and Nielsen [1885]; it is contained in Table 160. The differences between the values of the simple fundamental frequencies of the C_2H_3Cl molecule, used in paper [1885], and the values of the corresponding frequencies, given in Table 160, do not exceed 4 cm^{-1}, i.e., according to the spectroscopic data available, the deviation is within the limits of probable error connected with the determination of the fundamental frequencies of this molecule.

The structural parameters of the C_2H_3Cl molecule were determined as the result of electron diffraction studies [959, 60] and investigations of the microwave spectra of chlorethylene and its isotope modifications [3679, 2428].

In early electron-diffraction studies of the molecular structure of C_2H_3Cl [959] the C = C bond length was falsely assumed as equal to 1.38 A, so that the following values were obtained: $r_{C-Cl} = 1{,}69 \pm 0{,}02$ Å, $\angle C-C-Cl = 122 \pm 2°$. Later on Goldstein and Bragg [1795] investigated the microwave spectra of $C_2H_3Cl^{35}$ and $C_2H_3Cl^{37}$ and determined with high accuracy the values of the rotational constants of the vibrational ground state of these molecules. These data were used by Sekino and Nikishawa [3679] to calculate $r_{C=C} = 1{,}34 \pm 0{,}02$, $r_{C-Cl} = 1{,}724 \pm 0{,}015$ Å, $\angle C-C-Cl = 120°3' \pm 30'$ under the supposition that in the C_2H_3Cl molecule the C-H bond length and the angle in C – C – H are just the same as in the C_2H_4 molecule: $r_{C-H} = 1{,}07$ Å, $\angle C-C-H = 120°$ (according to data of [1646]). Another electron-diffraction study of the molecular structure of C_2H_3Cl was made by Akishin, Bilkov and Vesnin [60]. Under the assumption that $r_{C-H} = 1.07$ A and $\angle C-C-H = 120°$, the following values were obtained in [60] for the C_2H_3Cl molecule: $r_{C=C} = 1{,}32 \pm 0{,}02$, $r_{C-Cl} = 1{,}72 \pm 0{,}01$ Å, $\angle C-C-Cl = 125 \pm 2°$.

The most careful investigation of the molecular structure of C_2H_3Cl was made by Kivelson, Wilson and Lide [2428], on the basis of an analysis of the microwave spectra of nine isotope modifications of the chlorethylene molecule. In paper [2428] the values of the rotational constants B_0 and C_0 of these molecules were determined with high accuracy and the corresponding values of the moments of inertia, I_B and I_C were calculated. From the changes of the moments of inertia I_B and I_C connected with the substitution of an isotope (according to the method of Costain-Kraitchman [1186, 2471]), the following values of the structural parameters of the C_2H_3Cl molecule* were calculated in paper [2428] r_{C-H}(CH_2 group) = 1.078 and 1.090, r_{C-H}(CHCl group) = 1.079, $r_{C=C} = 1{,}332$, $r_{C-Cl} = 1{,}726$ Å, $\angle C-C-H$ (CH_2 group) = 119°32′ and 121°1′, $\angle H-C-H$ (CH_2 group) = 119°27′, $\angle C-C-H$ (CHCl group) = 123°49′, $\angle H-C-Cl = 113°35′$, $\angle C-C-Cl =$

~ 122°18′ . The error of the value of the C = C bond length obtained in paper [2428] was estimated by Kivelson, Wilson and Lide as amounting to ±0.005 A, the error of the other bond lengths were estimated as not exceeding ±0.01 A.

The following values of the principal moments of inertia correspond to the values of the rotational constants of the vibrational ground state of the $C_2H_3Cl^{35}$ molecule and the $C_2H_3Cl^{37}$ molecule, determined in papers [1795, 2428] (in 10^{-40} g·cm^2): for $C_2H_3Cl^{35}$ $I_A = 14{,}95$, $I_B = 139{,}14$, $I_C = 154{,}10$; for $C_2H_3Cl^{37}$ $I_A = 14{,}92$, $I_B = 142{,}13$, $I_C = 157{,}09$.
The values of the products of the principal moments of inertia of C_2H_3Cl, given in Table 160, are based on these data.

The ultraviolet spectrum of C_2H_3Cl has not been investigated.

$\underline{C_2H_2FCl}$. The spectra and the molecular structure were only studied for the asymmetric form of fluorchlorethylene CH_2CFCl.*

The infrared spectrum of gaseous CH_2CFCl was investigated by Torkington and Thompson [4005] (500-3200 cm^{-1}), Mann, Acquista and Plyler [2754] (192-6350 cm^{-1}) and Nielsen and Albright [3088]** with prism spectrometers of low and medium dispersions. The most thorough investigation of the infrared spectrum of CH_2CFCl was carried out by Mann, Acquista and Plyler [2754]. The Raman spectrum of gaseous CH_2CFCl was studied by Nielsen and Albright [3088] by means of a three-prism spectrometer with a linear dispersion of 15 A/mm, at 4358 A. The vibrational spectra of the deuterium derivatives of fluorchlorethylene were not investigated.

An exhaustive interpretation of the vibrational spectra CH_2CFCl stems from Mann, Acquista and Plyler [2754] and Nielsen and Albright [3088]. In paper [2754] the fundamental frequencies of the CH_2CFCl molecule are identified and the observed infrared spectrum of this compound is interpreted on the basis of an investigation of the intensity distribution in the infrared spectrum of CH_2CFCl, an analysis of the band contours and a comparison of the values of the fundamental frequencies of the molecules of CH_2CF_2, CH_2CFCl, CH_2CCl_2, CH_2CBr_2. Nielsen's and Albright's investigation [3088] of the Raman spectrum of gaseous CH_2CFCl and the infrared spectrum verified perfectly the correctness of the attributions of the fundamental frequencies of this molecule, carried out by Mann, Acquista and Plyler [2754].

The values of the fundamental frequencies of the CH_2CFCl molecule recommended in paper [2754] have been adopted in the present Handbook and are given in Table 160.

The microwave spectra of CH_2CFCl^{35} and CH_2CFCl^{37} were investigated by Bragg, Madison and Sharbraugh [892] who used the purely rotational transitions to the vibrational ground states of these molecules to determine with high accuracy the values of the rotational constants A_0, C_0 and the asymmetry parameter $\varkappa = \frac{2B_0 - A_0 - C_0}{A_0 - C_0}$. The values of the principal moments of inertia corresponding to it are in the case of CH_2CFCl^{35} equal to (in 10^{-40} $g \cdot cm^2$): $I_A = 78{,}554$, $I_B = 164{,}457$, $I_C = 243{,}328$ and in the case of CH_2CFCl^{37}: $I_A = 78{,}556$, $I_B = 169{,}342$, $I_C = 248{,}215$. In Table 160 we find the value of the product of the principal moments of inertia of CH_2CFCl, based on these data.

Mann, Acquista and Plyler [2754], on the basis of experimental values of the structural parameters of the molecules of C_2F_4, CH_2CF_2 and C_2Cl_4 and the values of the rotational constants of the molecules of CH_2CFCl^{35} and CH_2CFCl^{37}, obtained by Bragg, Madison and Sharbraugh [892], determined the following values of the structural parameters of CH_2CFCl: $r_{C=C} = 1{,}31$, $r_{C-F} = 1{,}32$, $r_{C-Cl} = 1{,}734$, $r_{C-H} = 1{,}07$ Å, $\angle C{-}C{-}F = 124°4'$, $\angle C{-}C{-}Cl = 123°$, $\angle C{-}C{-}H = 121°$.

The ultraviolet spectrum of C_2H_2FCl has not been investigated.

C_2HF_3. The infrared spectra of gaseous C_2HF_3 and C_2DF_3 were investigated by Mann, Acquista and Plyler [2752] in the 200-5000 cm^{-1} range by means of a prism spectrometer with changeable optics. Other investigations of the vibrational spectra of these compounds have not been carried out.

In paper [2752] an assignment is given of the bounds in the infrared spectra of the C_2HF_3 and C_2DF_3 molecules, based on a comparison of the C_2HF_3 and C_2DF_3 spectra, a study of the shape of the band edges and a comparison of the supposed fundamental frequencies of these molecules with the earlier determined fundamental frequencies of C_2HF_2Cl, C_2HCl_3 and C_2DCl_3 molecules. The values of the fundamental frequencies of C_2HF_3, recommended in paper [2752], are adopted in the present Handbook and quoted in Table 160.

The structural parameters of C_2HF_3 have not been determined experimentally. On the basis of the results of investigations of the molecular structure of ethylene and its fluorine derivatives, the following ranges of the possible values of structural parameters of C_2HF_3 may be indicated: $r_{C=C} = 1{,}30-1{,}34$, $r_{C-F} = 1{,}30-1{,}35$, $r_{C-H} = 1{,}07-1{,}10$ Å, $\angle C-C-F = 120-128°$, $\angle C-C-H = 120-125°$. Hence, $r_{C=C} = 1{,}32 \pm 0{,}02$, $r_{C-F} = 1{,}32 \pm 0{,}03$, $r_{C-H} = 1{,}08 \pm 0{,}02$ Å, $\angle C-C-F = 124 \pm 4°$, $\angle C-C-H = 122 \pm 3°$ are adopted in the present Handbook, according to the values adopted in paper [2752] ($r_{C=C} = 1{,}31$, $r_{C-F} = 1{,}32$, $r_{C-H} = 1{,}07$ Å, $\angle C-C-F = 124°$, $\angle C-C-H = 122°$). The product of the principal moment of inertia of the C_2HF_3 molecule, quoted in Table 160, corresponds to these approximate values of the structural parameters, determined in this manner.

The ultraviolet spectrum of C_2HF_3 was not investigated.

C_2HF_2Cl. The spectra and the molecular structure of only the asymmetrical type of difluorochloroethylene, CF_2CHCl, have been investigated.

Nielsen, Liang and Smith [3092] investigated the infrared spectra of liquid and gaseous CF_2CHCl in the 262-5000 and 455-5000 cm^{-1} ranges, respectively, and the Raman spectrum of liquid CF_2CHCl. The infrared spectra were obtained by a prism spectrometer with changeable optics, and the Raman spectrum by a three-prism spectrograph with a linear dispersion of 15 A/mm at 4358 A. On the basis of an analysis of the Raman spectra of CF_2CHCl, carried out in [3092], and the comparison of the probable fundamental frequencies of this molecule with the corresponding frequencies of CF_2CH_2 and CF_2CCl_2, found earlier, Nielsen Liang and Smith interpreted the entire Raman spectra of asymmetrical difluorochloroethylene. The values of the fundamental frequencies of CF_2CHCl, determined by this interpretation, are quoted in Table 160. The values of the frequencies ν_1, ν_2, ..., ν_8 and ν_{10}, given in this Table, are determined according to the infrared gas spectrum, and the values of ν_9, ν_{11}, ν_{12} on the basis of the Raman spectrum of the liquid. The error in the values of the frequencies of CF_2CHCl, which are quoted in Table 160, may be estimated as equal to ± 3 cm^{-1}.

The purely rotational spectrum of CF_2CHCl^{35} and CF_2CHCl^{37} molecules was investigated by Jenkins and Sugden [2225] in the 0.63-0.84 cm^{-1} range. The analysis of the spectra enabled the authors to determine the following values of the rotational constants of the CF_2CHCl^{35} (in 10^{-6} cm^{-1}): $A_0 = 357\,260$, $B_0 = 76\,606$, $C_0 = 63\,050$ and for the CF_2CHCl^{37} molecule: $A_0 = 357\,273$, $B_0 = 74478$, $C_0 = 61\,596$ the error amounts to $\pm 1 \cdot 10^{-6}$ cm^{-1}.

The product of the principal moments of inertia of CF_2CHCl, quoted in Table 160, is based on the values of the rotational constants, determined by Jenkins and Sugden [2225], taking into account the proportion of the isotopes Cl^{35} and Cl^{37} in natural chlorine, adopted in the Handbook.

The data obtained in paper [2225] are insufficient for a total determination of the structure of the CF_2CHCl molecule. Nevertheless, Jenkins and Sugden carried out calculations in order to elucidate the peculiarities of the CF_2CHCl structure, taking into account the well-known data on the structure of the C_2H_4 molecule and its halogen derivatives. The use of the Kraitchman method [2471] enabled the authors of [2225] to determine only the distance of the chlorine atom to the center of gravity of the CF_2CHCl molecule, and the ratio of the parameters r_{C-Cl} and $\angle C - C - Cl$, corresponding to the found moments of inertia. It is pointed out in paper [2225] that the most probable value of r_{C-Cl} is 1.72 A; to this value corresponds $\angle C - C - Cl = 118°$. In paper [2225] the same values as those for the C_2H_4 molecule are adopted for r_{C-H} and $\angle C - C - H$: $r_{C-H} = 1.07$ A, and $\angle C - C - H = 120°$ (according to [1646]). Under this condition and using the moments of inertia of CF_2CHCl^{35} and CF_2CHCl^{37}, Jenkins and Sugden calculated the values of the parameters r_{C-F} and $\angle F - C - F$ which correspond to the adopted values $r_{C=C} = 1.32$ and 1.34 A.* The results of the investigations of the molecular structure of CH_2CCl_2 [2631, 2093], C_2H_3Cl [2428], C_2H_3F [626, 2949], C_2H_4 [1398, 664], CH_2CF_2 [3227] support the assumption that the length of the C = C bound in the CF_2CHCl molecule lies within 1.32 and 1.34 A, corresponding, according to Jenkins' and Sugden's calculations, to the values $r_{C-F} \cong 1.35$ Å and $\angle F-C-F \cong 106°$. Thus, the length of the C – F bond in the CF_2CHCl molecule is considerably greater than in the CH_2CF_2 and C_2F_4 molecules (see pages 1145 and 1138). Jenkins and Sugden [2225] explain this fact by a weakening of the C – F bonds and a strengthening of the C – Cl bond. It must be noted that the value $r_{C-F} \cong 1.35$ Å found in paper [2225], conforms with the length of the C – F bond in the C_2H_3F molecule, in accordance to the data of papers [626, 2949].

The ultraviolet spectrum of C_2HF_2Cl has not been investigated.

C_2HFCl_2. Experimental data on the vibrational frequencies and the structure of the C_2HFCl_2 molecule are lacking. Data on the calculation of the fundamental frequencies of the C_2HFCl_2 molecule on the basis of the molecular force constants of other halogen derivatives of ethylene, and presumable estimates of the structural parameters are also lacking in literature.

It is assumed in the present Handbook that, like the cases of fluorochloroethylene and difluorochloroethylene, the asymmetrical form of $CHFCCl_2$ is the most stable isomeric form of fluorodichloroethylene. On the basis of the data obtained by Jenkins and Sugden [2225] on the structural parameters of the CF_2CHCl molecule, and also on the values of the structural parameters of C_2H_3F and C_2HCl_3 molecules, adopted in the present Handbook, the following values of the structural parameters of the $CHFCCl_2$ molecule are assumed: $r_{C=C} = 1{,}32 \pm 0{,}02$, $r_{C-F} = 1{,}34 \pm 0{,}02$, $r_{C-Cl} = 1{,}72 \pm 0{,}01$, $r_{C-H} = 1{,}08 \pm 0{,}02$ Å, $\angle C-C-Cl = 122 \pm 2°$, $\angle C-C-F = 125 \pm 3°$, $\angle C-C-H = 120 \pm 2°$. The product of the principal moments of inertia of the $CHFCCl_2$ molecule, quoted in Table 160, is calculated on the basis of the adopted values of the structural parameters.

With respect to the fundamental frequencies of the $CHFCCl_2$ molecule, one may affirm that they must possess values intermediate between the values of the corresponding frequencies of CF_2CHCl and C_2HCl_3 (see Table 160). However, in the writing of the present Handbook, the fundamental frequencies of the $CHFCCl_2$ molecule were not calculated because it was found that the vibrational components of the thermodynamic functions of C_2HFCl_2 may be determined with sufficient accuracy on the immediate basis of the corresponding values of these quantities for ethylene halides (see page 1189).

C_2HCl_3. The infrared spectrum of gaseous trichloroethylene was investigated by Wu [4336] in the 400-5000 cm^{-1} range, and Bernstein [759] in the 400-4000 cm^{-1} range by means of prism spectrometers with low dispersion. The position of the individual, most intense bands in the infrared spectrum of gaseous trichloroethylene was determined in papers [3991, 4107]. The infrared spectrum of liquid trichloroethylene was investigated by Bernstein [759] in the 400-4000 cm^{-1} range.

The Raman spectrum of liquid trichloroethylene was studied by several investigators whose results are discussed in the monographs by Kohlrausch [236] and Hibben [2065]. The Raman spectra of solutions of C_2HCl_3 in CCl_4 have been investigated by Allen and Bernstein [498]. The Raman spectrum of gaseous trichloroethylene has not been investigated. The Raman spectra of C_2DCl_3 have been investigated in papers [759, 498, 2132].

A current interpretation of the Raman spectra of C_2HCl_3 is given by Bernstein in paper [759]. Subsequent investigations of the Raman spectra of C_2HCl_3 [498, 2132] confirmed Bernsteins' interpretation [759] and made possible a more accurate determination of the fundamental frequencies.

In the present Handbook, the values of the fundamental frequencies of the C_2HCl_3 molecule are adopted, which were determined by Allen and Bernstein [498] on the basis of their investigation of Raman spectra of C_2HCl_3 solutions in CCl_4. The adopted values of the fundamental oscillation frequencies of C_2HCl_3 are quoted in Table 160. The error of their determination is estimated as equal to ±2%. The difference of the fundamental frequencies of the C_2HCl_3 molecule in gaseous and liquid state does not exceed this amount.

The structural parameters of the C_2HCl_3 molecule were determined by Brockway, Beach and Pauling [959] and Lipscom (see [517]) on the basis of an electron diffraction study. However, the method used by these investigators for recording the electron diffraction patterns and for interpreting them, was insufficiently perfect for the determination of the accurate structural parameters of C_2HCl_3. Assuming $r_{C=C} = 1{,}38$ Å. Brockway, Beach and Pauling [959] obtained from their electron diffraction pattern: $r_{C-Cl} = 1{,}71 \pm 0{,}03$ Å, $\angle C-C-Cl = 123 \pm 2°$ Lipscom (see [517]) found $r_{C=C} = 1{,}36 \pm 0{,}04$, $r_{C-Cl} = 1{,}72 \pm 0{,}02$ Å, $\angle C-C-Cl$ (CCl_2 group) = 121.5 ± 1°, $\angle C - C - Cl$ (CHCl group) = 124 ± 2°.

The results of investigations of the molecular structure of ethylene and its halogen derivatives led to the ascertainment that the C = C bond in halogen derivatives of ethylene is shorter than in the C_2H_4 molecule. According to the most accurate investigations [510, 664, 1398], the length of the C = C bond in the C_2H_4 molecule is equal to 1.335 ± 0.005A. The minimum length of the C = C bond in halogen derivatives of ethylene takes place in the C_2F_4 molecule, where it is equal to 1.313 ±0.010 A, according to the data of paper [2327]. On the basis of investigations of microwave spectra of CH_2CCl_2 [3679] and CF_2CHCl [2225], the length of the C = C bond was determined as equal to 1.32 ± 0.02 A in the caae of CH_2CCl_2, and as laying within 1.32 and 1.34 A in the case of CF_2CHCl. The length of the C − Cl bond is equal to 1.72 ± 0.01 A in all chlorine derivatives of ethylene. The length of the C − H bond in the C_2HCl_3 and C_2HF_3 molecules may be considered as identical within the accuracy limits of its determination in C_2HF_3 (see page 1166). The angle between the C = C and C − Cl bonds in the CCl_2 group is equal to 122 ± 2°, according to the data obtained by electron diffraction studies of the C_2HCl_3 structure (see [517]) and also the data obtained for CH_2CCl_2 [3679 and C_2Cl_4 [517, 2328]. A value equal to 125 ± 3° is assumed for the analogous angle in the CHCl group, based on data obtained by Lipscom (see [517]) for C_2HCl_3, and Akishin, Volkov and Vesnin [60] for C_2H_3Cl. The angle between the C = C and C − H bonds may be assumed as equal to 120 ± 2°. Thus, the following structural parameters of the C_2HCl_3 molecule are adopted in the present Handbook: $r_{C=C} = 1{,}32 \pm 0{,}02$, $r_{C-Cl} = 1{,}72 \pm 0{,}01$, $r_{C-H} = 1{,}08 \pm 0{,}02$ Å, $\angle$ C—C—Cl (CCl_2 group) $= 122 \pm 2^\circ$, $\angle$ C—C—Cl (CHCl group) $= 125 \pm 3^\circ$, $\angle$ C—C—H $= 120 \pm 2^\circ$.

The adopted values of the structural parameters of C_2HCl_3 have been used for the calculation of the product of principal moments of inertia, the value of which is quoted in Table 160.

The ultraviolet C_2HCl_3 spectrum has been investigated by Lacher, Hummel, Bohmfalk and Park [2509].

C_2F_3Cl. The infrared vibrational spectrum of gaseous trifluorochloroethylene was investigated by Smith and co-workers [3772],* Mann, Acquista and Plyler [2751] (185-4000 cm^{-1}) and Plyler** (110-220 cm^{-1}) by means of prism spectrometers of low dispersion. The Raman spectrum of liquid trifluorochloroethylene was investigated by Smith and co-workers [3772], and Rolfe and Woodward [3474]. In paper [3772], the Raman spectrum of liquid trifluorochloroethylene at room temperature was obtained (under pressure). Measurements of polarization were not carried out in this case. Rolfe and Woodward [3474] obtained the Raman spectrum of liquid trifluorochloroethylene, cooled to -75°C, which enabled them to carry out measurements of polarization and to observe a series of new bands of C_2F_3Cl. The Raman spectrum of gaseous trifluorochloroethylene was not investigated.

An interpretation of the Raman spectra of C_2F_3Cl was suggested first in paper [3772]. However, after the calorimetric investigations [3130, 1635] made it possible to determine $S^\circ_{244.80}(C_2F_3Cl$, gas), a very considerable divergence between the experimental and calculated values of this quantity was found, ascribed to errors in the assignment of the fundamental frequencies of the C_2F_3Cl molecule suggested in paper [3772]. In order to eliminate this non-alignment, Mann, Acquista and Plyler [2751] investigated the infrared spectrum of C_2F_3Cl in a considerably larger range than in paper [3772] and interpreted anew the Raman spectra of this compound. Mann, Acquista and Plyler [2751] made essential changes in the assignment of the fundamental frequencies of the molecule, suggested earlier in paper [3772]. However, the new interpretation of the Raman spectra of C_2F_3Cl, suggested in paper [2751] could also not be considered as completely reliable. It not only used incomplete data on the Raman spectrum, obtained in [3772], but also the torsional frequency ν_{12} was not determined on the basis of spectral data but calculated by means of the value of $S^{\circ}_{244.8}(C_2F_3Cl$, gas), found by calorimetric measurements, and the values of the other frequencies and structural parameters of the C_2F_3Cl molecule, adopted in paper [2751]. The investigation of the Raman spectrum, carried out by Rolfe and Woodward [3474], made dubious the assignment of the ν_9 and ν_{12} frequencies in paper [2751], and corroborated, at the same time, the correct assignment of the other frequencies. The true values of the ν_9 and ν_{12} frequencies, equal to 188 and 169 cm^{-1}, respectively, have been determined by Plyler (see [2758]), who investigated the infrared vibrational spectrum of C_2F_3Cl in the 110-220 cm^{-1} range. The appropriately corrected assignment of the fundamental frequencies of C_2F_3Cl, suggested in paper [2751], was confirmed by the theoretical calculations of [2758].

In the present Handbook, the values of fundamental frequencies, recommended in paper [2758], are adopted and quoted in Table 160. The error of the adopted values of fundamental frequencies of C_2F_3Cl is estimated as equal to ± 2 cm^{-1}.

The structural parameters of the C_2F_3Cl molecule were first determined by Akishin, Vilkov and Vesnin [60] on the basis of their own electron diffraction studies. Using visual methods of processing of the electron diffraction patterns, the authors of paper [60] found

$r_{C-F} = 1{,}32 \pm 0{,}01$, $r_{C-Cl} = 1{,}72 \pm 0{,}02$ Å, $\angle F-C-F = 114 \pm 2°$, $\angle C-C-F$ (CF_2 group) $= 123 \pm 1°$, $\angle C-C-Cl = 127 \pm 1°{,}5$ assuming $r_{C=C} = 1{,}31$ Å and $\angle Cl-C-F = 114°$.

The structural parameters of the C_2F_3Cl molecule, determined in paper [60], are used in the present Handbook to calculated the products of principal moments of inertia of C_2F_3Cl, the values of which are quoted in Table 160.

The ultraviolet spectrum of C_2F_3Cl was investigated by Lacher, Hummel, Bohmfalk and Park [2509].

$\underline{C_2FCl_3}$. The infrared spectra of gaseous fluorotrichloroethylene have been investigated by Mann and Plyler [2760] (200-5000 cm^{-1}), and Nielsen, Gullikson and Woollett [3091] (450-5000 cm^{-1}), who used prism spectrometers with changeable optics. The Raman spectrum of liquid fluorotrichloroethylene was also obtained in [2760, 3091]. In paper [3091] it was obtained by a device with a higher dispersion.

Mann and Plyler [2760] interpreted the vibrational spectra of C_2FCl_2, obtained by them, on the basis of the fundamental frequencies of the C_2FCl_3 molecule, which they also calculated.* The investigation of the vibrational spectra of C_2FCl_3, carried out by Nielsen, Gullikson and Woollett [3091], confirmed the interpretation of these spectra, given by Mann and Plyler.

The values of the fundamental frequencies of the C_2FCl_3 molecule, determined by Mann and Plyler in paper [2760], are quoted in Table 160. With the exception of ν_5, ν_9 and ν_{12}, the values of all fundamental frequencies of the C_2FCl_3 molecule are determined on the basis of the infrared spectrum of gaseous fluorotrichloroethylene. The frequencies ν_5 and ν_9, quoted in Table 160, are determined by means of the Raman spectrum of liquid fluorotrichloroethylene. The frequency ν_{12} of the torsional vibration was determined by Mann and Plyler [2760] as equal

130 cm^{-1} on the basis of Mann's calculations [2758] ($\nu_{12}^{\mathrm{rasch}} = 129\ \mathrm{cm}^{-1}$) and the two weak lines at 123 and 144 cm^{-1}, observed by the authors of paper [2760] in the Raman spectrum of C_2FCl_3. The error of the values of fundamental frequencies of C_2FCl_3, adopted in Table 160, is estimated as equal to ±3 cm^{-1}.

The values of the structural parameters of the C_2FCl_3 molecule have not been determined in experiments. Mann and Plyler [2760], guided by the data on the structure of C_2F_4 and C_2Cl_4 molecules, obtained in papers [2327, 2328], suggested the following values of these quantities: $r_{C=C} = 1{,}31$, $r_{C-F} = 1{,}31$, $r_{C-Cl} = 1{,}72$ Å, $\angle C-C-F = \angle C-C-Cl = 123°$,

In the present Handbook, the structural parameters of C_2FCl_3 are assumed as equal to $r_{C=C} = 1{,}32 \pm 0{,}02$, $r_{C-F} = 1{,}32 \pm 0{,}02$, $r_{C-Cl} = 1{,}72 \pm 0{,}01$ Å, $\angle C-C-Cl$ (CCl_2 group)$CCl_2) = 123 \pm 3°$, $\angle C-C-Cl$(CFCl group) $= 125 \pm 3°$, $\angle F-C-Cl = 114 \pm 3°$ — , on the basis of a comparison of the adopted structural parameters of C_2F_4, C_2F_3Cl, $C_2F_2Cl_2$ and C_2Cl_4 molecules (see pages 1138,1173,1154 and 1140).The mentioned values of structural parameters of C_2FCl_3 are used for the calculation of the product of principal moments of inertia (see Table 160).

The ultraviolet spectrum of C_2FCl_3 was investigated by Lacher, Hummel, Bohmfalk and Park [2509].

Part 2. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of gaseous ethylene and of 14 of its fluorine-chlorine derivatives, calculated in the harmonic osccilator-rigid rotator model approximation for the temperature range from 293.15 to 6000°K, are quoted in the second volume of the Handbook (see Vol. 2, Tables 213, 216, 218-230). The calculations have been carried out on the basis of the molecular constants of these compounds, quoted in Tables 157-160, not taking into account the effect of intermolecular interaction (for ideal gases).

The values of the virial coefficients and of their derivatives for C_2H_4, by means of which corrections for non-ideality may be taken into account, are quoted in Table 419 (II).

The data on the thermodynamical functions of ethylene and its halogen derivatives, published in literature, are calculated on the basis of the harmonic oscillator - rigid rotator model approximation. Therefore, the calculation method used is not mentioned when comparing the thermodynamic functions of these compounds, calculated for the present edition of the Handbook, with the values published in literature.

§74. ETHYLENE AND ITS FLUORINE-CHLORINE DERIVATIVES OF THE C_2X_4 TYPE

The thermodynamic functions of gaseous C_2H_4, C_2F_4 and C_2Cl_4, quoted in Tables 213, 216 and 221 of the 2nd volume of the Handbook, are calculated by Eqs. (II.243) and (II.244) in the harmonic oscillator-rigid rotator model approximation, using the molecular constants, given in Table 157, and without taking into account the effect of intramolecular interactions. The values of the constants θ_n, C'_Φ and C'_S, used in the calculations, are quoted in Table 162.

TABLE 162

Values of the Constants for the Calculation of Thermodynamic Functions of Gaseous C_2H_4, C_2F_4 and C_2Cl_4.

1 Вещество	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7	θ_8	θ_9	θ_{10}	θ_{11}	θ_{12}	C'_Φ	C'_S
	2 град												3 кал/моль·град	
C_2H_4	4354,4	2334,6	1931,1	1478	4463,5	1778	1365,7	1357	4468,2	1165,9	4301,3	2076,9	−1,4239	6,5252
C_2F_4	1119	2693	567	273	1928	793	584	731	1924	314	1706	803	10,2922	18,2413
C_2Cl_4	643	2260	338	158	1439	499	414	737	1306	253	1118	446	14,8283	22,7774

1) Substance; 2) degree; 3) cal/mole·degree.

The errors in the values of thermodynamic functions of C_2H_4, C_2F_4 and C_2Cl_4, quoted in Tables 213 (II), 216 (II) and 221 (II), are mainly caused by the inaccuracy of the adopted values of molecular constants and the disregarding of the anharmonicity of the molecular vibrations. The first cause prevails at T ≤ 1000°K, the second at higher temperatures. The errors in the values of $\Phi^*_{298.15}$ for C_2H_4, C_2F_4 and C_2Cl_4 are estimated as equal to ±0.02 and ±0.56 and ±0.87 cal/mole·degree, respectively, and the errors in the Φ^*_{3000} values as equal to ±1.6; ±3.7 and ±4.6 cal/mole·degree, respectively.

The calculations of thermodynamic functions of C_2H_4, C_2F_4 and C_2Cl_4, carried out earlier, are discussed below, and a comparison of the results of these calculations with those carried out in processing the present edition of the Handbook is given.

$\underline{C_2H_4}$. The thermodynamic functions of gaseous ethylene have been calculated by a great number of investigators. A review of data on the calculations carried out is given in Table 163. In this Table Handbooks and monographs are also mentioned, in which thermodynamic functions of C_2H_4, calculated in the corresponding papers, are cited.

The earlier calculations of thermodynamic functions of ethylene [2331, 430, 3783] are based on estimated values of structural parameters of the C_2H_4 molecule and on the assignment of the fundamental frequencies suggested by Mecke [2830] (see Table 156). The frequency of the torsional vibration of the C_2H_4 molecule was estimated in these calculations on the basis of calorimetric measurements of the specific heat of ethylene.

In Kassel's paper [2331], the thermodynamic functions of C_2H_4 were calculated in two variants, corresponding to two assumptions on the quantity of the frequency of torsional vibration: $\nu_4 = 0$ and 950 cm^{-1}. The structural parameters were assumed as equal to $r_{C=C} = 1{,}18, r_{C-H} = 1{,}08$ Å, $\angle$ H—C—H = 109°28′ ; to which correspond $I_A I_B I_C = 3{,}423\cdot10^{-117}$ $(g\cdot cm^2)^3$. In Frost's calculations [430], the values of the fundamental frequencies of the C_2H_4 molecule, recommended by Mecke [2830], were not rounded off like those in paper [2331], and the value of 950 cm^{-1}, calculated on the basis of experimental data of the specific heat of ethylene [432], was assumed for the frequency ν_4 of the torsional vibration. Erroneous values, found in one of the earlier spectroscopical investigations, to which corresponds $I_A I_B I_C = 3{,}187 \cdot 10^{-117}$ $(g \cdot cm^2)^3$ (cf. Table 157), were assumed for the moments of inertia of C_2H_4 in Frost's calculations. The values of thermodynamic functions of C_2H_4, calculated in papers [2331, 430], are comparable to the corresponding values quoted in Table 213 (II) only after subtraction of the nuclear spin component 4R ln 2. Then, the difference of the Φ^*_{1000} values, given in Table 213 (II) and in papers [2331, 430], amounts to 0.40 and 0.50 cal/ /mole·degree, respectively. These discrepancies are mainly caused by the difference of the product of the principal moments of inertia of the C_2H_4 molecule, assumed in the calculations.

TABLE 163

Review of the Data on Calculations of Thermodynamic Functions of Gaseous Ethylene

1 **Авторы**	2 **Год опубликования**	3 **Термодинамические функции**	4 **Справочники и монографии**
5 Кассель [2331][а]	1933	15 $S^\circ_{298,16}$ и Φ°_T для $T = 300 - 3000°$ K	[426]
6 Фрост [430][а]	1934	S°_{300} и C°_p, Φ°_T для $T = 300 - 1000°$ K	[426]
7 Смит и Вон [3783] . . .	1935	S°_T, $H^\circ_T - H^\circ_0$ для $T = 298 - 973°$ K	—
8 Питцер [3253]	1937	$S^\circ_{298,16}$ и $\Delta G^\circ f_T/T$ для $T = 300 - 1500°$ K	—
9 Юсти [2312]	1938	C°_p и $S^\circ_T - S^\circ_{273,16}$ для $T = 273{,}16 - 1273{,}16°$ K	—
10 Гуггенгейм [1877] . . .	1941	Φ°_T для $T = 355 - 973°$ K	—
11 Томпсон [3971][а]	1941	Φ°_T, S°_T, $H^\circ_T - H^\circ_0$, C°_p для $T = 291{,}16 - 1500°$ K	[426]
12 Килпатрик и Питцер [2399]	1946	Φ°_T, S°_T, $H^\circ_T - H^\circ_0$, C°_p для $T = 298{,}16 - 1500°$ K	[4384, 3680, 3426, 427, 119]
13 Первое издание Справочника [420]	1956	Φ°_T, S°_T, $H^\circ_T - H^\circ_0$, I°_T для $T = 293{,}16 - 6000°$ K	—
14 Крёпелин и др. [248[illegible]] . .	1958	Φ°_T для $T = 1000 - 6000°$ K	—

[a]The thermodynamic functions of C_2H_4 were calculated taking into account the nuclear spin component 4R ln 2.

1) Authors
2) year of publication
3) thermodynamic functions
4) handbooks and monographs
5) Kassel
6) Frost
7) Smith and Vaughan
8) Pitzer
9) Justi
10) Guggenheim
11) Thompson
12) Kilpatrick and Pitzer
13) first edition of the Handbook
14) Kroepelin et al
15) for.

For the calculation of the thermodynamic functions of C_2H_4, Pitzer [3253], Justi [2312], and Guggenheim [1877] used the values of fundamental frequencies of the ethylene molecule (see Table 156), recommended in Bonner's paper [864]. In Pitzer's calculations [3253], those values of the moments of inertia are used, which were found by Badger [597]; to these values corresponds the value $I_A I_B I_C = 5{,}20\cdot 10^{-117}$ $(g\cdot cm^2)^3$ (cf. Table 157). Owing to the smaller difference between the values of the molecular constants, used in these calculations, the discrepancy between the values of thermodynamic functions of C_2H_4 quoted in Table 213 (II) and in papers [3253, 2312, 1877] is smaller than the one between the values adopted in the present Handbook and those given in the earlier papers [2331, 430, 3783].

The calculations by Thompson [3971] are based on the assignment of the fundamental frequencies of the C_2H_4 molecule, recommended by Conn and Sutherland [1160] (see Table 156). Here, a value equal to 820 cm^{-1}, resulting from experimental measurements of the specific heat of gaseous ethylene and of its entropy at 298°K (see below), was assumed for the frequency ν_4 of the torsional vibration. In the calculations of [3971], the product of the principal moments of inertia was assumed as equal to $5.22\cdot 10^{-117}$ $(g\cdot cm^2)^3$ on the basis of the results of an analysis of the rotational structure of a number of bands in the infrared spectrum, obtained in papers [3968, 3790]. If we eliminate the nuclear spin component (4R ln 2) from the values of Φ_T^* and S_T°, calculated by Thompson [3971], the values of these quantities become very similar to those quoted in Table 213 (II). The difference in the values of $\Phi_{298.15}^*$ and Φ_{1000}^* amounts to 0.02 and 0.16 cal/mole·degree, respectively, mainly due to the difference in the assumed frequencies ν_4 and ν_6.

The calculations by Kilpatrick and Pitzer [2399] are based on the molecular constants of C_2H_4, recommended by Gallaway and Barker [1646] (see page 1133 and Table 156). The values of the thermodynamic functions of C_2H_4, obtained in paper [2399], are similar to the values quoted in Table 213 (II). The differences in the values of $\Phi_{298.15}^*$ and Φ_{1000}^* amount to 0.01 and 0.12 cal/mole·degree, respectively, mainly owing to the difference in the assumed values of the frequencies ν_4 and ν_6. The thermodynamic functions of C_2H_4, calculated by Kilpatrick and Pitzer [2399], are cited in many Handbooks and monographs (see Table 163).* Kroepelin and co-workers [2489] continued the calculations of Φ_T^* led off by Kilpatrick and Pitzer, up to 6000°K, using the same values of the molecular constants of C_2H_4 as those in paper [2399].

The values of the thermodynamic functions of ethylene, quoted in the first and in the present edition of the Handbook, differ insignificantly, because the differences in the adopted values of the molecular constants of C_2H_4 are small. The differences in the Φ_T^* values at T = 298.15 and 6000°K are 0.005 and 0.003 cal/mole·degree, respectively.

It must be mentioned that in the case of ethylene the effect of the centrifugal stretching of the C_2H_4 molecules on the value of the thermodynamic functions can be approximately taken into account, because Wilson [4287] calculated for C_2H_4 the constant $\rho_1 = 0{,}79 \cdot 10^{-5}$ degree^{-1}. The regard for the anharmonicity of the vibrations, however, has a significantly greater influence.

The specific heat of gaseous ethylene was measured by many investigators in the temperature range from 150 to 460°K. The results of measurements carried out up to 1935 are cited in the Handbook [426]. In the following years, measurements of specific heat have been carried out by Burcik, Easter and Yost [1019] at $T = 270{,}7;\ 300{,}0$ and 320.7°K with an accuracy of ±0.5%. The results of experimental measurements of the specific heat of ethylene are in accordance with the values of the specific heat, calculated on the basis of the molecular constants of C_2H_4 and adopted in the present Handbook.

Egan and Kemp [1466] measured the specific heat of ethylene between 16.00 and 169.40°K and also carried out calorimetric measurements of the heats of melting and evaporation. On the basis of the results of the measurements carried out, Egan and Kemp calculated $S^{\circ}_{169.40}$ (C_2H_4, gas) $= 47{,}36 \pm 0{,}10$ cal/mole·degree. The value of this quantity, calculated by means of the molecular constants of C_2H_4 and adopted in the present Handbook, is equal to 47.354 cal/mole·degree.

<u>C_2F_4</u>. The thermodynamic functions of gaseous tetrafluoroethylene were calculated not only by Mann, Acquista and Plyler [2753] $(T = 197{,}53-1500°K)$ but also during the preparation of the first edition of this Handbook $(T = 293{,}16-6000°K)$. In the latter calculations, the same values of the fundamental frequencies and structural parameters of the C_2F_4 molecule were used as in the present edition of the Handbook. The differences between the corresponding values of thermodynamic functions of C_2F_4, quoted in paper [2753], in the first and in the present edition of the Handbook [see Table 216 (II)], are insignificant. They are caused by a certain difference in the values of the physical constants, assumed in the calculations, and in the values of the product of principal moments of inertia of the C_2F_4 molecule.

Furukawa, McCoskey and Reilly [1634] carried out very accurate calorimetric measurements of the specific heat ($T=16-210°K$), melting heat and heat of evaporation of tetrafluoroethylene and also of the pressure of C_2F_4 vapor. On the basis of these data, the authors of paper [1634] calculated $S^\circ_{197.53}$ (C_2F_4, gas) $= 64,55 \pm 0,09$ cal/mole·degree. The value of $S^\circ_{197.53}$, calculated on the basis of the molecular constants of C_2F_4 and adopted in the present Handbook, is equal to 64.53 cal/mole·degree.

$\underline{C_2Cl_4}$. The thermodynamic functions of gaseous tetrachloroethylene have been calculated by Torkington [4003], Mann, Acquista and Plyler [2753], and Mann, Meel and Plyler [2759] from 298,15—1500° K.

Torkington's calculations [4003] are erroneous because they are based on an incorrect assignment of the fundamental frequencies of the C_2Cl_4 molecule and on estimated values of the structural parameters.

The calculations by Mann, Acquista and Plyler [2753] are based on the assignment of the fundamental frequencies of the C_2Cl_4 molecule, suggested by these authors, and on values of the structural parameters, determined by I. Karle and J. Karle [2328] by electron diffraction studies and corresponding to the value $I_A I_B I_C = 316 \cdot 10^{-117}$ $(g \cdot cm^2)^3$ (cf. Table 157). The values of Φ^*_T and S°_T quoted in paper [2753], are higher than the corresponding values of these quantities in Table 221 (II) by approximately 0.5 and 0.8 cal/mole·degree owing to the fact that lower values of the ν_7 and ν_{12} frequencies are assumed in the calculation of [2753].

The same values of the fundamental frequencies of the C_2Cl_4 molecule as those in the present Handbook, and values of structural parameters according to the data of [2328], are used in the paper by Mann, Meel and Plyler. The discrepancy between the corresponding values of thermodynamic functions of C_2Cl_4, quoted in paper [2759] and in Table 221 (II), is caused by a difference in the adopted values of the structural parameters of the C_2Cl_4 molecule and of the physical constants. For Φ^*_T, it amounts to 0.014 cal/mole·degree at 298,15° K and to 0.007 cal/mole·degree at 1500° K.

During the preparation of the first edition of the Handbook, the thermodynamic functions of gaseous tetrachloroethylene were not calculated.

§75. FLUORINE AND CHLORINE DERIVATIVES OF ETHYLENE OF THE $C_2X_2Y_2$ TYPE

TABLE 164

The values of S°_T (in cal/mole·degree) for Isomers of $C_2H_2Cl_2$ and $C_2F_2Cl_2$

$T°$, K	$C_2H_2Cl_2$			$C_2F_2Cl_2$		
	1 несимм.	2 цис-	3 транс-	1 несимм.	2 цис-	3 транс-
298,15	68,8545	69,190	69,250	78,453	77,863	77,974
1000	94,842	94,846	95,036	109,186	108,974	109,074
2000	114,423	114,405	114,598	130,286	130,082	130,180
4000	135,670	135,649	135,842	152,073	151,869	151,968
6000	148,404	148,383	148,576	164,918	164,713	164,813

1) Asymmetrical; 2) cis; 3) trans.

TABLE 165

Values of the Constants for the Calculation of the Thermodynamic Functions of gaseous $C_2H_2F_2$, $C_2H_2Cl_2$ and $C_2F_2Cl_2$

1 Вещество	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7	θ_8	θ_9	θ_{10}	θ_{11}	θ_{12}	C'_Φ	C'_S
	2 град												3 кал/моль·град	
4 несимм. $C_2H_2F_2$	4403	2486	1986	1332	791	4465	1873	1374	630	1155	879	1027	7,5495	15,4986
цис- $C_2H_2Cl_2$ 5	249	584	822	1023	1220	1696	1862	2283	1260	1003	4420	4427	11,0950	19,0441
транс.-$C_2F_2Cl_2$ 6	2456	1706	909	611	414	479	201	761	1712	1283	613	252	14,1446	22,0937

1) Substance; 2) degree; 3) cal/mole·degree; 4) asymmetrical; 5) cis; 6) trans.

The thermodynamic functions of gaseous difluoroethylene, dichloroethylene and difluorodichloroethylene, quoted in Tables 219, 223, and

226 of the 2nd volume of the Handbook, are calculated by means of Eqs. (II.243) and (II.244) in the harmonic oscillator-rigid rotator model approximation on the basis of the molecular constants of CH_2CF_2, cis-$C_2H_2Cl_2$ and trans-$C_2F_2Cl_2$, quoted in Table 159, without taking into account intermolecular effects. This choice is due to the fact that experimental values of molecular constants are known only for the asymmetrical isomer of $C_2H_2F_2$. As regards to $C_2H_2Cl_2$ and $C_2F_2Cl_2$, the calculation of the thermodynamic functions was carried out on the basis of the molecular constants of cis-$C_2H_2Cl_2$ and trans-$C_2F_2Cl_2$ because the values of the thermodynamic functions of these isomers are intermediate between the values of the corresponding thermodynamic functions of the other two isomers (at least at $T < 1500°K$), as follows from Table 164.

The values of the constants in the formulas for the calculation of the thermodynamic functions of $C_2H_2F_2$, $C_2H_2Cl_2$ and $C_2F_2Cl_2$, based on the corresponding data of Table 159, are quoted in Table 165.

The errors in the thermodynamic functions of $C_2H_2F_2$, $C_2H_2Cl_2$, $C_2F_2Cl_2$, quoted in Tables 219 (II), 223 (II) and 226 (II), are caused by the inaccuracy of the initial molecular constants and the approximate method of calculation (not taking into account the anharmonicity of the vibrations, etc.). The total errors in the values of $\Phi^*_{298.16}$ for $C_2H_2F_2$, $C_2H_2Cl_2$ and $C_2F_2Cl_2$ are estimated as equal to 0.1; 0.25 and 0.6 cal/mole·degree, respectively, and those of Φ^*_{3000} as equal to 2.5; 3 and 4 cal/mole·degree.

In the first edition of the Handbook, the thermodynamic properties of $C_2H_2F_2$, $C_2H_2Cl_2$ and $C_2F_2Cl_2$ were not dealt with. Below, information is given on other calculations of the thermodynamic functions of these gases.

<u>$C_2H_2F_2$</u>. Mears, Stahl, et al [2826] calculated the values of $H^\circ_T - H^\circ_0$

of the gaseous (asymmetrical) difluoroethylene for $T = 233,15-298,15°K$. The values of $(H_T^\circ - H_0^\circ) - (H_{233,15}^\circ - H_0^\circ) + \Delta H_{233,15}^\circ$ are quoted in paper [2826]. In the calculations of [2826], the fundamental frequencies of the CH_2CF_2 molecule are used, which were determined by Smith et al. [3773] on the basis of the vibrational spectra of gaseous difluoroethylene (see page 1143).

$\underline{C_2H_2Cl_2}$. The thermodynamic functions of the isomers of gaseous dichloroethylene are calculated on the basis of the corresponding molecular constants by Godnev and Filatova [160] (Φ_T^* at $T = 298,1 - 1500°K$ for cis- and trans-$C_2H_2Cl_2$), Tatevskiy and Frost [415] ($S_{298.1}^\circ$ for all three isomers), Pitzer and Hollenberg [3260] (at $T = 200-1500°$ for cis- and trans-$C_2H_2Cl_2$), and Hildenbrand and co-workers [2072] (at $T = 298,15 - 1500°K$ for CH_2CCl_2).

The thermodynamic functions of cis-$C_2H_2Cl_2$ were calculated by Godnev and Filatova [160] on the basis of obsolete data for the fundamental frequencies of the cis-$C_2H_2Cl_2$ molecule [4339] and of their structural parameters [959]. This fact is the principal cause of the difference in the Φ_T^* values, quoted in paper [160] and in Table 223 (II) amounting to 0.1 cal/mole•degree at $T = 298,15°K$ and to 0.5 cal/mole••degree at $T = 1500°K$. In the calculations of Pitzer and Hollenberg [3260], the same values of the fundamental frequencies of cis-$C_2H_2Cl_2$ are adopted those as in the present Handbook. Owing to this fact, the differences between the corresponding values of thermodynamic functions of cis-$C_2H_2Cl_2$, given in paper [3620] and in Table 223 (II), are small; nevertheless, in the calculations of [3260] the likewise obsolete values of structural parameters, found in the earlier electron diffraction study [959], have been used. The difference in the corresponding Φ_T^* values amounts to about 0.05 cal/mole•degree. The values of $S_{298,1}^\circ$ calculated by Tatevskiy and Frost [415] for all three isomers of $C_2H_2Cl_2$

are also based on obsolete values of molecular constants. Owing to this fact, [415], the values of $S^{\circ}_{298.1}$ of the $C_2H_2Cl_2$ isomers are by 0.5-1 cal/mole·degree lower than the corresponding values of these quantities, quoted in Table 223 (II) (for cis-$C_2H_2Cl_2$), in paper [3260] (for cis- and trans-$C_2H_2Cl_2$) and in paper [2072] (for CH_2CCl_2).

Hildenbrand and co-workers [2072] measured the specific heat of solid and liquid asymmetrical dichloroethylene at temperatures from 13 to 290°K, and also the heat of melting and evaporation, and the vapor pressure. On the basis of these data, the value $S^{\circ}_{298.15}$(CH_2CCl_2 , gas) = 69.04 ± 0.20 cal/mole·degree was calculated in paper [2072], which is in accordance with the value of this quantity, calculated by means of the molecular constants.

$\underline{C_2F_2Cl_2}$. The thermodynamic functions of gaseous trans-difluorodichloroethylene have been calculated by Mann and Plyler [2761] from 200 to 1500°K on the basis of the same values of molecular constants of trans-$C_2F_2Cl_2$ as those adopted in the present Handbook. The results of the corresponding calculations are in accordance.

The thermodynamic functions of the other isomers of difluoro-dichloroethylene have not been calculated.

§76. FLUORINE AND CHLORINE DERIVATIVES OF ETHYLENE OF THE TYPES C_2X_3Y AND C_2X_2YZ

The thermodynamic functions of fluorine and chlorine substituted ethylene drivatives of the types C_2X_3Y and C_2X_2YZ, calculated by Eqs. (II.243) and (II.244) in the harmonic oscillator-rigid rotator model approximation on the basis of the molecular constants, adopted in Table 160, are quoted in Tables 218, 220, 222, 224, 225, 227, 228, 229, 230 of the 2nd Volume of the Handbook. The values of the constants in the corresponding formulas are quoted in Table 166.

TABLE 166

Values of the Constants for the Calculation of Thermodynamic Functions of Gaseous Fluorine and Chlorine Derivatives of Ethylene of the Types C_2X_3Y and C_2X_2YZ.

1 Вещество	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7	θ_8	θ_9	θ_{10}	θ_{11}	θ_{12}	C'_{Φ}	C'_S
	2 град												3 кал/моль·град	
C_2H_3F	2380	4431	4482	4532	1879	1986	1335	1663	695	1340,0	1242	1024	5,6439	13,5930
C_2H_3Cl	2316	4360	4431	4503	1042	1971	568	1842	1482	1356,1	1290,3	892	7,7709	15,7200
C_2H_2FCl	2383	4339	4416	1990	1706	1363	1006	622	534	1203	873	741	10,7962	18,7453
C_2HF_3	2573	4532	1960	1819	1337	1685	698	896	334	1079	799	439	11,3327	19,2818
C_2HF_2Cl	2511	4503	1918	1725	1216	1396	623	833	289	1081	823	350	12,7860	20,7351
C_2HFCl_2	—	—	—	—	—	—	—	—	—	—	—	—	14,3954	22,3445
C_2HCl_3	2286	4431	1787	1341	1209	904	394	548	247	1122	647	304	15,6084	23,5575
C_2F_3Cl	2578	1922	1748	1522	991	744	486	666	270	774	531	239	14,3901	22,3392
C_2FCl_3	2367	1699	1422	1233	748	586	360	515	250	773	450	187	16,6513	24,6004

1) Substance; 2) degree; 3) cal/mole•degree.

The errors in the thermodynamic functions of the compounds in question are caused by the inaccuracy of the adopted values of molecular constants and the approximate nature of the calculation method. The error in the $\Phi^*_{298.15}$ values amounts from 0.1 cal/mole•degree (for C_2H_3F, C_2H_3Cl, C_2H_2FCl, C_2HF_3, C_2HF_2Cl) to 0.5-0.7 cal/mole•degree (for C_2HCl_3, C_2F_3Cl, C_2FCl_3, C_2HFCl_2). The total error in the Φ^*_{3000} values changes from 2-2.5 cal/mole•degree (for C_2H_3F, C_2H_3Cl, C_2H_2FCl, C_2HF_3, C_2HF_2Cl) to 4-5 cal/mole•degree (for C_2HCl_3, C_2F_3Cl, C_2FCl_3, C_2HFCl_2).

The thermodynamic properties of the fluorine and chlorine derivatives of ethylene of the types C_2X_3Y and C_2X_2YZ were not dealt with in the first edition of the Handbook. Below, information is given on calculations of the thermodynamic functions of these gases, which have been carried out earlier.

C_2H_3F. The thermodynamic functions of gaseous fluoroethylene have not been calculated earlier.

C_2H_3Cl. The thermodynamic functions of gaseous chloroethylene have been calculated by Godnev and Filatova [160] (Φ^*_T for $T = 298{,}1—1500° K$), Tatevskiy and Frost [415] ($S^\circ_{298.1}$) , Richards [3432] ($\Phi^\circ_T, S^\circ_T, H^\circ_T - H^\circ_0, C^\circ_p$ for $T = 291{,}16—1500° K$) and Gullikson and Nielsen [1885] ($\Phi^\circ_T, S^\circ_T, (H^\circ_T - H^\circ_0)/T, C^\circ_p$ for $T = 273{,}16—500° K$). The differences between the corresponding values of Φ^*_T, quoted in the mentioned papers and in table 222 (II), do not exceed 0.07 cal/mole•degree and are caused by the difference in the adopted values of molecular and physical constants.

<u>C_2H_2FCl, C_2HF_3</u>. The thermodynamic functions of gaseous asymmetrical difluorochloroethylene and trifluoroethylene were calculated by Mann, Acquista and Plyler in papers [2754, 2752] for the range $T = 200—1500°$ using almost the same values of molecular constants of CH_2CFCl and C_2HF_3 as in the present Handbook.* The values of thermodynamic functions of CH_2CFCl and C_2HF_3, quoted in papers [2754, 2752], are in accordance with the values of the corresponding quantities, quoted in Tables 228 (II) and 220 (II).

<u>C_2HF_2Cl</u>. The thermodynamic functions of gaseous (asymmetrical) difluorochloroethylene have been calculated by Nielsen, Liang and Smith [3092] ($\Phi^\circ_T, S^\circ_T, (H^\circ_T - H^\circ_0)/T, C^\circ_p$ for $T = 253{,}46—600° K$) and Mears and co-workers [2826] ($H^\circ_T - H^\circ_0$ at $T = 233{,}15 — 393{,}15° K$).

In the calculations of [3092], the same values of the fundamental frequencies of the C_2HF_2Cl are assumed as in the present Handbook. The corresponding values of the thermodynamic functions of C_2HF_2Cl, quoted in paper [3092] and in Table 229 (II) differ insignificantly. These discrepancies are caused mainly by the difference in the adopted values of the principal moments of inertia of the C_2HF_2Cl molecule.

The results of the calculations by Nielsen, Liang and Smith [3092] supplemented somewhat by interpolations and extrapolations, are cited in Zeise's Handbook [4384].

<u>C_2HFCl_2</u>. The thermodynamic functions of gaseous fluorodichlorothy-

lene have not been calculated earlier due to the lack of data on the molecular constants of this compound.

In the present Handbook, the translational and rotational components of the thermodynamic functions of (asymmetrical) fluorodichloroethylene are calculated by Eqs. (II.8) and (II.9) and (II.179), (II.180) The values of the constants C'_Φ and C'_S quoted in Table 166, are calculated by Eqs. (II.247) and (II.248).

The vibrational components of the thermodynamic functions of C_2HFCl_2 may be calculated on the basis of the assumption that the increase in these quantities is equal to zero in the exchange reactions between fluoro- and chloro ethylenes. For the exchange reactions, in qhich C_2HFCl_2 participates, the following equations can be written down:

$$C_2HFCl_2 + C_2HF_2Cl = C_2HF_3 + C_2HCl_3, \qquad (XVIII.\ 1)$$

$$2C_2HFCl_2 = C_2H_2Cl_2 + C_2F_2Cl_2, \qquad (XVIII.\ 2)$$

$$2C_2HFCl_2 = C_2HF_2Cl + C_2HCl_3, \qquad (XVIII.\ 3)$$

$$2C_2HFCl_2 = C_2H_3FCl + C_2FCl_3. \qquad (XVIII.\ 4)$$

Assuming that $\Delta\Phi^{\bullet}_{\text{кол}} = 0$ and $\Delta S_{\text{кол}}=0$, are valid for these reactions, we have the following relations:

$$\Phi^{\bullet}_{\text{кол}}(C_2HFCl_2) = \Phi^{\bullet}_{\text{кол}}(C_2HF_3) + \Phi^{\bullet}_{\text{кол}}(C_2HCl_3) - \Phi^{\bullet}_{\text{кол}}(C_2HF_2Cl), \qquad (XVIII.\ 5)$$

$$\Phi^{\bullet}_{\text{кол}}(C_2HFCl_2) = \frac{1}{2}\left[\Phi^{\bullet}_{\text{кол}}(C_2H_2Cl_2) + \Phi^{\bullet}_{\text{кол}}(C_2F_2Cl_2)\right], \qquad (XVIII.\ 6)$$

$$\Phi^{\bullet}_{\text{кол}}(C_2HFCl_2) = \frac{1}{2}\left[\Phi^{\bullet}_{\text{кол}}(C_2HF_2Cl) + \Phi^{\bullet}_{\text{кол}}(C_2HCl_3)\right], \qquad (XVIII.\ 7)$$

$$\Phi^{\bullet}_{\text{кол}}(C_2HFCl_2) = \frac{1}{2}\left[\Phi^{\bullet}_{\text{кол}}(C_2H_2FCl) + \Phi^{\bullet}_{\text{кол}}(C_2FCl_3)\right]. \qquad (XVIII.\ 8)$$

Analogous relations take place for the vibrational entropy components.

The results of calculations of the vibrational components of Φ^*_T of fluorodichloroethylene for $T = 298.15;\ 1000\ (1000)\ 6000°\ K$ by means ofEqs. (XVIII.5)-(XVIII.8) on the basis of the vibrational components of Φ^*_T of the other components of reactions (XVIII.1)-(XVIII.4), calculated by means of the experimental frequency values, are quoted in Table 167.

It follows from the data of this Table that the calculation by means of the approximate formulas of the thermodynamic functions of C_2HFCl_2 (XVIII.5)-(XVIII.8) results in very similar values of the corresponding quantities. The values of $\Phi^*_{kol}(C_2HFCl_2)$, quoted in Table 167, are similar to the values calculated by Eq. (XVIII.5). Owing to this fact, the vibrational components of Φ^*_T and S°_T are determined by Eq. (XVIII.5) and the analogous relationship for S_{kol} when calculating the thermodynamic functions of C_2HFCl_2 for Table 230 (II).

TABLE 167

Values (in cal/mole·degree) of the Vibrational component of Φ^*_T of Fluorodichloroethylene Calculated by Formulas (XVIII.5)-(XVIII.8).

T, °K	(XVIII.5)	(XVIII.6)	(XVIII.7)	(XVIII.8)
298,15	2,960	3,081	2,878	2,979
1000	13,683	13,683	13,393	13,723
2000	24,278	24,249	23,926	24,362
3000	31,691	31,654	31,318	31,799
4000	37,364	37,324	36,980	37,483
5000	41,954	41,912	41,563	42,081
6000	45,805	45,763	45,410	45,939

C_2HCl_3. The thermodynamic functions of gaseous trichloroethylene have been calculated earlier by Allen and Bernstein [498] in the temperature range from 298.16—1500° K. In the calculations of [498], not only the same values of the fundamental frequencies but also other values of the structural parameters of the C_2HCl_3 molecule are assumed than those in the present Handbook. Owing to this fact and also to the difference in the values of the physical constants, the Φ^*_T values, quoted in paper [498] and in Table 224 (II), differ by 0.01 cal/mole·

•degree.

Allen and Bernstein [498] calculated also the thermodynamic functions of C_2DCl_3.

C_2F_3Cl, C_2FCl_3. The thermodynamic functions of gaseous trifluorochloroethylene and fluorotrichloroethylene were calculated by Mann and Plyler in papers [2751, 2760] for the 200—1500° K. temperature range. In the present Handbook, somewhat other values of the molecular constants of C_2F_3Cl and C_2FCl_3 are adopted than in papers [2751, 2760]. This fact explains the small differences in the values of the thermodynamic functions of trifluorochloroethylene and fluorotrichloroethylene, quoted in Tables 225 (II), 227 (II) and in papers [2751, 2760]. The difference in the corresponding Φ_T^* values amounts to 0.01 cal/mole••degree.

In papers [3128, 1635], values of $S^\circ_{244.80}$ (C_2F_3Cl, gas) are calculated on the basis of results of calorimetric measurements. The most accurate value $S^\circ_{244.80}$ (C_2F_3Cl, gas) = 73.28 ± 0.10 cal/mole•degree based on calorimetric measurements, was obtained by Furukawa, McCoskey and Reilly [1635]. The value of this quantity, calculated on the basis of the molecular constants of C_2F_3Cl, adopted in the present Handbook, is equal to 73.264 cal/mole•degree.

Part 3. THERMOCHEMICAL QUANTITIES

§77. HEATS OF FORMATION AND ENERGIES OF DISSOCIATION

C_2H_4 (gas). The heat of combustion of ethylene has, since 1838, been repeatedly determined. The majority of results of these investigations are only of historical interest. A review of the data published up to 1936, is given by Rossini and Knowlton [3505].

In 1935, Kistiakowsky and co-workers [2417] carried out a determination of the heat of ethylene hydrogenation, using the method of calorimetric bomb. The use of catalyst enabled these investigators to exclude side reactions and to obtain very accurate results. In 1936, Kistiakowsky and co-workers [2420] reviewed the results obtained in paper [2417] and obtained a somewhat more accurate value of the heat of the hydrogenation reaction: C_2H_4 (gas) + H_2 (gas) = C_2H_6 (gas), $\Delta H^{\circ}_{298\cdot 15} = -32{,}618 \pm 0{,}060$ kcal/mole. This result, together with the heat of formation of ethane, recommended in Handbook [3508], leads to the value $\Delta H^{\circ}f_{298.15}$ (C_2H_4, gas) = 12.4 ± 0.2 kcal/mole.

In 1937 Rossini and Knowlton [3505] determined with great accuracy the combustion heat of ethylene $\Delta Hc_{298\cdot 15} = -337{,}234 \pm 0{,}072$ kcal/mole by means of a precise method of calorimetric measurements, developed by them. In accordance with the values of the heats of formation of CO_2 and H_2O, adopted in the present Handbook, the results of the measurements by Rossini and Knowlton lead to the following value of the heat of formation of ethylene

$$\Delta H^{\circ}f_{298,15}(C_2H_4, \text{gas}) = 12{,}50 \pm 0{,}10 \text{ kcal/mole}.$$

This value, corresponding within the measurement error to the results obtained by Kistiakowsky and co-workers [2420], is adopted in the present Handbook. The energy of dissociation of C_2H_4 in atoms, corresponding to it, is equal to

$$D_0(C_2H_4) = 531{,}208 \pm 0{,}9 \text{ kcal/mole}.$$

$\underline{C_2H_3F(\text{gas})}$ Experimental data which make it possible to determine the heat of formation of fluoroethylene are lacking.

A graphic comparison of the heats of formation of fluorine derivatives of ethylene, fluorine-chlorine derivatives of ethylene, and fluorine derivatives of methane by the Karapet'yants method gives the value

$$\Delta H^{\circ}f_{298,15}(C_2H_3F, \text{gas}) = -33 \pm 3 \text{ kcal/mole},$$

which is in accordance with the results of calculations by means of the simple additive scheme (see [468]) and by the interpolation formula of the Bernstein type, developed by the authors of the Handbook on the basis of the adopted values of heats of formation of C_2H_4, $C_2H_2F_2$ and C_2F_4.* The values of the heat of formation of fluoroethylene obtained by this method is adopted in the present Handbook.

In paper [293], the value $\Delta H^\circ f_{298}(C_2H_3F$, gas) = -28 kcal/mole is quoted, calculated on the basis of the simple additive scheme by means of data differing from those addopted in the present Handbook.

To the adopted value of the heat of formation of C_2H_3F corresponds

$$D_0(C_2H_3F) = 543{,}726 \pm 3{,}2 \text{ kcal/mole.}$$

C_2H_3Cl (gas). The value of the heat of formation of chloroethylene (+7.5 kcal/mole), adopted in the thermochemical Handbooks [3508, 813] is based on the data by Thomsen [3983] who measured the heat of combustion of gaseous C_2H_3Cl. The error of this value is of the order of 2-3 kcal/mole.

In 1956, Lacher and co-workers [2508, 2510] measured the heat of the reaction C_2H_3Cl (gas) + $2H_2$ (gas) = C_2H_6 (gas) + HCl (gas), $\Delta H^\circ_{521} = -52{,}61 \pm 0{,}26$ kcal. The calculation of the heat of formation of chloroethylene by means of the measurements results, obtained in papers [2508, 2510] and other thermochemical data [3508, 1678] gives the value:**

$$\Delta H^\circ f_{298,15}(C_2H_3Cl, \text{gas}) = 8{,}9 \pm 0{,}3 \text{ kcal/mole,}$$

which is adopted in the present Handbook. The value of the dissociation energy which corresponds to it, is equal to

$$D_0(C_2H_3Cl) = 511{,}947 \pm 0{,}9 \text{ kcal/mole.}$$

$C_2H_2F_2$ (gas). The combustion heat of asymmetrical difluoroethylene was determined by Neugebauer and Margrave [3050]: $\Delta H^\circ c_{298,15} = -262{,}15 \pm 0{,}8$ kcal/mole. This result, in combination with the thermochemical data of [3508], enabled Neugebauer and Margrave to determine the heat of formation of asymmetrical difluoroethylene:

$$\Delta H^\circ f_{298,15}(CH_2CF_2, \text{gas}) = -77{,}5 \text{ kcal/mole.}$$

The authors of paper [3050] assumed the error of the cited value of $\Delta H^\circ f_{298,15}(C_2H_2F_2)$ as equal to ±0.8 kcal/mole. In the report of MGU [35] however, it is pointed out that the error calculated by Neugebauer and Margrave is too small and must be estimated as equal to ±2 kcal/mole.* With regard to this error, the value of the heat of formation of difluoroethylene, found by Neugebauer and Margrave, is adopted in the present Handbook. To it corresponds

$$D_0(C_2H_2F_2) = 555{,}281 \pm 2{,}5 \text{ kcal/mole.}$$

C_2H_2FCl (gas). The value of the heat of formation of fluorochloroethylene has not been determined in experiments. The results of calculation, carried out in simple additive manner (see [468]), prove that the value of the heat of formation of C_2H_2FCl lies between -32 and -39 kcal/mole.** A value equal to -38 kcal/mole results when using the Kharasch method (see [468]).

In order to determine the most probable value of the heat of formation of C_2H_2FCl, the graphic method by Karapet'yants was applied. Here, the values of the heats of formation of $CF_3Cl, CHF_2Cl, CH_2FCl, CH_3Cl$ and C_2F_3Cl, C_2HF_2Cl, C_2H_3Cl are used which are adopted in the present Handbook. The value

$$\Delta H^\circ f_{298,15}(C_2H_2FCl, \text{gas}) = -35 \pm 3 \text{ kcal/mole}$$

corresponds better than other values to the heats of formations of the mentioned compounds, and it is, therefore, adopted in the present Handbook. The corresponding value of the dissociation energy is equal to

$$D_0(C_2H_2FCl) = 522{,}995 \pm 3{,}2 \text{ kcal/mole.}$$

$C_2H_2Cl_2$ (gas). The heat of combustion of the liquid isomers of dichloroethylene was determined by Smith and co-workers [3786] by means of the "quartz helix" method (see [3502, 471]). The authors of paper

[3786] attributed the values $\Delta Hc_{298.15}$ (asymm. $C_2H_2Cl_2$, liquid) = -261.077 ± 0.4 kcal/mole and $\Delta Hc_{298,15}$ (symm. $C_2H_2Cl_2$, liqu.) = -261.649 ± 0.4 kcal/mole to the following final states of the products of combustion: CO_2 (gas), HCl (1 : 600 H_2O). The findings of Smith and co-workers, combined with the thermochemical data of the Handbook [3508], yield the values (in kcal/mole)

$$\Delta H^\circ f_{298,15}(\text{unsym. - } C_2H_2Cl_2,\ \text{liq.}) = -6{,}2 \pm 0{,}4,$$
$$\Delta H^\circ f_{298,15}(\text{sym. - } C_2H_2Cl_2,\ \text{liq.}) = -6{,}8 \pm 0{,}4,$$
$$\Delta H^\circ f_{298,15}(\text{unsym. - } C_2H_2Cl_2,\ \text{gas}) = +0{,}8 \pm 0{,}5,\ *$$
$$\Delta H^\circ f_{298,15}(\text{sym. - } C_2H_2Cl_2,\ \text{gas}) = +0{,}4 \pm 0{,}5\ .\ *$$

The two latter values agree well with the data by Kirkbride [2407] on the heats of chlorination of ethylene and its chlorine derivatives.

Sinke and Stull [3750] measured the heat of combustion of asymmetrical dichloroethylene and calculated on the basis of the data obtained $\Delta H^\circ f_{298.15}$ (asymm. $C_2H_2Cl_2$, liqu.) = -6.0 ± 0.3 kcal/mole, the value of which is in agreement with the results of [3786, 2407] within the limits of the experimental error.

In the present Handbook, the values of the heat of formation of $C_2H_2Cl_2$, resulting from the data by Smith and co-workers [3786], are adopted for the subsequent calculations. Owing to the fact that the thermal effect of isomerization of $C_2H_2Cl_2$ lies within the limits of the experimental error of [3786, 2407], the value

$$\Delta H^\circ f_{298.15}(C_2H_2Cl_2,\text{gas}) = 0{,}6 \pm 0{,}5\ \text{kcal/mole.}$$

is adopted in the present Handbook. The value

$$D_0(C_2H_2Cl_2) = 497{,}542 \pm 1{,}0\ \text{kcal/mole.}$$

corresponds to the adopted heat of formation of $C_2H_2Cl_2$.

<u>C_2HF_3 (gas)</u>. Skuratov, Kolesov, Martynov, Shtekher and Zenkov [41a] were the first to determine the experimental value of the heat of formation of trifluoroethylene:

$$\Delta H^\circ f_{298,15}(C_2HF_3,\ \text{gas}) = -114,6 \pm 2,4\ \text{kcal/mole}$$

on the basis of the heat of combustion ($\Delta Hc_{298,15} = -232,1 \pm 2,4$ kcal/mole) measured by them. Earlier, the heat of formation of gaseous trifluoroethylene was estimated in papers [35] (-127 kcal/mole) and [293] (-110 kcal/mole) on the basis of the thermochemical data of other halogen derivatives of ethylene.

The value of the heat of formation of C_2HF_3, determined in paper [41a], is adopted in the present Handbook. To it corresponds

$$D_0(C_2HF_3) = 559,682 \pm 3\ \text{kcal/mole}.$$

C_2HF_2Cl (gas). The heat of hydrogenation of difluorodichloroethylene ($C_2F_2Cl_2$ (gas) + H_2 (gas) = C_2HF_2Cl (gas) + HCl (gas)) equal to $\Delta H^\circ_{298} = -21,559 \pm 1,0$ kcal, was measured by Lacher and his co-workers [2510]. The value of the heat of formation

$$\Delta H^\circ f_{298,15}(C_2HF_2Cl,\ \text{gas}) = -77,5 \pm 3,0\ \text{kcal/mole}$$

which corresponds to it, is adopted in the present Handbook. To it corresponds

$$D_0(C_2HF_2Cl) = 532,735 \pm 3,3\ \text{kcal/mole}.$$

C_2HFCl_2 (gas). Experimental data which make it possible to determine the heat of formation of fluorodichloroethylene are unknown. According to calculations by means of the simple additive method (see [468]), this value lies between -38 and -41 kcal/mole.* Calculations by Kharasch's method (see [468]) yield a value equal to -38 kcal/mole.

The graphical comparison of the heats of formation of CHF_3, CHF_2Cl, $CHFCl_2$, $CHCl_3$ and C_2HF_3, C_2HF_2Cl, C_2HCl_3 by the Karapet'yants method yields the value

$$\Delta H^\circ f_{298,15}(C_2HFCl_2,\text{gas}) = -39 \pm 3\ \text{kcal/mole},$$

which is adopted in the present Handbook. To this value corresponds

$$D_0(C_2HFCl_2) = 504,505 \pm 3,2\ \text{kcal/mole}.$$

C_2HCl_3 (gas). The heat of combustion of liquid trichloroethylene,

$\Delta Hc_{298.15} = -230{,}029 \pm 0{,}4$ kcal/mole, was determined by Smith and co-workers [3786] by the "quartz helix" method (see [3502, 471]). The findings of Smith and co-workers, combined with the wellknown thermochemical data on the heats of formation of aqueous HCl solutions [3508] yield the value $\Delta H^\circ f_{298.15}(C_2HCl_3$, liqu.) = -9.4 ± 0.4 kcal/mole, to which corresponds*

$$\Delta H^\circ f_{298.15}(C_2HCl_3, \text{gas}) = -1{,}8 \pm 0{,}5 \text{ kcal/mole.}$$

The later value, adopted in the present Handbook, agrees well with the data by Kirkbride [2407] on the heats of chlorination of ethylene and its halogen derivatives. To this value corresponds

$$D_0 (C_2HCl_3) = 477{,}46 \pm 1{,}0 \text{ kcal/mole.}$$

C_2F_4 (gas). The heat of formation of C_2F_4 was first determined by Kirkbride and Davidson [2408] on the basis of the results of calorimetric measurements of the heat of combustion of potassium in gaseous tetrafluoroethylene. The value $\Delta H^\circ f_{298.15}$ (C_2F_4 , gas) = -162 kcal/mole with an uncertainty of ±1 kcal/mole was found in paper [2408]. The authors of paper [2408] point out, however, that the effective uncertainty of the heat of formation of C_2F_4, found by them, may acount to ±5 kcal/ /mole. Shortly after, analogous measurements were carried out by Wartenberg and Schiffer [4169] who found $\Delta H^\circ f_{298.15}$ (C_2F_4 ,gas) = -164 kcal/mole with an uncertainty of ±5 kcal/mole.

Duus [1430] measured the thermal effects of the thermal decomposition, hydrogenation and combustion in oxygen of gaseous tetrafluoroethylene and obtained the following results: 1) C_2F_4 (gas) = C(graphite + CF_4 (gas), $\Delta H^\circ_{298.15} = 61{,}43$ kcal; 2) C_2F_4 (gas) + $2H_2$ (gas) = 2C (graphite) + 4HF (gas), $\Delta H^\circ_{298.15} = -132{,}72$ kcal, and 3) C_2F_4 (gas) + O_2 (gas) = = CO_2 (gas) + CF_4 (gas) $\Delta H^\circ_{298.15} = -151{,}$ kcal. Starting from the heat of hydrogenation of tetrafluoroethylene, Duus calculated $\Delta H^\circ f_{298.15}$ (C_2F_4 , gas) = -151.3 kcal/mole. In paper [1430], the value $\Delta H^\circ f_{298.15}$ (CF_4 , gas) =

-212.7 kcal/mole was calculated on the basis of the heat of thermal decomposition of C_2F_4. Calculations, carried out on the basis of the values of thermal effects of the mentioned reactions, found by Duus, and the thermochemical quantities adopted in the present Handbook, yield the following values; $\Delta H^{\circ}f_{298.15}$ (C_2F_4, gas): -158.6; -151.3, and -156.9 kcal/mole. The significant scattering of the obtained results is caused by an imperfect analysis of the composition of the final reaction products, carried out in [1430], and an insufficient regard for possible side reactions.

Thermochemical investigations of the reactions of thermal decomposition and hyrodenation of gaseous tetrafluoroethylene were also carried out by Neugebauer and Margrave [3050]. These authors analyzed the composition of the reaction products much more accurately than Duus, and carried out a special measurement of the heat of combustion of the carbon formed during the thermal decomposition and hydrogenation of tetrafluoroethylene. On the basis of the value of the thermal effect of the hydrogenation reaction of C_2F_4,* determined in paper [3050], Neugebauer and Margrave calculated $\Delta H^{\circ}f_{298.15}$ (C_2F_4, gas) = -151.7 ± 1.1 kcal/mole. On the basis of this result and the value of the thermal effect of the reaction of thermal decomposition of C_2F_4,** found in paper [3050], Neugebauer and Margrave calculated $\Delta H^{\circ}f_{298.15}$ (CF_4, gas) = = -217.1 kcal/mole. When using the value $\Delta H^{\circ}f_{298.15}$ (CF_4, gas), adopted in the present Handbook, $\Delta H^{\circ}f_{298.15}$ (C_2F_4, gas) = -154.6 kcal/mole corresponds to the heat of thermal decomposition of C_2F_4, found in paper [3050].

The definitive solution of the problem of the true heat of formation of C_2F_4 was obtained by thermochemical investigation of the heat of combustion of sodium in tetrafluoroethylene, carried out by Skuratov, Kolesov and Zenkov [40a]. The method, used earlier by Kirkbride and Davidson [2408] and Wartenberg and Schiffer [4169], was significantly improved in this investigation, strictly observing the whole of the investigated reaction by analysis of the composition of both the initial components and the final products of reaction. Unlike the investigations carried out earlier in [2408, 4169], Skuratov, Kolesov and Zenkov used the lower active sodium instead of potassium and succeeded in avoiding certain side processes. Moreover, in contrast to the investigations [2408, 4169], distinction was drawn between the carbon, formed by combustion of Na in C_2F_4, and graphite, and its heat of combustion was determined in paper [40a]. Corresponding to the thermal effect of the reaction C_2F_4 (gas) + 4Na (solid) = 2C (amorphous) + 4NaF (solid), ($\Delta H^{\circ}_{298.15} = -385.0 \pm 1$ kcal), determined in paper [40a], is $\Delta H^{\circ}f_{298.15}$ (C_2F_4, gas) = -152.6 ± 1.5 kcal/mole,* the value of which agrees excellently with the value determined by Neugebauer and Margrave [3050] by means of the heat of hydrogenation of C_2F_4. All other values obtained for $\Delta H^{\circ}f_{298.15}$ (C_2F_4, gas) are undoubtedly less accurate. In the present Handbook, the value

$$\Delta H^{\circ}f_{298.15}(C_2F_4, \text{gas}) = -152 \pm 2 \text{ kcal/mole}$$

is adopted on the basis of the results of thermochemical investigations obtained in papers [40a, 3050]. The value of the dissociation energy, which corresponds to it, is equal to

$$D_0(C_2F_4) = 564{,}383 \pm 3 \text{ kcal/mole.}$$

C_2F_3Cl (gas). The heat of formation of trifluorochloroethylene was determined in 1954 by Kirkbride and Davidson [2408] by measuring the heat of combustion of potassium in gaseous C_2F_3Cl. Corresponding to the heats of formation of KF and KCl, adopted in the present Handbook (see Table 284), the results of the measurements carried out by Kirkbride and Davidson yield the value

$$\Delta H^{\circ}f_{298.15}(C_2F_3Cl, \text{gas}) = -127 \pm 2 \text{ kcal/mole.}$$

Wartenberg and Schiffer [4169] repeated the measurements carried out by Kirkbride and Davison [2408]. The value of the heat of formation of C_2F_3Cl (-118 kcal/mole), based on the results of [4169], differs by 9 kcal/mole, from the value calculated on the basis of the data of Kirkbride and Davidson. The latter authors, using a more perfect analytical method and a precision measuring technique, were more successful in avoiding side factors which influence the experiment than Wartenberg and Schiffer. Moreover, the results by Kirkbride and Davidson [2408] for other compounds (in particular, for CF_4, CF_3Cl, $CFCl_3$) in contrast to those of Wartenberg and Schiffer, agree well with the most accurate determinations of other authors. Taking this into consideration, the value of $\Delta H^\circ f_{298,15}$ obtained by Kirkbride and Davidsnn, is adopted in the present Handbook. To this value corresponds

$$D_0(C_2F_3Cl) = 549,583 \pm 2,6 \text{ kcal/mole.}$$

$C_2F_2Cl_2$ (gas). The heats of formation of the isomers of difluorodichloroethylene were determined by Wartenberg and Schiffer [4169] by measuring the heat of combustion of potassium in gaseous $C_2F_2Cl_2$. In accordance with the heats of formation of KF and KCl, adopted in the present Handbook (see Table 284), the results by Wartenberg and Schiffer lead to $\Delta H^\circ f_{298,15}$ (cis-$C_2F_2Cl_2$, gas) = -77 ± 2 kcal/mole and $\Delta H^\circ f_{298,15}$ (trans-$C_2F_2Cl_2$, gas) = -79 ± 2 kcal/mole. The comparison of these values with the experimentally determined heats of formation of CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4 and C_2F_4, C_2F_3Cl, C_2Cl_4, by means of the graphic Karapet'yants method proves that they are sufficiently reliable within the indicated limits. Taking into account the fact that the thermal effect of isomerization of $C_2F_2Cl_2$ lies within the limits of the experimental error of [4169], the value

$$\Delta H^\circ f_{298,15}(C_2F_2Cl_2, \text{gas}) = -78 \pm 3 \text{ kcal/mole,}$$

is adopted, which is the mean value of the values for both isomers. Corresponding to the adopted heat of formation of $C_2F_2Cl_2$ is

$$D_0(C_2F_2Cl_2) = 510,805 \pm 3,3 \text{ kcal/mole,}$$

$C_2F_2Cl_3$ (gas). The heat of formation of fluorotrichloroethylene has not been determined experimentally. A comparison of the heats of formation of CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4 and C_2F_4, C_2F_3Cl, $C_2F_2Cl_2$ C_2Cl_4 by means of the graphic Karapet'yants method results in the value

TABLE 168

Values Adopted (in kcal/mole) for the Thermodynamic Quantities of Ethylene and its Fluorine- and Chlorine-Substituted Derivatives in the Gaseous State.

1 Вещество	D_0	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{293.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
C_2H_4	531 208	14 490	12 537	12 500	2465	2516
C_2H_3F	543 726	—31 160	—32 971	—33 000[a]	2652	2712
C_2H_3Cl	511 947	10 669	8 928	8 900	2761	2825
$C_2H_2F_2$	555 281	—75 847	—77 479	—77 500	2875	2945
C_2H_2FCl	522 995	—33 511	—34 985	—35 000[a]	3073	3150
$C_2H_2Cl_2$	497 542	1 992	617	600	3212	3289
C_2HF_3	559 682	—113 380	—114 590	—114 600	3342	3424
C_2HF_2Cl	532 735	—76 384	—77 491	—77 500	3484	3570
C_2HFCl_2	504 505	—38 103	—38 997	—39 000[a]	3738	3830
C_2HCl_3	477 460	—1 008	—1 800	—1 800	3880	3976
C_2F_4	564 383	—151 213	—152 002	—152 000	3807	3903
C_2F_3Cl	549 583	—126 363	—127 005	—127 000	3994	4094
$C_2F_2Cl_2$	510 805	—77 535	—78 006	—78 000	4205	4309
C_2FCl_3	480 983	—37 663	—38 010	—38 000[a]	4369	4477
C_2Cl_4	457 301	—3 931	—4 113	—4 100	4574	4687

[a] Estimate.

1) Substance.

$$\Delta H^\circ f_{298.15}(C_2FCl_3, \text{ gas}) = -38 \pm 3 \text{ kcal/mole},$$

which agrees well with the calculation by the simple additive method* (see [468]). When using the Kharasch method, the value $\Delta H^\circ f_{298}$ (C_2FCl_3, gas) = -39 kcal/mole is obtained. In the present Handbook, the value of the heat of formation of C_2FCl_3, obtained by the Karapet'yants method, is adopted. The value of the dissociation energy of C_2FCl_3, which corresponds to it, is equal to

$$D_0(C_2FCl_3) = 480{,}983 \pm 3{,}2 \text{ kcal/mole}.$$

C_2Cl_4 (gas). In the thermochemical Handbooks [3508, 813], the value $\Delta H^\circ f_{298.15}(C_2Cl_4$, liqu.) = -3 kcal/mole is adopted. As was pointed out by Bichowsky and Rossini [813], this value, based on the data by Berthelot [769] for the heat of combustion of liquid C_2Cl_4, is too low.**

The heat of combustion of gaseous tetrachloroethylene was determined by Thomsen [3983]. According to Thomsen's data [3983], the heat of formation of C_2Cl_4 (gas) is equal to +7.0 kcal/mole. This value cannot be considered as reliable owing to the principal shortcomings of the "universal burner" method used by Thomsen (in detail, see [471]).

In 1953, Smith and co-workers [3786] determined anew the heat of combustion of liquid C_2Cl_4 using the "quartz helix" method.*** The value $\Delta Hc_{298.15}(C_2Cl_4$, liqu.) = -198.622 ± 0.4 kcal/mole was attributed by the authors of [3786] to the following final combustion products: CO_2

(gas), HCl (1 : 600 H_2O). The results of the measurements by Smith and co-workers, combined with the data of the Handbook [3508] lead to the value $\Delta H^\circ f_{298,15}(C_2Cl_4$, liqu.) = -12.4 ± 0.4 kcal/mole, to which corresponds

$$\Delta H^\circ f_{298,15}(C_2Cl_4, \text{gas}) = -4,1 \pm 0,5 \quad \text{kcal/mole},$$

The latter value, adopted in the present Handbook, agrees well with the data by Kirkbride [2407] on the heats of chlorination of ethylene and its chlorine derivatives. To the adopted value of the heat of formation of C_2Cl_4 corresponds

$$D_0(C_2Cl_4) = 457,301 \pm 1,0 \quad \text{kcal/mole}.$$

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1126	Earlier attributions of the fundamental frequencies of C_2H_4, suggested in the papers [2830, 864], have been critically studied by Conn and Sutherland [1160]. Therefore they will not be considered in the present Handbook.
1127	In paper [1547] a spectrograph with linear inverse dispersion of 10.5cm^{-1} at λ 4358 A was used.
1128	After having finished the calculation of the thermodynamic functions of ethylene based on the values of the fundamental of the C_2H_4 molecule adopted in the Handbook (see Tables 156 and 157), the authors learned of the results of an analysis of the fine structure of the ν_{11} band, obtained by Allen and Plyler [510]. In paper [510] the rotational structure of the ν_{11} band is much better resolved than in paper [1646], and its analysis is made with greater preciseness (see page)! The beginning of the ν_{11} band was determined by Allen and Plyler as equal to 2988.66 cm^{-1}, where the error does not exceed ±0.05 cm^{-1}.
1129	A band with its center at 2046.5 cm^{-1} was observed by Levin and Meyer [2597] in the infrared spectrum of gaseous ethylene. A band with its center at 1656 cm^{-1} was observed in the Raman spectrum of gaseous [810, 1547] and liquid [864, 1781]

ethylene as well as in the infrared spectrum of strongly compressed gaseous ethylene [3160].

1130 The attempts undertaken in [1547] to observe the ν_8 band in the Raman spectrum of gaseous ethylene remained without success.

1131 A line at about 3075 cm^{-1} was observed in the Raman spectrum of liquid ethylene [864, 1988, 1781, 3382] and a line at 3272 cm^{-1} in the Raman spectrum of gaseous ethylene [;335]. It must be mentioned, however, that Daure [1269] observed a line at 3080 cm^{-1} in the Raman spectrum of gaseous ethylene.

1132 Eucken and Parts [1503] calculated $\nu_4 \cong 775$ см$^{-1}$ from data on the specific heat of ethylene found by them. Later on, Bonner [864] proposed for the line in the Raman spectrum at 1656 cm^{-1} two attributions possible to his opinion: either to the frequency $\nu_4 + \nu_7$, or to the harmonic $2\nu_4$. In paper [864] the second interpretation was preferred and the frequency ν_4 was estimated as 825 cm^{-1}. Conn and Sutherland [1160] preferred the first interpretation of Bonner for the line at 1656 cm^{-1} and therefore estimated $\nu_4 = 700$ cm^{-1}. In the publications of Wu [4340], of Gallaway and Barker [1646] and of Herzberg [510] the line at 1656 cm^{-1} in the Raman spectrum of C_2H_4 was attributed to the frequency of the harmonic of the torsion vibration and ν_4 was estimated as 825 and 828 cm^{-1}. In the papers [4340, 1646, 152] this estimate is confirmed by making reference to the coincidence with the value of ν_4, estimated from the specific heat of gaseous ethylene [1503, 1019]. The accuracy of this estimate of ν_4 seemed to Herzberg [152] to be also verified by the fact that Rasmussen (according to a preliminary report on the results [3401] and Thompson and Harris [3973] observed a weak band at about 800 cm^{-1}. He considered it very likely that this band belonged to the frequency of the torsion vibration, supposing that the latter may become active in the infrared spectrum in relation with the transition from high rotational levels owing to the Coriolis interaction. But this proposal proved not justified since in papers [3401, 568, 3382] the infrared band about 800 cm^{-1} was shown to belong to the fundamental frequency ν_{10}, and the band at 1656 cm^{-1} observed in the Raman spectrum was the frequency of the harmonic $2\nu_{10}$.

1133* In the first edition of the Handbook we adopted for the fundamental frequencies of C_2H_4 the values recommended by Arnett, Crawford, Rank and others in the papers [568, 3382] (see Table 156), except the frequency ν_5, for which we chose the value of $\nu_5 = 3102.5$ cm^{-1}, obtained by Stoicheff [3872].

1133** Analogous calculations were also made by Crawford, Lancaster and Incskeep [1213].

1134 The reason for this was the similarity of the values of the moments of inertia, I_B and I_C.

1135 The first experimental studies of the structure of the C_2H_4 molecule were carried out by Wierl [4264], who obtained $r_{C=C} = 1,30 \pm 0,10$ Å. with the electron-diffraction method. Later on, Badger [597] determined approximately the principal moments of inertia of C_2H_4, based on the data of Levin and Meyer [2597] and Lewis and Houston [2602] on the fine structure of the bands in the spectra of the ethylene. With the help of these data and the value $r_{C-H} = 1,04$ Å estimated by him, Badger found $r_{C=C} = 1,37$ Å, $\angle H-C-H = 126°$. Penney [3217] proposed a length of the bond C – H of the C_2H_4 molecule equal to 1.08 A, assuming that it must be somewhat smaller than in the CH_4 molecule. Using also the values of the moments of inertia of C_2H_4, determined by Badger [597], Penney calculated $r_{C=C} = 1,33$ Å and $\angle H-C-H = 118°$. Thompson [3968] determined the moments of inertia of C_2H_4 by analyzing the fine structure of the rotation-vibration bands of C_2H_4 with their centers at 10,126 and 10,294 cm^{-1} and from these data and the value $r_{C-H} = 1,085$ Å estimated by him, he calculated $r_{C=C} = 1,331$ Å, $\angle H-C-H = 118°$. Pauling and Brockway [3204] found $r_{C-H} = 1,06 \pm 0,03$, $r_{C=C} = 1,34 \pm 0,02$ Å, $\angle H-C-H = 110 \pm 5°$ as a result of an analysis of electron diffraction pictures by the method of visual curves of the radial distribution.
Gallay and Barker [1646] obtained $r_{C-H} = 1,071$, $r_{C=C} = 1,353$ Å, $\angle H-C-H = 119°55'$ from an investigation of the fine structure of a series of vibration-rotation bands in the infrared spectra of C_2H_4 and C_2D_4. The insufficient accuracy of the values of the structure parameters of C_2H_4, discovered by Gallaway and Barker, is due to the insufficiently high resolution of the rotational structure of the bands and to the application of the theory of the energy level of symmetric rotators and of the approximate relation $\frac{1}{A_0} = \frac{1}{B_0} + \frac{1}{C_0}$ used to determined the rotational constants of C_2H_4.

1137 In the infrared spectrum of C_2F_4 Mann, Acquista and Plyler

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[2753] observed a weak band with a maximum at 205 cm^{-1}, which they ascribed to the frequency ν_4 supposing it active in the infrared spectrum because of the Coriolis interaction with the vibration ν_{10}. In the work of Nielsen, Claasen and Smith [3090] the authors chose $\nu_4 = 210\ cm^{-1}$, based on approximate calculations from the complex frequencies of C_2F_4.

1138 In paper [2753] it is reported that the range of investigation of the infrared spectrum of liquid tetrachloroethylene was extended by Pitzer to 135 cm^{-1}, who observed an intense band at 176 cm^{-1} and a weak band at 152 cm^{-1}.

1139* See [152, 4340, 4002, 760, 2753, 2759, 2758].

1139** This affirmation applies to a large part of frequencies.

1140* In paper [4336] on the infrared spectrum of gaseous tetrachloroethylene only two fundamental frequencies of the molecule C_2Cl_4 ν_9 and ν_{11} were determined.

1140** The work of Lipscomb, accomplished in 1950, has not been published. The values of the structure parameters of C_2Cl_4 discovered by him are given in the summary of Sutton and Allen [517].

1140*** In paper [2328] the sector-microphotometric method was used, and in paper [3387] the sector-visual method.

1141 In 1961 an investigation of the microwave spectrum of cis-difluorethane [2570a] has been published, which resulted in the determination of the values of the rotational constants of the vibrational ground states of the molecules of $C_2^{12}H_2F_2$ $C^{12}C^{13}H_2F_2$ and the following values were obtained for the structural parameters of the molecule of cis-$C_2H_2F_2$: $r_{C=C} = 1{,}324$, $r_{C-F} = 1{,}337$, $r_{C-H} = 1{,}080$ Å, $\angle F-C-C = 122°9'$, $\angle H-C-C = 121°16'$. In paper [2570a] the rotational constants of the excited vibrational state ($\nu_5 = 1$) of the molecule of cis-$C_2^{12}H_2F_2$ were also determined.

1146 In paper [2570a] the structural parameters of the CH_2CF_2 molecule were recalculated according to data of Edgell, Kinsey and Any [1457] and the following values were obtained: $r_{C=C} = 1{,}320$, $r_{C-F} = 1{,}321$ (chosen according to [2327]) $r_{C-H} = 1{,}076$ Å, $\angle F-C-F = 109°26'$, $\angle H-C-H = 121°$.

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1150 If the fundamental frequencies obtained by Torkington and Thompson are used [2975], this agreement is not achieved.

1151 In 1960 Shimitsu and Takuma [3708a] investigated the microwave spectrum of cis-$C_2H_2Cl_2$ in the frequency band of from 20 to 25 Mc. A spectrum analysis enabled the authors of paper [3708a] to determine the values of the principal moments of inertia of the molecules of $CHCl^{35}CHCl^{35}$ and $CHCl^{35}CHCl^{37}$ and the structural parameters of cis-$C_2H_2Cl_2$ ($r_{C-Cl} = 1{,}724$ Å, $\angle C-C-Cl = 121°33'$, under the assumption that $r_{C=C} = 1{,}32$, $r_{C-H} = 1{,}07$ Å, $\angle C-C-H = 120°$).

1152 Nielsen, Claassen and Smith [3089] were the first who measured the degree of polarization of the lines in the Raman spectrum of CF_2CCl_2 and analyzed the band contours in the infrared spectrum.

1154 According to the designations adopted in paper [2761], Fermi resonance takes place between $\nu_5 + \nu_{10}$ and ν_9.

1160 In paper [2949] the analogous transitions to the lowest excited vibrational state, corresponding to the excitation of the torsional oscillation (ν_{12}) were also investigated for the molecule of $C^{13}H_2C^{13}HF$

1161* In 1961 Laurie [2570b] published the values of the structural parameters of the C_2H_3F molecule, recalculated on the basis of data obtained in the papers [626, 2949]: $r_{C=C} = 1{,}332$, $r_{C-F} = 1{,}348$, r_{C-H} (group CHF) $= 1{,}071$, r_{C-H} (CH_2 group) = 1.086 and 1,079 Å, $\angle F-C-C = 121°10'$, $\angle F-C-H = 117°55'$, $\angle H-C-H = 120°31'$, $\angle C-C-H = 120°43'$.

1161** In the papers [626, 2949] the values of the rotational constants B_0 and C_0 of the isotope modifications of the C_2H_3F molecule were determined immediately from the spectroscopic data. Mirri, Guarnieri and Favero [2924a] were the first who, in 1961, obtained an accurate value of the constant A_0 (and the dipole moment) of the C_2H_3F molecule, on the basis of an analysis of the pure rotational spectrum of C_2H_3F in the microwave range, corresponding to the transitions J = 5-6 and J = 7-8: A_0 = 64,582.7 Mc = 2,154243 cm^{-1}. Using the values of the constants B_0 and C_0 obtained by Morgan and Goldstein [2949], the authors of paper [2924a] determined also the values of a series of centrifugal constants of the C_2H_3F molecule.

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1163 According to the terminology suggested by Costain [1186] they are the so-called r_s parameters, intermediate between the structural parameters of the equilibrium configuration (r_e) and the usual r_0 parameters, calculated immediately from the moments of inertia of the vibrational ground state.

1164* In 1961 the results of investigations of the microwave spectra of two isotope modifications of cis-C_2H_2ClF were published [2134a]. The following values of structural parameters correspond to the values of the moments of inertia of $CHCl^{35}CHF$ and $CHCl^{37}CHF$ obtained in paper [2134a]: $r_{C=C} = 1{,}333$, $r_{C-Cl} = 1{,}726$, $r_{C-F} = 1{,}348$, $r_{C-H} = 1{,}079$ Å, $\angle C-C-Cl = 123°{,}6$, $\angle C-C-H = 123°{,}2$, $\angle C-C-F = 121°$.

1164** In paper [3088] the infrared spectrum of CH_2CFCl was obtained in a lower spectral range than in paper [2754] but the results of the spectroscopic measurements proved to be virtually identical with those obtained previously in paper [2754]. Therefore, in paper [3088], Nielsen and Albright published only the values of the fundamental frequencies of the CH_2CFCl molecule, they had determined from the infrared spectrum. The difference between the corresponding values of the fundamental frequencies of CH_2CFCl in the papers [2754, 3088] amounts to 1 cm^{-1} for most of the frequencies, only in the case of ν_{11} and ν_2 it is equal to 3 and 4 cm^{-1}, respectively.

1168 According to these calculations, $r_{C-F} = 1{,}351 \pm 0{,}004$ Å and $\angle F-C-F = 105°36' \pm 1°40'$, correspond to the value $r_{C=C} = 1{,}32$ Å, and $r_{C-F} = 1{,}340 \pm 0{,}005$ Å $\angle F-C-F = 106°50' \pm 1°20'$. correspond to the value $r_{C=C} = 1{,}34$ Å

1172* The results obtained in paper [3772] are cited in papers [2751, 3474].

1172** The results of the investigation of the infrared C_2F_3Cl spectrum in the 110-220 cm^{-1} range are reported in paper [2758].

1174 The calculation was carried out by means of the force constants of the C_2F_4 and C_2Cl_4 molecules.

1180 The tables of thermodynamic properties of ethylene, quoted in the Handbook [137], are based on the calculations by Kilpatrick and Pitzer [2399].

1188 An insignificant difference is present in the values of the adopted moments of inertia.

1193* This formula is stated as following: $\Delta H°f_{298,16}(C_2H_{4-n}F_n, \text{газ}) = 12{,}5 - 46{,}38n + 0{,}688n^2$, $n = 0, 1, 2, 3, 4$.

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1193**	The value $\Delta H^\circ f_{298.15} = 8.889$ kcal/mole is quoted in papers [2508, 2510].
1194*	Repeated measurements of the heat of combustion of asymmetrical difluoroethylene were carried out in 1960 in the Thermochemical Laboratory of MGU [41a], resulting in the values $\Delta H^\circ c_{298.15} = -259.8 \pm 2.4$ and $\Delta H^\circ f_{298.15} = -79.6 \pm 2.4$ kcal/mole.
1194**	The value -32 kcal/mole was obtained in paper [293] by means of the simple additive method.
1195	The value of the heat of evaporation of the isomers of $C_2H_2Cl_2$ at 298.15°K is quoted in the Handbook of the US Bureau of Standards [3508].
1196	$\Delta H^\circ f_{298}$ (C_2HFCl_2 , gas) = -36 kcal/mole was obtained in paper [293] by means of the simple method of addition.
1197	The heat of evaporation of C_2HCl_3 at 298.15°K is quoted in the Handbook of the US Bureau of Standards [3508].
1198*	$C_2F_4(\text{gas}) + 2H_2(\text{gas}) + \text{aq} = 2C(\text{amorphous}) + 4HF(\text{aq})$, $\Delta H^\circ_{298.15} = -63.5$ kcal.
1198**	$C_2F_4(\text{gas}) = 2C(\text{amorphous}) + CF_4(\text{gas})$; $\Delta H^\circ_{298.15} = -63.5$ kcal.
1199	The value of the heat of formation of NaCl, adopted in the present Handbook, is used in the calculations.
1201*	The value -40 kcal/mole, obtained by the simple additive method, is quoted in paper [293].
1201**	This may be explained by the fact that in the work [789] a total reduction of Cl_2 to HCl was not provided for. As later measurements proved, up to 14% of free chlorine remains in the Berthelot bomb after combustion of the chlorine-containing compounds (see [471]).
1201***	See [3502, 471].

Manuscript Page No.	[Transliterated Symbols]
1189	кол = kol = kolebatel'nyy = vibrational
1175	расч = rasch = raschet = calculation
1194	МГУ = MGU = Moskovskiy gosudarstvennyy universitet = Moscow State University.

Chapter 19

ACETYLENE AND THE FLUORINE SUBSTITUTION PRODUCTS OF ACETYLENE

(C_2H_2, C_2HF, C_2F_2)

Acetylene belongs to those substances that were studied in a most detailed manner whereas its fluorine substitution products are not well known substances. At the first stage of preparation of data for the Handbook the experimental data needed to calculate the thermodynamic properties were only known for acetylene. A special work was, therefore, undertaken in order to estimate the molecular constants and the heat of C_2HF and C_2F_2 formation. Fluoroacetylene was obtained for the first time in 1959 [2899, 482]. Difluoroacetylene was not obtained in pure form,* and its properties were not studied experimentally.

It is well known that acetylene and its halogen substitution products polymerize in the gaseous state. In the present Handbook, only monomeric molecules of these compounds are considered.

The radicals C_2H, C_2F and C_2, considered in the Chapters 20 (C_2H, C_2F) and 16 (C_2) are dissociation products of the C_2H_2, C_2F_2 and C_2HF molecules.

§78. MOLECULAR CONSTANTS

C_2H_2. A great number of papers delaing with the investigation of acetylene spectra are known. The results of these investigations show that in the electronic ground state the C_2H_2 molecule has a linear symmetric structure (symmetry point group $D_{\infty h}$). Molecules of this type are characterized by five normal vibrations: three valency vibrations of the Σ_g^+, Σ_g^+ and Σ_u^+ symmetry types and two doubly degenerate deformation vibrations of the Π_g and Π_u symmetry types. The fundamental frequencies of the corresponding vibrations are designated in the present Handbook by ν_1, ν_2, ν_3, ν_4, ν_5. In the infrared spectrum of C_2H_2 the frequencies ν_3 and ν_5, and in yhe Raman spectrum the frequencies ν_1, ν_2 and ν_4 are active.

The studies on the spectra of C_2H_2, but also on those of C_2HD and C_2D_2 carried out up to 1944 were critically reviewed by Herzberg [152]. In this period, the absorption spectra of C_2H_2 were studied in a very detailed way in the photographic range (8700-15,600 cm^{-1}), where the bands corresponding to overtones and composite frequencies lie. The most accurate studies on the C_2H_2 bands in this range were carried out by Levin and Meyer [2597], Herzberg and Spinks [2048], Funke [1629], and Mecke and Ziegler [2833]. The spectrum C_2H_2 in the neighboring infrared range where the bands of the fundamental frequencies and lower overtones lie had been studied very incompletely and inaccurately before the semiconductor photoresistors were introduced into the practice of spectroscopic measurements. Consequently, only recently it became possible to determine sufficiently reliable values of the vibrational constants of C_2H_2.

In the past, repeated attempts were made to determine the vibrational constants of C_2H_2 from the existing spectral data (see [2833, 2048, 1629, 4341, 1809, 4121]). All these attempts, however, cannot be considered statisfactory since they were based on unreliable and incomplete results of studies on bands lying in the neighboring infrared range and were carried out without allowing for the resonance between the vibrational states of C_2H_2. Herzberg [152] was the first to point out the fact that between the vibrational states of the C_2H_2 molecule of the form ν_1, ν_2, ν_3, $\nu_4^{\ell_4}$, $\nu_5^{\ell_5}$, and ($\nu_1 + 2$, ν_2, $\nu_3 - 2$, $\nu_4^{\ell_4}$, $\nu_5^{\ell_5}$) an anharmonic resonance interaction analogous to the Darling-

Dennison resonance in the H_2O molecule must exist. This assumption was verified by Nordin and Haslam [3101], who determined the resonance interaction constant of C_2H_2 equal to 52.65 cm^{-1}.

In 1950, Bell and Nielsen [719] and Talley and Nielsel [3920] began a detailed study on the bands of C_2H_2 lying in the nearby infrared range. Bell and Nielsen [719] investigated the infrared spectrum of C_2H_2 in the range from 625-4000 cm^{-1} and carried out a partial analysis of the rotational structure of 30 bands in this range. The authors of the work [719] assigned these bands and approximately determined the band heads, which permitted an estimate of the values of some anharmonicity constants of C_2H_2. Talley and Nielsen [3920] studied the spectral range from 4300 to 8500 cm^{-1}, in which they discovered 19 bands. In the work [3920] the wave numbers of the zero lines of these bands and their assignment are given.

Allen, Tidwell and Plyler [515] obtained the infrared spectrum of C_2H_2 in the range from 1900 - 8500 cm^{-1} with considerably higher resolution* than in the works [719, 3920], which permitted them to carry out a more comprehensive analysis of the rotational structure of 28 bands in this range. In particular, in the work [515] the zero lines of 28 bands re determined, and their assignment to the vibrational frequencies of the C_2H_2 molecule is given. On the basis of these data, the frequency $\nu_4^1 + \nu_5^1$ and the values of the frequencies ν_1 and ν_2 found by Bell and Nielsen [719] and adopted in the book by Herzberg [152], Allen, Tidwell and Plyler calculated the values of 22 vibrational constants in the quadratic expression for the unperturbed levels of the vibrational energy of C_2H_2, as well as the value of the resonance interaction constant $W_D = 49$ cm^{-1} between the vibrational states $(v_1, v_2, v_3, v_4^{\ell_4}, v_5^{\ell_5})$ and $(v_1 + 2, v_2, v_3 - 2, v_4^{\ell_4}, v_5^{\ell_5})$. With the help of these vibrational constants, however, the experimental values of the vibrational levels of C_2H_2 connected with the excitation of deformation vibrations cannot be reproduced exactly enough. Thus, the discrepancies between the experimentally found values of the levels $(0, 0, 0, 2^2, 1)(0, 1, 0, 4^0, 1^1)$, $(1, 3, 0, 3^1, 1^1)$ and $(1, 3, 0, 5^1, 1^1)$ and those calculated are, respectively, equal to 16.23; 40.0; 53.99 and 113.21 cm^{-1}. Allen, Tidwell and Plyler expressed the assumption that these discrepancies are due to the existence of a resonance interaction between the vibrational states $(v_1, v_2, v_3, v_4^{\ell_4}, v_5^{\ell_5})$ and $(v_1, v_2, v_3, (v_4 + 2)^{\ell_4}, (v_5 + 2)^{\ell_5})$. Without excluding the possibility of other resonance interactions between the vibrational states of the C_2H_2 molecule, besides the Darling-Dennison resonance, it is hardly possible to agree with the explanation of the essential discrepancies between the experimental and calculated values of the C_2H_2 vibrational energy levels, as proposed by Allen, Tidwell and Plyler, since the values of the vibrational constants of C_2H_2 obtained in the work [515] are not exact enough.

In order to represent the dependence of the vibrational energy levels of C_2H_2 on the vibrational quantum numbers, Allen, Tidwell and Plyler assumed a quadratic expression* which Shaffer and Nielsen [3690] had founded theoretically for lineal X_2Y_2 molecules in the second approximation of quantum-mechanical perturbation theory. If, however, the differences between the series of experimental values of the C_2H_2 vibrational energy levels corresponding to the variation of any vibrational quantum number are considered it is not difficult to satisfy oneself of the fact that even for lower levels terms proportional to the third power of the quantum numbers v_n must be taken into account. Some of them were used to supplement the quadratic expression for $G_0(v_1, v_2, v_3, v_4^{\ell_4}, v_5^{\ell_5})$ also in the earlier attempts to determine the vibrational constants of C_2H_2 [2048, 1629, 4341]. The necessity of taking account of these terms in the expression for the vibrational energy levels of C_2HD was shown in the work [514] by Allen, Tidwell and Plyler. Besides, even the quadratic expression for $G_0(v_1, v_2, v_3, v_4^{\ell_4}, v_5^{\ell_5})$, used in the work [515] to obtain the vibrational constants C_2H_2, is not complete. Keller, Nielsen and Shaffer [2351, 2352] showed that in the derivation of this expression in the work [3690] fourth-power terms were not taken into account in the expansion of the potential energy of the linear X_2Y_2 molecules with respect to powers of the relative displacements of the atoms. If these terms are taken into account, the quadratic expression for G_0 $(v_1, v_2, v_3, v_4^{\ell_4}, v_5^{\ell_5})$ obtained in the work [3690] is supplemented by the term $g_{45}l_4l_5$. The value of the constant g_{45} was determined by Keller, Nielsen and Shaffer [2352] from the zero lines of some bands, and by Coburn, Rao and Nielsen [1140] on the basis of an analysis of the rotational structure of the $v_4 + v_5$ band. According to calculations carried out in the work [2352] $g_{45} = 4.91$ cm^{-1}, whereas in the work [1140] the value of $g_{45} = 9.8$ cm^{-1} was found.

Additional data on the vibration frequencies of the C_2H_2 molecule were obtained by Feldman, Shepherd and Welsh [1548], who studied the rotational structure of the v_1, v_2 and v_4^1 bands, and by Coburn, Rao and Nielsen [1140], who investigated the rotational structure of the $v_4^1 + v_5^1$ band. The results of these studies agree with the corresponding results of an investigation carried out by Allen, Tidwell and Plyler [515].

In the present Handbook, the values found by Allen, Tidwell and Plyler in the work [515] and supplemented by allowing for the constant y_{444} (see Table 169) were adopted for the vibrational constants of C_2H_2. This constant must be taken into account since the anharmonicity constant x_{44} of the C_2H_2 molecule has a positive value as was not only shown in the work [515], but also in the works [1629, 719, 2176]. Consequently, if we restrict ourselves to the purely quadratic approximation of the vibrational energy levels of C_2H_2, the energy levels of the states (0, 0, 0, v_4, 0) prove to increase unlimitedly if the quantum number v_4 grows gradually. This is in contradiction to the experimental facts on the limited stability of the C_2H_2 molecule and leads to difficulties and errors in the calculation of the thermodynamic functions of acetylene when account is taken of the anharmonicity of vibrations at high temperatures. If the quadratic expression for G_0 $(v_1, v_2, v_3, v_4^{\ell_4}, v_5^{\ell_5})$ is supplemented by the term $y_{444} \cdot v_4^3$, these difficulties are eliminated and the aforementioned discrepancies between the experimental and calculated values of the vibrational energy levels of C_2H_2 are reduced.

TABLE 169

Adopted Values (in cm^{-1}) of the Molecular Constants of C_2H_2 in the Electronic Ground state

Постоянная 1	Значение 2	Постоянная 3	Значение 4	Постоянная 5	Значение 6
$\omega_1^{\bullet}$	3397,78	x_{12}	−16,94	y_{444}	−1
$\omega_2^{\bullet}$	1981,72	x_{13}	−99,01	g_{44}	−1,10[a]
$\omega_3^{\bullet}$	3307,62	x_{14}	−16,46	g_{55}	+2,49
$\omega_4^{\bullet}$	608,28	x_{15}	−11,75	B_0	1,17658
$\omega_5^{\bullet}$	729,03	x_{23}	− 1,38	α_1	0,00692
x_{11}	−24,08	x_{24}	− 6,15	α_2	0,00635
x_{22}	− 7,92	x_{25}	− 0,85	α_3	0,00549
x_{33}	−25,69	x_{34}	− 9,06	α_4	−0,0021
x_{44}	+ 5,38	x_{35}	− 5,73	α_5	−0,0022
x_{55}	− 2,27	x_{45}	−12,65	D_0	$1{,}0 \cdot 10^{-4}$

[a] In the work [515] the erroneous value of +1.10 cm^{-1} is given for g_{44}. 1) Constant; 2) value; 3) constant; 4) value; 5) constant; 6) value.

The value of the constant y_{444} given in Table 169 was calculated on the basis of the differences between the experimental values of the vibrational energy levels (0104^01^1), (1303^11^1) and (1305^11^1) and the values calculated with the help of the vibrational constants of C_2H_2 obtained in the work [515] (see page 1214). Table 169 does not give the value of the constant g_{45} since it was not taken into account by Allen, Tidwell and Plyler [515] in obtaining the vibrational constants of C_2H_2. An introduction of this constant into the calculation of the vibrational energy levels of C_2H_2 would require a new determination of the values of all vibrational constants.

The rotational constants B_{00000} and D_{00000} of the C_2H_2 molecule were determined in the works [2048, 1629, 2833, 719, 515, 1548, 1140, 4265 1101, 1049] on the basis of the results of a study on the structure of the rotational and vibration-rotation spectra of C_2H_2 obtained with high resolution by the methods of infrared spectroscopy [2048, 1629, 2833, 719, 515, 1140, 4265, 1101] and Raman effect [1548, 1049]. The values of the constants B_{00000} and D_{00000} of the C_2H_2 molecule obtained in the mentioned works agree with each other. In the present Handbook, the values determined by Wiggins, Shearer, Shull and Rank [4265] as a result of analyzing the rotational structure of the Q branch of the $\nu_1 + \nu_5^1$ band obtained with a resolution into 145,000 are adopted for these constants (see Table 169).

The vibration-rotation interaction constants α_i were determined in the works [2048, 1629, 2833, 1548, 1101]. The values of these constants given in Table 169 were determined by Christensen, Eaton, Green and Thompson [1101], who carried out a careful analysis of the rotational structure of the C_2H_2 bands in the range from 625 to 3340 cm^{-1}, and calculated the values of the corresponding constants of the C_2HD and C_2D_2 molecules. The authors of the work [1101] found a value for B_{00000} which coincides within the limits of accuracy of their determination with the more accurate value of this quantity obtained in the work [4265], and calculated B_e and the equilibrium values of the bond lengths in the C_2H_2 molecule: $r_e(C-H) = 1.0585$, $r_e(C \equiv C) = 1.2047$ A. Very similar values of these quantities are given in the monograph by Herzberg [152] and in the work [3156a].*

A survey of the studies on the ultraviolet spectrum of C_2H_2 carried out up to 1953 is given in the works by Walsh [4141] and Ingold and King [2173]. In the following years, a detailed investigation of the electronic band systems of C_2H_2 in the ultraviolet range (1970-2500 A) was carried out by Ingold and King [2173] and Innes [2176]. Wilkinson [4274] studied the band systems of C_2H_2 in the range from 1280-1520 Å. A theoretical analysis of the problem of the possible electronic states of the C_2H_2 molecule was carried out by Walsh [4141] and Mulliken [3002] on the basis of the results of studies on the infrared spectrum, and quantum-mechanical calculations of the excitation energies of the electronic states of C_2H_2 were carried out by Ross [3489]** and Howard and King [2134].***

Ingold and King [2173] carried out a detailed investigation of the C_2H_2 band system in the wavelength range from 1970-2500 Å; this system corresponds to transitions from the electronic ground state $^1\Sigma_g^+$ into the first excited electronic state ^1A_u. On the basis of a theoretical analysis [2174] Ingold and King [2173] showed that in the first excited electronic state ^1A_u the C_2H_2 molecule has a curved plane <u>trans</u> configuration corresponding to the symmetry point group C_{2h} and determined the values of the rotational constants and structural parameters of the C_2H_2 molecule in this state. In the following, the band system $^1A_u \leftarrow {}^1\Sigma_g^+$ was studied in detail by Innes [2176] with the help of spectrograms obtained with a considerably higher resolution than those obtained by Ingold and King [2173]. An analysis of the C_2H_2 spectrum carried out by Innes [2176] verified the fundamental results obtained by Ingold and King [2173] increased their accuracy and supplemented them by several new results. Innes [2176] carried out an analysis of the rotational spectrum of the band system $^1A_u \leftarrow {}^1\Sigma_g^+$, which permitted bim to determine the excitation energy of the state ^1A_u (ν_{00} = 42197.69 cm^{-1}), the values of the rotational constants and the vibration frequencies ν_2 and ν_3 of the C_2H_2 molecule in the excited electronic state ^1A_u.* The structural parameters of the C_2H_2 molecule in the excited state ^1A_u are the following, according to data obtained by Innes [2176]: r_0 (C – H) = 1.08 ± 0.01, r_0 (C ≡ C) = 1.388 ± 0.008 A, ∠C – C – H = 120 ± 2°. (as to the results of the works [2173, 2176] see also [4276b]).

C_2F_2, C_2HF. The molecular properties of fluoro acetylene and difluoro acetylene can be roughly estimated by a comparison of the experimental data obtained for C_2H_2, C_2Cl_2, C_2HCl, C_2DCl, C_2Br_2 and C_2I_2. The results of the corresponding estimates for the fundamental frequencies of C_2HF proved to be in good agreement with the experimental values of these quantities found from the infrared spectrum of C_2HF [2899, 482]. This enables us to assume that the hypotheses made in the present Handbook on the structure and vibrational frequencies of the C_2HF and C_2F_2 molecules are close to reality.

In the present Handbook we assume that in the electronic ground state the C_2F_2 and C_2HF molecules have a linear structure, as well as the studied molecules C_2H_2, C_2Cl_2, C_2HCl, C_2Br_2, C_2HBr, and C_2I_2. For C_2HF this assumption is verified by the clear results of the spectral studies (see below).

The ≡C – H bond length in C_2H_2 is equal to 1.0585 Å [1101], in C_2HCl equal to 1.0525 Å [4220], in C_2HCN, C_2HCH_3, C_2HCF_3 equal to 1.056 Å [164], i.e., varies within very narrow limits. The given data enable us to assume that within the limits of accuracy of ± 0.005 Å the ≡C – H bond length in C_2HF is equal to 1.055 A.

The ≡C – F bond length in the C_2F_2, C_2HF and FCN molecules must have very similar values. This statement follows from a comparison of the experimental values of the ≡C – X (X = H, Cl, Br, J) bond lengths in the molecules of the XCN, C_2X_2, C_2HX and CH_3C_2X types, given in Table 170.

TABLE 170

Experimental Values (in Å) of the ≡C – X (X = = H, Cl, Br, J) bond lengths in the molecules of the XCN, C_2X_2, C_2HX and CH_3C_2X types.

≡C – X	XCN	C_2X_2	C_2XH	CH_3C_2X
≡C – H	1,064 [164]	1,0585 [1101]	1,0585 [1101]	1,056 [164]
≡C – Cl	1,629 [164]	1,640 [517]	1,632 [4220]	1,637 [164]
≡C – Br	1,790 [164]	1,80 [101]	1,80 [517]	1,793 [164]
≡C – J	1,995 [164]	2,03 [101]	—	1,991 [164]

Such a comparison permits the assumption that the ≡C – F bond lengths in the C_2F_2, C_2HF and FCN molecules are equal within the limits of ±0.01 A. The ≡C – F bond length in the FCN molecule is estimated within 1.28 ± 0.02 A. (see page 1323). The same value is adopted also for the ≡C – F bond length in the C_2F_2 and C_2HF molecules. A comparison of the experimental values of the C – H bond lengths in the C_2H_6, C_2H_4 and C_2H_2 molecules and the C – F bond lengths in the C_2F_6 and C_2F_4* molecules shows that the adopted value for the ≡C – F bond length in the C_2F_2 and C_2HF molecules is correct.

The triple bond length –C ≡ C varies only slightly if the hydrogen atoms in the acetylene molecule are replaced by halogen or other radicals. According to [1101], the –C ≡ C– bond length in the C_2H_2 molecule is equal to 1.2047 A. The –C ≡ C– bond length in the C_2HCl and CH_3C_2Cl molecules was determined equal to, respectively, 1.211 and 1.2069 A, on the basis of a study on the microwave spectra of their isotopic modifications [4220, 164]. If these data on the –C ≡ C– bond lengths are compared with the values of the force constant of the stretching of the –C ≡ C– bond in the C_2H_2, C_2HF and C_2HCl* molecules, we have to admit that the $r_{c\equiv c}$ (C_2H_2) bond lengths in the C_2F_2 and C_2HF molecules must be very similar to –C ≡ C–, but somewhat shorter than the latter. In the present Handbook, the –C ≡ C– bond length in the C_2F_2 and C_2HF molecules is adopted equal to 1.20 ± 0.01 A.

Like the C_2H_2 molecule, the molecules C_2F_2 and C_2HF have five fundamental frequencies: three frequencies ν_1, ν_2, ν_3 of the valency vibrations and two frequencies of the deformation (doubly degenerate) vibrations ν_4, ν_5. In the case of C_2F_2 the frequencies ν_1 and ν_3 correspond to the symmetric and antisymmetric valency vibrations accompanied by a change of the C – F bond length. In the case of C_2HF, a vibration connected basically with a stretching of the C – H bond length corresponds to the frequency ν_1, whereas a vibration accompanied by a stretching the C – F bond corresponds to the frequency ν_3. Frequencies with a stretching of the –C ≡ C– bond correspond to the frequency ν_2 of the C_2F_2 and C_2HF molecules.

The C_2F_2 and C_2HF molecules belong to the symmetry point groups $D_{\infty h}$ and $C_{\infty v}$, for which reason the selection rules for the vibrational frequencies of these molecules are different. If the selection rules of the C_2F_2 molecule are analogous to the selection rules of C_2H_2 (see page 1211), all fundamental frequencies are active both in the infrared spectrum and in the Raman spectrum in the case of the asymmetric C_2HF molecule.

Middleton and Sharkey [2899] obtained the infrared absorption spectrum of gaseous fluoro acetylene in the range from 665-6500 cm^{-1}, and Yakubovich, Smirnov and Dubov [482] in the range from 665-4000 cm^{-1}.

The microphotometric curve of the C_2HF spectrum given in the work [2899] shows nine bands of moderate and strong intensities with centers at 730, 951, 1058, 1150, 2110, 2230, 3355, 3875 and 6330 cm^{-1}. In the work [2899] we find the remark that the most intense bands with centers at 3355, 2230 and 1058 cm^{-1} correspond to the fundamental frequencies ν_1, ν_2, ν_3 of the C_2HF molecule. The rest of the frequencies in the spectrum of C_2HF was not interpreted by Middleton and Sharkey.

Up to the publication of the works [2899, 482] the authors of the Handbook calculated the fundamental frequencies of the C_2HF molecule with the help of the approximate values of the force constants.* The values of the frequencies ν_1, ν_2, ν_3 calculated in this way proved to be similar to the experimental values of the centers of the corresponding bands in the infrared spectrum [2899]. Using the results of these calculations and taking into account the form of the band outlines in the infrared spectrum of C_2HF, it proved to be possible to assign the remaining six intense bands in the infrared spectrum of C_2HF. The bands with the centers at 730, 951, 1150, 2110, 3875 and 6330 cm^{-1} were assigned, respectively, to the frequencies $2\nu_5$, $\nu_4 + \nu_5$, $2\nu_4$, $2\nu_3$, $\nu_1 + \nu_4$ and $2\nu_1$.

On the basis of this assignment for the fundamental frequencies of the C_2HF molecule the values given in Table 171 are adopted in the Handbook.** The values of the frequencies ν_1, ν_2, ν_3 were determined from the centers of the corresponding bands of the infrared spectrum [2899], and the values of ν_4, ν_5 from the band centers of the overtones $2\nu_4$ and $2\nu_5$. Table 171 gives also the value of the principal moment of inertia of the C_2HF molecule, calculated on the basis of the values of the structural parameters given above.***

From the experimental values of the frequencies ν_1, ν_2, ν_3 of the C_2HF molecule given in Table 171 and Eqs. (P4.34) the values of the

Force constants f_{d_2}, f_{d_3}, $f_{d_2d_3}$, corresponding to a stretching of the —C≡C— and ≡C—F bands and their mutual interaction, can be calculated if the values of the constants f_{d_1} and $f_{d_1d_2}$ corresponding to a stretching of the ≡C—H band and the interaction of the —C≡C— and ≡C—H bands are fixed. Assuming that the constants f_{d_1} and $f_{d_1d_2}$ of the C_2HF molecule are equal to the corresponding constants of C_2H_2: $f_{d_1} = 5.90$, $f_{d_1d_2} = -0.302\cdot10^5$ dyn·cm^{-1}, we obtain $f_{d_2} = 17.62$, $f_{d_3} = 7.79$ and $f_{d_2d_3} = 1.005\cdot10^5$ dyne·cm^{-1}. The calculations from Eqs. (P4.34), based on the values of the deformation vibration frequencies ν_4 and ν_5 shown in Table 171 and using the adopted values of the structural parameters of the C_2HF molecule, yield the following values of the force constants f_{α_2} and f_{α_2}: $f_{\alpha_1} = 0.256$, $f_{\alpha_2} = 0.190\cdot10^5$ dyn·cm^{-1}.

TABLE 171

Adopted Values of the Molecular Constants of C_2HF C_2F_2

Молекула 1	ν_1	ν_2	ν_3	$\nu_4(2)$	$\nu_5(2)$	I	σ
	см$^{-1}$ 2					10^{-39} г·см^2 3	
C_2HF C_2F_2	3355 2400	2230 800	1058 1350	365 450	575 200	8,7 23,7	1 2

1) Molecule; 2) cm^{-1}; 3) g·cm^2.

If we assume the force constants of the C_2F_2 molecule to be equal to the corresponding force constants of the C_2HF molecule and carry out the calculations with the help of Eqs. (P4.35), we obtain the following values (in cm^{-1}) for the fundamental frequencies of the C_2F_2 molecule: $\nu_1 = 2366$, $\nu_2 = 781$, $\nu_3 = 1340$, $\nu_4 = 480$, $\nu_5 = 190$. Except for ν_1, the given frequency values are close to the values of the fundamental frequencies of C_2F_2 adopted in the first edition of the Handbook on the basis of a rough estimate of the force constants ($\nu_1 = 2550$, $\nu_2 = 780$, $\nu_3 = 1400$, $\nu_4 = 475$, $\nu_5 = 180$ cm^{-1}). Since the errors in the calculated values of the valency vibration frequencies of C_2F_2 (ν_1, ν_2, ν_3) are of the order of ±100 cm^{-1}, and those of the deformation vibration frequencies (ν_4, ν_5) are of the order of ±50 cm^{-1}, the present Handbook gives rounded-off values of the fundamental frequencies of C_2F_2, as shown in Table 171. This table also gives the value of the principal moment of inertia adopted in the Handbook and based on the afore-indicated assumption on the structure of this molecule.

§79. THERMODYNAMIC FUNCTIONS OF THE GASES

The thermodynamic functions of C_2H_2, C_2HF and C_2F_2 calculated in the temperature interval from 293.15-6000°K for the corresponding perfect gases are given in the Tables 212, 217 and 215 of Volume 2 of the Handbook. For C_2H_2 Table 417 (2) gives the values of the virial coefficients and their derivatives.

C_2H_2. The thermodynamic functions of gaseous acetylene given in Table 212 (2) were calculated taking account of the anharmonicity of the vibrations and the centrifugal stretching of the C_2H_2 molecules by means of Gordon's method (see formulas (II.195), (II.196)) with the help of the molecular constants given in Table 169. The excited electronic states of C_2H_2 were not taken into account in the calculations since the influence of these states on the values of the thermodynamic functions of C_2H_2 is much smaller than their errors. The vibrational components of C_2H_2 corresponding to a deformation vibration with the frequency ν_4, but also the quantities $\bar{\nu}4$, $\bar{\nu}_4^2$, $\bar{s}_4$ and $\bar{s}_4^2$ were calculated by an immediate summation over the Gordon formulas for degenerate vibrations. In doing so, the values of $G_0(0, 0, 0, \nu_4, 0)$ were determined according to the data of Table 169 taking into account of the cubic term $y_{444} \cdot \nu_4^3$. The maximum value of the vibrational quantum number ν_4 was assumed to be equal to 16 on the basis of solving an equation of the form (I.14b). The rest of the vibrational components was determined in the usual way from the tables of the thermodynamic functions of the harmonic oscillator and the corrections to the anharmonicity of the vibrations. The values of the constants in Eqs. (II.195), (II.196), (II.247) and (II.248), calculated with the help of the values of the molecular constants adopted in Table 169 are given in Table 172.

TABLE 172

Values of the Constants Used to Calculate the Thermodynamic Functions of C_2H_2[a]

Постоянная 1	Значение 2	Постоянная 3	Значение 4	Постоянная 5	Значение 6	Постоянная 7	Значение 8
θ_1	4923,34, град	a_2	$5,397\cdot10^{-3}$	c_{14}	$-21,00\cdot10^{-4}$	$y_{15}\cdot T$	16,906, град
θ_2	2862,67, град	a_3	$4,666\cdot10^{-3}$	c_{15}	$-21,99\cdot10^{-4}$	$y_{23}\cdot T$	1,986, град
θ_3	4795,93, град 9	a_4	$-1,785\cdot10^{-3}$	c_{23}	$50,36\cdot10^{-4}$	$y_{24}\cdot T$	8,849, град
θ_5	1052,19, град	a_5	$-1,870\cdot10^{-3}$	c_{24}	$-19,27\cdot10^{-4}$	$y_{25}\cdot T$	1,223, град
x_{11}	$7,037\cdot10^{-3}$	b_{11}	$34,59\cdot10^{-4}$	c_{25}	$-20,18\cdot10^{-4}$	$y_{34}\cdot T$	13,035, град
x_{22}	$3,981\cdot10^{-3}$	b_{22}	$29,13\cdot10^{-4}$	c_{34}	$-16,66\cdot10^{-4}$	$y_{35}\cdot T$	8,244, град 9
x_{33}	$7,707\cdot10^{-3}$	b_{33}	$21,77\cdot10^{-4}$	c_{35}	$-17,45\cdot10^{-4}$	$y_{45}\cdot T$	18,201, град
x_{55}	$3,104\cdot10^{-3}$	b_{44}	$3,19\cdot10^{-4}$	c_{45}	$6,675\cdot10^{-4}$	$y_{l_4}\cdot T$	−0,1102, град
$q_0\cdot T^{-1}$	0,59072, $град^{-1}$ 9	b_{55}	$3,50\cdot10^{-4}$	$y_{12}\cdot T$	24,373, град	$y_{l_5}\cdot T$	−5,275, град
$d_0\cdot T^{-1}$	$1,004\cdot10^{-4}$, $град^{-2}$	c_{12}	$63,48\cdot10^{-4}$	$y_{13}\cdot T$	142,455, град 9	C_Φ	0,0093, кал/моль·град
a_1	$5,881\cdot10^{-3}$	c_{13}	$54,88\cdot10^{-4}$	$y_{14}\cdot T$	23,682, град 9	C_S 10	6,9647, кал/моль·град

[a] The vibrational components of the thermodynamic functions corresponding to the frequency ν_4 were calculated by immediate summation 1) Constant; 2) value; 3) constant; 4) value; 5) constant; 6) value; 7) constant; 8) value; 9) degree; 10) cal·mol^{-1}.

The errors in the values of the thermodynamic functions of C_2H_2 given in the Tables 212 (2) for $T \leq 1500$°K are mainly due to the inaccuracy in the adopted values of the vibrational constants. At higher temperatures the errors are also due to the approximation method of calculation and, in particular, to the fact that the restriction with respect to J was not taken into account, but also that terms proportional to the third and higher powers of the vibrational quantum numbers were neglected in the power expansions of $Q^{(X)}_{kol.vr}$. The total errors in the values of Φ_T^* of acetylene at T = 298.15; 3000 and 6000°K are estimated within 0.01; 0.2 and 0.5 cal·mol^{-1}·deg, respectively.

The thermodynamic functions of acetylene were calculated in many works and are presented in several Handbooks and monographs. In Table 173, we find a list of the works in which calculations of the thermodynamic functions of C_2H_2 with the help of the molecular constants were carried out, but also the Handbooks and monographs in which the results of the corresponding calculations are given are enumerated.

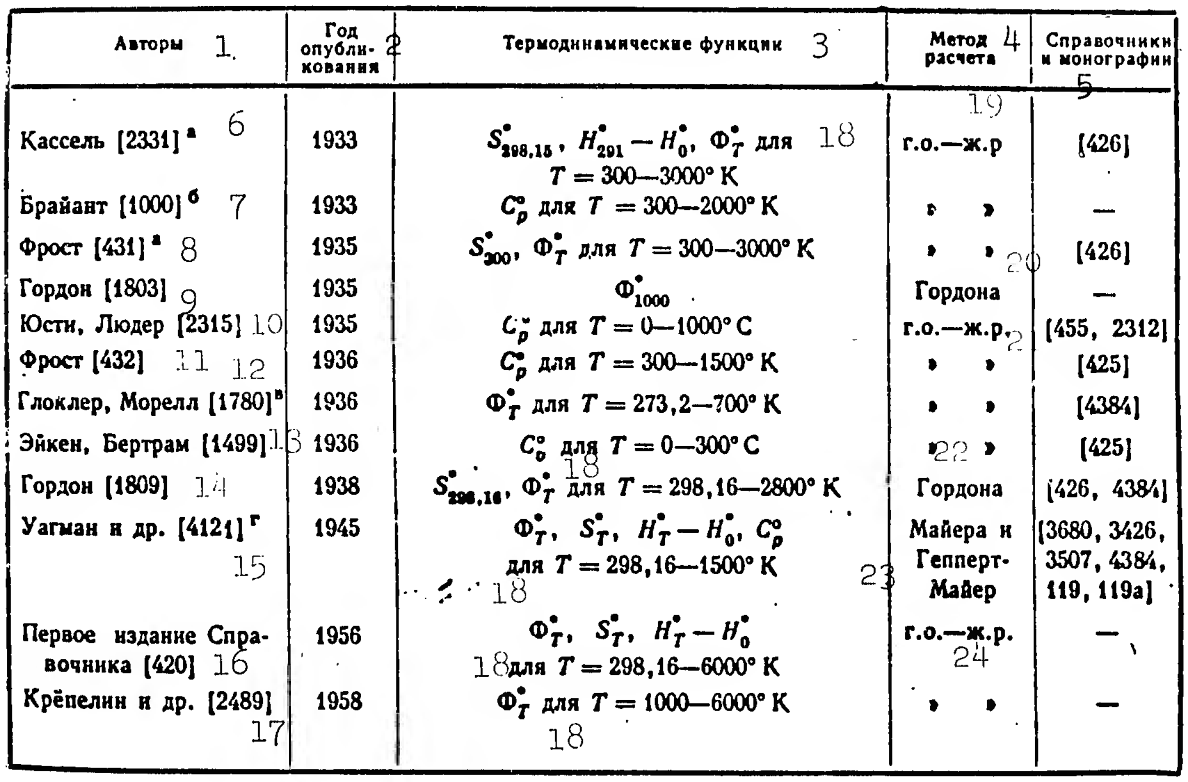
It follows from Table 173 that in the majority of works the thermodynamic functions of C_2H_2 were calculated in the approximation of the harmonic oscillator-rigid rotator model (g.o. – zh.r.). The thermodynamic functions of C_2H_2 were calculated by Gordon [1803, 1809] and Wagman, Kilpatrick, Pitzer and Rossini [4121] taking account of the anharmonicity of vibrations, the vibration-rotation interaction and the centrifugal stretching. In the Handbook [426] Frost compared the values of Φ_T^* calculated in the works [2331, 431] in the approximation of the harmonic oscillator-rigid rotator model, with values of Φ_T^* calculated in the work [1809] taking the anharmonicity of the vibrations into account. This comparison showed that at T $\leq$ 1000°K the influence of the vibrational anharmonicity on the values of the thermodynamic functions of C_2H_2 is unimportant. At 2800°K the contribution of the vibrational anharmonicity to the value of Φ_{2800}^* is about 0.5 cal/mol^{-1}·deg.

The vibrational anharmonicity and other deviations from the harmonic oscillator-rigid rotator model were taken into account in the work [1809] according to Gordon's method, and in the work by Wagman et al. [4121] according to Mayer and Goeppert-Mayer. The anharmonicity constants of C_2H_2 adopted in the works [1809, 4121] were calculated by the authors of these works from the insufficient and inaccurate data of the works [2833, 1630, 4342] on the vibration frequencies of the C_2H_2 molecule and without taking account of the Darling-Dennison resonance between the vibrational states. Consequently, the individual values of the anharmonicity constants of C_2H_2 adopted in the works [1809, 412] are widely different from the values of the corresponding quantities adopted in the present Handbook. All these constants, however, permitted the influence of the vibrational anharmonicity on the values of the thermodynamic functions to be taken into account approximately. Consequently, in spite of the considerable differences in the adopted values of the molecular constants, the thermodynamic functions of C_2H_2 calculated by Gordon [1809] do not differ considerably from those given in Table 212 (2).* At the same time, the values of the thermodynamic functions of C_2H_2 obtained in the work [4121] essentially from those given in Table 212 (2). The discrepancies between them increase with rising temperature and attain 0.311 cal/mol^{-1} ·deg. at a value of Φ^*_{1500}. We must note that the values of the thermodynamic functions of C_2H_2 obtained in the work [4121] are lower than those calculated in the approximation of the harmonic oscillator-rigid rotator model. This attests to the fact that the method by which the vibrational anharmonicity of C_2H_2 was taken into account and which was used by the authors of the work [4121] is not satisfactory or that errors were committed in this work.

In the first edition of the Handbook the thermodynamic functions of acetylene were calculated in the approximation of the harmonic oscillator-rigid rotator model. For this reason, discrepancies attaining 0.7 cal/mol^{-1}·deg at T = 6000°K for Φ^*_T exist between the values of the thermodynamic functions of C_2H_2 as given in Table 212 (2) and in the first edition of the Handbook.

TABLE 173

Summary of the Data on the Calculations of the Thermodynamic Functions of Gaseous Acetylene



Авторы 1	Год опубликования 2	Термодинамические функции 3	Метод расчета 4	Справочники и монографии 5
Кассель [2331] [а] 6	1933	$S^\circ_{298,15}$, $H^\circ_{291}-H^\circ_0$, Φ°_T для 18 $T = 300$—$3000°$ K	19 г.о.—ж.р	[426]
Брайант [1000] [б] 7	1933	C°_p для $T = 300$—$2000°$ K	» »	—
Фрост [431] [а] 8	1935	S°_{300}, Φ°_T для $T = 300$—$3000°$ K	» » 20	[426]
Гордон [1803] 9	1935	Φ°_{1000}	Гордона	—
Юсти, Людер [2315] 10	1935	C°_p для $T = 0$—$1000°$ C	г.о.—ж.р. 21	[455, 2312]
Фрост [432] 11	1936	C°_p для $T = 300$—$1500°$ K	» »	[425]
12 Глоклер, Морелл [1780] [в]	1936	Φ°_T для $T = 273{,}2$—$700°$ K	» »	[4384]
Эйкен, Бертрам [1499] 13	1936	C°_v для $T = 0$—$300°$ C	» 22 »	[425]
Гордон [1809] 14	1938	$S^\circ_{298,16}$, Φ°_T для 18 $T = 298{,}16$—$2800°$ K	Гордона	[426, 4384]
Уагман и др. [4121] [г] 15	1945	Φ°_T, S°_T, $H^\circ_T-H^\circ_0$, C°_p для $T = 298{,}16$—$1500°$ K 18	23 Майера и Гепперт-Майер	[3680, 3426, 3507, 4384, 119, 119a]
Первое издание Справочника [420] 16	1956	Φ°_T, S°_T, $H^\circ_T-H^\circ_0$ 18 для $T = 298{,}16$—$6000°$ K	г.о.—ж.р. 24	—
Крёпелин и др. [2489] 17	1958	Φ°_T для $T = 1000$—$6000°$ K 18	» »	—

[a] The thermodynamic functions of C_2H_2 were calculated taking account for the nuclear spin components.

[b] The results of the calculations are given in the form of an empirical equation.

[c] The values of Φ^*_T of the deuteron substitution products of acetylene (C_2HD, C_2D_2) were also calculated.

[d] Plooster and Reed [3266] continued the calculations carried out by Warman et al. [4121] for Φ^*_T up to 3000°K.

1) Authors;
2) year of publication;
3) thermodynamic function;
4) method of calculation;
5) handbooks and monographs;
6) Kassel;
7) Bryant;
8) Frost;
9) Gordon;
10) Justi, Lueder;
11) Frost;
12) Glockler, Morell;
13) Eucken, Bertram;
14) Gordon;
15) Warman et al.;
16) first edition of the Handbook;
17) Kroepelin et al.;
18) for;
19) harmonic oscillator-rigid rotator;
20) Gordon's;
21) harmonic oscillator-rigid rotator;
22) Gordon's'
23) Mayer's and Goeppert-Mayer;
24) harmonic oscillator-rigid rotator.

Table 173 shows the Handbooks in which (with small additions) the values of the thermodynamic functions of C_2H_2 calculated in the original works are presented. The thermodynamic functions of gaseous acetylene are also given in the Handbooks [2363, 137]. Kelley [2363] gives the values of $H_T^\circ - H_{298.16}^\circ$ and $S_T^\circ - S_{298.16}^\circ$ for T = 400-2000°K as calculated from em irical formulas based on the calculations of Kassel [2331] and Wagman et al.[4121]. In the Handbook [137] compiled by Vukalovich et al. the values of the specific heat, the enthalpy and the entropy of acetylene are given in the temperature interval from 0-1200°C, based on calculations carried out by Warman et al. [4121].

The entropy of acetylene was not determined from specific heat measurements at low temperatures.

C_2HF, C_2F_2. The thermodynamic functions of gaseous fluoro acetylene and difluoro acetylene given in the Tables 217 (2) and 215 (2) were calculated from Eqs. (II.243), (II.244) in the approximation of the harmonic oscillator-rigid rotator model on the basis of the values of the molecular constants given in Table 171. Table 174 shows the values of the constants for the calculation of the thermodynamic functions of C_2HF and C_2F_2.

TABLE 174

Values of the Constants Needed to Calculate the Thermodynamic Functions of Gaseous C_2HF and C_2F_2

Вещество 1	θ_1 (1)	θ_2 (1)	θ_3 (1)	θ_4 (2)	θ_5 (2)	C_Φ	C_S
	град 2					3 кал/моль·град	
C_2HF	4827	3209	1522	525	827	5,5295	12,4850
C_2F_2	3453	1151	1942	647	288	7,1648	14,1203

1) Substance; 2) degree; 3) cal/mol^{-1}·deg.

The errors in the calculated values of the thermodynamic functions of C_2HF and C_2F_2 are due to the application of an approximate method of calculation and the inaccuracy in the adopted values of the molecular constants. Since we have no experimental data on the fundamental frequencies of the C_2F_2 molecule the errors of the thermodynamic functions of C_2F_2 are essentially greater than those of C_2HF. The errors in the values of Φ^*_T of fluoro acetylene at T = 298.15, 3000 and 6000°K are, respectively, estimated within 0.1; 1.0 and 1.5 cal/mol^{-1}·degree and those of difluoro acetylene within 0.5; 2.5 and 3.0 cal//mol^{-1}·degree.

The thermodynamic functions of C_2HF were not calculated earlier. The thermodynamic functions of C_2F_2 were calculated when the first edition of the Handbook was prepared. The differences in the values of the thermodynamic functions of C_2F_2 given in the first edition of the Handbook and in Table 215 (2) are about 0.2 cal/mol^{-1}·degree at $T < 1000$°K and about 0.05 cal/mol^{-1}·degree at T = 6000°K. They are due to the differences in the adopted values of the molecular and physical constants.

§80. THERMODYNAMIC QUANTITIES

C_2H_2 (gas). The heat of combustion of acetylene was measured by Berthelot [784, 796], Thomsen [3983] and Mixter [2927]. The results of these measurements agree with each other within the experimental error limits ($\pm 1 - \pm 2$ kcal/mol^{-1}) Mixter's data [2927] for the heat of thermal dissociation of C_2H_2 are considerably more accurate. On the basis of these data Bichowsky and Rossini [813] calculated $\Delta H°f_{291}$ (C_2H_2 gas) = 53.9 kcal/mol^{-1}.

In 1938, Conn, Kistiakowsky and Smith [1161, 1162] determined the heat of hydrogenation of acetylene at 355°K. Rossini et al. [4121, 3507] converted the experimental data of Mixter [2927] and Conn, Kistiakowsky and Smith [1162, 1161] and obtained $\Delta H^\circ f_{298.15}$ (C_2H_2, gas) = 54.194 ± 0.190 kcal/mol . This value was adopted in the Handbooks [3507, 3508, 4384, 3426, 249]. In the present Handbook the value

$$\Delta H^\circ f_{298.15}(C_2H_2, \text{gas}) = 54{,}2 \pm 0{,}2 \text{ kcal/mole},$$

is adopted on the basis of the data given in the works [2927, 1161, 1162, 4121], to which value corresponds

$$D_0(C_2H_2) = 388{,}14 \pm 0{,}9 \text{ kcal/mole}.$$

C_2HF (gas), C_2F_2 (gas). The values of the heats of formation of C_2HF and C_2F_2 were estimated by two methods: by the mean bond energies and by Kharasch's method.

When the first method of calculation is applied the mean bond energies of $\equiv C - F$, $\equiv C - H$ and $-C \equiv C$ in the fluorine substitution products of acetylene must be determined. Since the $\equiv C - H$ and $\equiv C - F$ bonds in the HCN, FCN, C_2H_2, C_2HF and C_2F_2 molecules are analogous (see §84 and 78) the mean bond energies of $\equiv C - H$ and $\equiv C - F$ in the fluorine substitution products of acetylene are assumed to be equal to the dissociation energies of these bonds in the corresponding cyanides.* This assumption permits the calculation of the bond energy of $-C \equiv C-$ in acetylene equal to $E(C\equiv C)$ = 173 kcal/mol and, respectively, the values of the heats of formation of C_2HF and C_2F_2: $\Delta H^\circ f_{298.15}$ (C_2HF, gas) = +5 kcal/mol and $\Delta H^\circ f_{298.15}$($C_2F_2$, gas) = = -43 kcal/mol with errors of the order of ±15 kcal/mol .

When Kharasch's method was used the values of the thermao corrections to the triple bond and fluorine were adopted according to the work [468]. The values of $\Delta H^\circ f_{298.15}$ (C_2HF, gas) = +5 kcal/mol and $\Delta H^\circ f_{298.15}$($C_2F_2$, gas) = -45 kcal/mol which are close to those found above from the bond energies correspond to the calculated values of the heats of combustion $\Delta Hc_{298.15}$ (C_2HF, gas) = -252 kcal/mol and $\Delta H^\circ c_{298.15}$ (C_2F_2, gas) = -203 kcal/mol .

TABLE 175

Adopted Values (in cal/mol^{-1}) of the Thermodynamic Quantities of C_2H_2, C_2HF and C_2F_2 in Gaseous State

Вещество 1	D_0	$\Delta H°f_0$	$\Delta H°f_{293,15}$	$\Delta H°f_{298,15}$	$H°_{293,15} - H°_0$	$H°_{298,15} - H°_0$
C_2H_2	388 140	54 294	54 201	54 200	2341	2393
C_2HF	404 513	4 789	4 993	5 000	2682	2744
C_2F_2	421 755	—45 585	—45 015	—45 000	3093	3164

1) Substance

The calculation of the heats of combustion of the acetylene series compounds according to Kharasch's method shows that the deviations of the calculated values from the corresponding experimental values do not exceed ± 6 kcal/mol^{-1}.

Making use of the estimates carried out for the heats of formation of C_2HF and C_2F_2 the following values are adopted in the Handbook:*

$$\Delta H°f_{298,15}(C_2HF, \text{gas}) = 5 \pm 10 \text{ kcal/mole},$$
$$\Delta H°f_{298,15}(C_2F_2, \text{gas}) = -45 \pm 10 \text{ kcal/mole},$$

to which

$$D_0(C_2HF) = 404{,}513 \pm 10 \text{ kcal/mole},$$
$$D_0(C_2F_2) = 421{,}755 \pm 10 \text{ kcal/mole}.$$

correspond.

Manu-script Page No.	[Footnotes]
1210	According to [2048] it is shown in the American patents 2831,835, 22.4. 1958 and 2546,997,5.9. 1947 that the presence of difluoro acetylene was established in a carbon fluoride mixture.
1212	In the range from 4000 to 8500 cm^{-1} the resolution was about 0.1 cm^{-1}, in the range from 1900-3500 cm^{-1} it was about 0.2 cm^{-1}.

121** [3] $G_0(v_1, v_2, v_3, v_4^{l_4}, v_5^{l_5}) = \sum_{i=1}^{5} \omega_i^{\circ} v_i + \sum_{i=1}^{5}\sum_{j=1}^{5} x_{ij}^{\circ} v_i v_j + g_{44} \cdot l_4^2 + g_{55} \cdot l_5^2$, where

$l_k = v_k, v_k - 2, \ldots 1$ or $0\ (k = 4, 5)$.

1217 I the work [3156a] the attempt was undertaken to give a theoretical interpretation of the negative values of the constants α_4 and α_5 of the C_2H_2 molecule and formulas for the calculation of these constants in terms of the moment of inertia and the structural parameters were obtained.

1217 For compounds in which a linear configuration of the C_2H_2 molecule is maintained.

1217 For compounds in which the C_2H_2 molecule has plane <u>cis</u> and <u>trans</u> configurations.

1218 Innes [2176] succeeded also in determining the values of the constants ω_{44}, x_{44} and q_{44} of the C_2H_2 molecule in the electronic ground state.

1219 [1] $r_{C-H}(C_2H_6) = 1{,}09 \pm 0{,}03$ Å [517], $r_{C-H}(C_2H_4) = 1{,}084 \pm 0{,}003$ Å [664], $r_{C-H}(C_2H_2) = 1{,}0585 \pm 0{,}005$ Å [1101], $r_{C-F}(C_2F_6) = 1{,}32 \pm 0{,}02$ Å [3909], $r_{C-F}(C_2F_4) = 1{,}313 \pm 0{,}010$ Å [2327].

1220 According to the calculations carried out the force constant of the $-C{\equiv}C-$ bond in the C_2H_2, C_2HF and C_2HCl molecules is, respectively, equal to 15.34; 17.62 and $13.27 \cdot 10^5$ $dyn \cdot cm^{-1}$.

1221 The latter were found on the basis of the experimental values of the corresponding force constants of C_2H_2, C_2HCl and C_2I_2 and the estimated value of the force constant of the $\equiv C - F$ bond stretching.

1221 In 1961, the results of the following studies on the infrared spectra of C_2HF [986a, 2158b] obtained with prism spectrometers were published. Brown and Tyler [986a] studied the infrared spectra of C_2HF and C_2DF in the range from 400-4000 cm^{-1}, which permitted them to observe the band ν_4, besides the bands ν_1, ν_2, ν_3. For C_2HF the following values of the fundamental frequencies (in cm^{-1}) were determined in the work [986]: $\nu_1 = 3370$, $\nu_2 = 2245$, $\nu_3 = 1064$, $\nu_4 = (370)$, $\nu_5 = 584$. The value of the frequency ν_4 was estimated by Brown and Tyler on the basis of the values of ν_4 and ν_5 determined from the microwave spectrum [4029] (see footnote three) and the value of ν_5. Hunt and Wilson [2158b] studied the infrared spectra of C_2HF, C_2HCl, C_2HBr and their deutron substitution products in the range from 250-3500 cm^{-1}. The following values of the fundamental frequencies (in cm^{-1}) were obtained in the work [2158b] for C_2HF: $\nu_1 = 3355$,

ν_2 = 2255, ν_3 = 1055, ν_4 = 367, ν_5 = 578. The values of the fundamental frequencies of the C_2HF molecule obtained in the works [986a, 2158b] are similar to the values of these quantities adopted in Table 171.

1221 In 1960, a report by Tyler and Sheridan [4029] on the results of a study on the microwave spectrum of six isotopic modifications of the C_2HF molecule was published. These authors found the following values of the structural parameters of the C_2HF molecule: $r_{C\equiv C} = 1{,}198$, $r_{C-H} = 1{,}053$, $r_{C-F} = 1{,}279$ Å, which they identified with the equilibrium values of the corresponding bond lengths within error limits of ±0.005 A. Thus, in the work [4029] the values of the structural parameters of the C_2HF molecule estimated by the authors of the present Handbook were verified. A value of $I = 8.645 \cdot 10^{-39}$ $g \cdot cm^2$ corresponds to the value of B_0 (C_2HF) = 9706.19 Mc found by Tyler and Sheridan; it is in good agreement with the value of $I(C_2HF)$ adopted in Table 171. In the microwave spectra of C_2HF and C_2DF Tyler and Sheridan [4029] observed also rotational transitions in the vibrational states (0, 0, 0, 1, 0) and (0, 0, 0, 0, 1), which permitted them to determine the approximate values of the frequencies ν_4, ν_5 and those of the constants α_4 and α_5 of the C_2HF and C_2DF molecules from the ℓ-doubling of the corresponding spectral lines. For the frequencies of C_2HF evidently too high values were obtained in the work [4029]: ν_4 = 430 and ν_5 = 650 cm^{-1}.

1226 The maximum difference does not exceed ±0.06 cal/mol^{-1}·deg.

1230 According to the data adopted in the present Handbook D_0(H – CN) = 110.4 ± 5 and D_0(F – CN) = 125 ± 10 kcal/mol.

1231 In the present edition of the Handbook the heat of formation of C_2F_2 was assumed to be equal to zero by extrapolating the heats of formation of C_2F_6 and C_2F_4 in a very rough way.

[Transliterated Symbols]

1222 П = P = Prilozheniye = Appendix

1224 кол.вр = kol.vr = kolebatel'no-vrashchatel'Nyy = vibrational-rotational

Chapter 20

THE SIMPLEST FREE RADICALS OF HYDROCARBONS AND THEIR FLUORINE AND CHLORINE SUBSTITUTION PRODUCTS

(CH, CH_2, CH_3, C_2H, CF, CF_2, CF_3, C_2F, CHF, CH_2F, CHF_2, CCl, CCl_2, CCl_3)

In the present chapter we consider the thermodynamic properties of some of the simplest radicals the dissociation products of methane, its fluorine and chlorine substitution products as well as those of acetylene and its fluorine substitution products. It can be assumed that the absence of data on other radicals, among them those containing two or more carbon atoms, has no important influence on the accuracy of the thermodynamic calculations since the radicals that are not considered in the Handbook are comparatively unstable. We must note that even the radicals considered in the Handbook are, for the most part, compounds of low stability, and that the remaining radicals are still less stable, except for, maybe, CBr_3, CI_3 CBr_2, and CI_2. I particular, we may expect that radicals simultaneously containing halogen and hydrogen should easily decompose into solid carbon, hydrogen halide and other dissociation products.

§81. MOLECULAR CONSTANTS

CH. The state $X^2\Pi_r$* is the electronic ground state of the CH molecule. As a result of numerous studies carried out by various authors [2061, 1854, 1694, 1520, 1695, 3349, 4051, 1424, 2394, 2476, 3707, 3104] three systems of bands were identified in the CH spectrum: $A^2\Delta - X^2\Pi$, $B^2\Sigma - X^2\Pi$ and $C^2\Sigma - X^2\Pi$. All three systems were observed in the emission spectra of various hydrocarbon flames and in the absorption spectrum (in studying explosive combustion of acetylene [3103a, 3104], in diazomethane photolysis [3406a], but also in the absorption spectrum of a pulsating discharge in the atmosphere of an inert gas with C_2H_2, C_2H_4, C_6H_6, $C_6H_5CH_3$ admixtures [832a]).

Since in the works carried out up to 1950 only bands connected with transitions between the first two vibrational levels of different electronic states had been studied, Herzberg [2020] calculated the values of the vibrational constants of methine in the ground state $X^2\Pi$ (ω_e = 2861.6 and $\omega_e x_e$ = 64.3 cm^{-1}) and in three excited electronic states, on the basis of the values of $\Delta G_{1/2}$ found for CH and CD by Gero [1695]. The values of ω_e and $\omega_e x_e$ calculated by Herzberg [2020] are recommended in the Handbook [649].

I 1952, a work by Durie [1424] was published, who studied the emission spectrum of CH using a hydrogen-oxygen flame with small admixtures of hydrocarbons as the radiation source. Analyzing the 1-0, 1,1 and 1-2 bands of the $A^2\Delta - X^2\Pi$ system, Durie obtained the following values of the vibrational constants of CH in the state $X^2\Pi$; ω_e = 2844 and $\omega_e x_e$ = 62.5 cm^{-1}. Khachkuruzov [436] compared the vibrational constants of the diatomic hydrides of the second-period elements and showed that the values of the constants obtained by Durie are less reliable than the values recommended by Herzberg [2020] and adopted in the Handbook [649].

This conclusion was verified in a subsequent work of Kiess and Broida [2394], who analyzed the 0-1 and 1-2 bands of the $A^2\Delta - X^2\Pi$ system of the CH molecule. An acetylene-oxygen flame was used as the radiation source. The spectrum was photographed in the first order of the grating. The wave numbers of the lines were measured with an accuracy of ±0.07 cm^{-1}. In each band up to 12 bands characteristic of the $^2\Delta - {}^2\Pi$ transition were found. The analysis of the rotational structure of the 0-1 and 1-2 bands was carried out using the formulas of Hill and Van Vleck for the energy of the rotational levels of the doublet states. The spin-orbit coupling constant of the $X^2\Pi$ state was found equal to 27.3 cm^{-1}. Thus, the coupling in the ground state of CH is similar to the Hund case b. The splitting in the excited state $A^2\Delta$ proved to be insignificantly small (about 1 cm^{-1}).

A analysis of the 0-1 and 1-2 bands together with the results of an investigation of the 0-0, 1-1 and 2-2 bands carried out by Gero [1695] permitted the authors of [2394] to increase the accuracy of the values of the molecular constants of CH in the states $X^2\Pi$ and $A^2\Delta$.

Kiess and Broida [2394] estimate the accuracy of their values found for the constants ω_e, $\omega_e x_e$ and B_e for the $X^2\Pi$ state equal to ± 1.0, ± 0.05 and ± 0.010 cm^{-1}, respectively. We must note that these values characterize only the inaccuracy of the experimental data. The total uncertainty in the values of the vibrational constants is, obviously, considerably higher since they are obtained as a result of studying the transitions to three lower levels of the ground-state vibrational energy. A linear extrapolation of the vibrational levels of the $X^2\Pi$ state with the help of the constants obtained in the work [2394] leads to a dissociation limit of 30,508 cm^{-1}, which is in satisfactory agreement with the value of $D_0(CH) = 27,989$ cm^{-1} found as a result of studying the predissociation in the CH spectrum.

In the present Handbook the molecular constants of CH in the $X^2\Pi$ and $A^2\Delta$ states found in the work of Kiess and Broida [2394], and the constants in the $B^2\Sigma$ and $C^2\Sigma$ states, recommended by Herzberg [2020] on the basis of a work by Gero [1695], are adopted. These constants are given in Table 176.

CF. The studies on the emission [556, 557, 2756, 55, 268] and absorption [2778] spectra of fluoro methine showed that the $X^2\Pi$ state is the electronic ground state of the CF molecule. Two systems of lines are wellknown in the CF spectrum: $A^2\Sigma - X^2\Pi$ and $B^2\Sigma - X^2\Pi$ lying in the range from 1950-2350 A.

Andrews and Barrow [556, 557] were the first to determine the molecular constants of CF. In the works [556, 557] the spectrum of CF was obtained with prism spectrometers of low and moderate dispersion using a discharge in fluorinated hydrocarbon vapors as the radiation source. In the $A^2\Sigma - X^2\Pi$ system Andrews and Barrow observed the 1-0, 0-0, 0-1 and 1-1 bands with resolved vibrational structure an analysis of which allowed them to obtain the values of the rotational constants of CF in the $X^2\Pi$ and $A^2\Sigma$ states. An analysis of the vibrational structure of the $A^2\Sigma - X^2\Pi$ system is not reliable since the edges of the 1-0 and 0-0 bands are diffuse owing to the superposition of lines belonging to other bands. In the B → X system Andrews and Barrow identified 18 bands($v'' \leq 3$, $v' \leq 6$) forming five sequences. Using the results of measurements of the positions of these band edges and the distances between the edges of different branches Andrews and Barrow found approximate values of the vibrational and rotational constants of CF in the state B. Since the rotational structure of the bands of the B → X system was not resolved in the work [557] the type of the state B could not be determined. The values of the molecular constants of CF in the states $X^2\Pi$, $A^2\Sigma$ and B found by Andrews and Barrow are given in the book by Herzberg [2020] and in the Handbook [649]. In order to increase the accuracy in determining the type of the state B and in the rotational constants of CF in this state the spectrum of the CF molecule was reinvestigated in the range from 1970-2100 A by Tatevskiy, Kuzyakov et al.[55]. A pulsed discharge in a flow of CF_4 vapors was used as the source of excitation. The spectrum was photographed in the range from 2000-2075 A with a DFS-3 spectrograph having a dispersion of 2 A/mm, and in the range of $\lambda < 2000$ A with a DFS-5 spectrograph having a dispersion of 3 A/mm.

The authors of [55] carried out an analysis of the rotational structure of the 0-0 and 1-0 bands of the B – X system. In view of the fact that the Q branches are the most intense branches of the bands under investigation, and that the formulas for the Q branches branches of the $^2\Sigma - {}^2\Pi$ band system satisfactorily describe the positions of the lines belonging to these branches, the authors of [55] drew the conclusion that the upper state of the studied bands is a state of the $^2\Sigma$ type. The values of the rotational constants in the state $B^2\Sigma$ found in the work [55] practically coincide with the constants recommended by Andrews and Barrow [557]. Table 176 shows the vibrational and rotational constants of the CF molecule adopted in the present Handbook, found by Andrews and Barrow [557], except for the rotational constants of CF in the state $B^2\Sigma$ which were adopted according to the work by Tatevskiy, Kuzyakov et al.[55].*

<u>CCl</u>. The state $X^2\Pi_r$ is the electronic ground state of the CCl molecule. A series of bands lying in the range from 2710 to 2940 A is connected with the CCl molecule. These bands were observed both in the emission spectrum [55, 269, 269a, 269b, 579, 580, 2124, 2247, 2756, 4090, 1819, 4102a] and in the absorption spectrum [4102a]. The CCl bands have a very complex structure; their interpretation is, therefore, connected with considerable difficulties. Several authors carried out an analysis of the vibrational structure of the CCl bands [579, 580, 2124, 55, 269, 269b, 4090, 1819, 4102a]. Herzberg [2020] and Rosen [649] recommended the values of the molecular constants of CCl obtained by Venkateswarlu [4090] making use of the results of works published up to 1950 ($\omega_e'' = 846$, $\omega_e''x_e'' = 1$, $\omega_e' = 867.5$ and $\omega_e'x_e' = 1.5$ cm^{-1}.

The same constants were adopted in the first edition of the present Handbook, where, however, a special remark is made that the anharmonicity constants found by Venjateswarky are too low and, obviously, erroneous.*

TABLE 176

Adopted Values of the Molecular Constants of CH, CF and CCl

Молекула 1	Состояние 2	T_e	ω_e	$\omega_e x_e$	B_e	α_1	D_e	r_e
		см$^{-1}$						Å
CH	$X^2\Pi$ d	0^a	2868,5	64,4	14,448	0,530	$1{,}43\cdot10^{-3}$ b	1,1198
	$A^2\Delta$	23151,8	2943,0	99,3	14,930	0,696	$1{,}47\cdot10^{-3}$ c	1,1026
	$B^2\Sigma^-$	25949	2542,5 d	373,8 d	12,887	0,485	$2{,}18\cdot10^{-3}$	1,1861
	$C^2\Sigma^+$	31821	2824,1 d	105,8 d	14,629	0,744	$1{,}55\cdot10^{-3}$	1,1132
CF	$X^2\Pi$ d	0^e	1308,4	10,86	1,4190	0,0190	$6{,}7\cdot10^{-6}$	1,2708
	$A^2\Sigma$	42705	1764	22 f	1,7277	0,0260	$6{,}8\cdot10^{-6}$	1,1516
	$B^2\Sigma$	49452	1191,0	19,4 g	1,323	0,027	$6{,}21\cdot10^{-6}$	1,318
CCl	$X^2\Pi_{1/2}$	0^h	875,1	7,0	0,69363 i	0,00672	$1{,}88\cdot10^{-6}$ k	1,6452 l
	$X^2\Pi_{3/2}$				0,6976 i	0,00678	$1{,}89\cdot10^{-6}$ k	
	$B^2\Delta$ m	36003,92	860	7,5	0,70620 i	—	$1{,}84\cdot10^{-6}$ k	1,6344 l

a) $A = 27.3$ cm^{-1}.

b) $\beta_1 = 2.6\cdot10^{-5}$ cm^{-1}.

c) $\beta_1 = 6.4\cdot10^{-5}$ cm^{-1}.

d) calculated by Herzberg from the isotopic relations on the basis of the wellknown values of $\Delta G_{1/2}$ for CH and CD.

e) $A = 77$ cm^{-1}.

f) since only $\Delta G_{1/2}$ is known for the state $A^2\Sigma$, the value of $\omega_e x_e$ given in the table is estimated from Eq. (I.38).

g) $\omega_e y_e = -0.4$ cm^{-1}.

h) $A = 134.92$ cm^{-1}.

i) the value of B_0 is given.

k) the value of D_0 is given.

l) the value of r_0 is given.

m) the existence of a $^2\Sigma$ state with an excitation energy below 36,000 cm^{-1} is possible (see [4102a]).

1) Molecule;

2) State.

In order to increase the accuracy of analyzing the vibrational structure of the bands Kuzyakov, Zvolinskiy and Tatevskiy [55, 269, 269b] reinvestigated the emission spectrum of CCl. A discharge tube of the Schuler tube type filled with helium and CCl_4 vapors was used as the excitation source. The spectrum was photographed in the first order of a DFS-3 spectrograph with a dispersion of 2 A/mm. The most intense group of bands in the range from 2777-2788 A was also photographed in the third order with a dispersion of 0.67 A/mm. In the works [55, 269, 269b] the wavelengths of 23 edges of five bands were measured, a new assignment of edges different from that proposed by Venkateswarlu was given, and the following molecular constants were obtained*: $\omega''_e = 858.0$ $\omega''_e x''_e = 5.0$, $\omega'_e = 879.5$ and $\omega'_e x'_e = 6.5$ cm^{-1}. Subsequently, Kuzyakov and Tatevskiy [269a] carried out an analysis of the rotational structure of two bands in the spectrum of CCl and found the values of the rotational constants equal to: $B''_0 = 0.6465 \pm 0.0032$, $B'_0 = 0.6589 \pm 0.0038$ and $B'_1 = 0.6551 \pm 0.0026$ cm^{-1}.

We must note that the authors of the works published up to 1960 considered the observed bands to be connected with the electronic transition $^2\Sigma \rightarrow X^2\Pi$. In 1960, however, Gordon and King [1819] anew photographed the spectrum of CCl with an instrument of higher resolution than in the preceding works. A detailed investigation of the fine structure of the band at 2780 A showed that the bands of CCl are connected with the transition $^2\Delta - {}^2\Pi_r$. All attempts of analysis based on the assumption that the observed bands are connected with the transition $^2\Sigma - {}^2\Pi_r$, had no success. In the work [1819] it was shown that the band in the region of 2780 A is a 0-0 band rather than a 1-1 band as Kuzyakov and Tatevskiy [269, 269b] had assumed. In the work [1819] it is also remarked that Kuzyakov and Tatevskiy [269a] erroneously numbered the lines without paying attention to the small deviations from the parabolic formula for small J. On the basis of the analysis carried out the authors of the work [1819] obtained the following values for the constants of CCl: ω''_e = 875.1, $\omega''_e x''_e$ = 7.0, ω'_e = 860, $\omega'_e x'_e$ = 7.5, B''_0 = 0.69199, B'_0 = 0.70533, A" = 134.96 cm^{-1}, r''_0 = 1.65115 and r'_0 = 1.63546 A. An extrapolation of the ground state vibrational levels to the dissociation limit with the help of constants recommended in the work [1819] leads to a value of $D_0(CCl)$ = 26940.5 cm^{-1} (77 kcal/mole.) which is in good agreement with the mean bond energy in the CCl_4 molecule.

In 1961, Verma and Mulliken [4102a] took the spectrum of CCl in the first, second and third orders of a grating with a resolving power of 320,000 and a dispersion in the third order equal to 0.23 A/mm. The authors of [4102a] carefully analyzed the fine structure of the bands at 2777 and 2788 A, regarded as two subbands of the 0-0 band of the transition $^2\Delta \rightarrow {}^2\Pi_r$ and that of the bands at 2846 and 2856 A (subbands of the 0-1 band of the same transition). The assignment of the bands at 2777 and 2788 A to the transition 0-0 agrees with the data obtained by Gordon and King [1819] and is corroborated by the presence of these bands in the absorption spectrum of CCl which was obtained by Herzberg.* Since in the work [4102a] the spectrum of CCl was obtained with still greater resolution than in the work by Gordon and King [1819] the authors of [4102a] could carry out a more detailed analysis of the rotational structure of the bands under investigation, and the rotational constants of CCl found by them are more accurate. This cannot be said of the vibrational constants in the electronic ground state: ω''_e = 875.9 ($^2\Pi_{1/2}$), 872.3 ($^2\Pi_{3/2}$), $\omega''_e x''_e$ = 4.6 ($^2\Pi_{1/2}$), 3.4 ($^2\Pi_{3/2}$), obtained on the basis of measuring the position of the lines in the $^OP_{12}$ and P_1 branches of the 0-0 bands of the isotopic molecules CCl^{35} and CCl^{37}.

In the present Handbook the values of the vibrational constants of CCl found by Gordon and King [1819], and the values of the rotational constants obtained by Verma and Mulliken [4102a] are adopted. Table 176 shows the adopted values of the constants.

We must note that considering the possible electronic configurations of the CCl molecule corresponding to low electronic states Verma and Mulliken found that the observed system in the spectrum of CCl is analogous to the B' – X system of the NO molecule and that the existence of a state $^2\Sigma$ can be expected, whose excitation energy must be lower than the energy of the state $^2\Delta$.

$\underline{CH_2}$. The existence of a free radical CH_2 was proved experimentally by many research workers [370, 2018, 2659]. The problem of the structure and type of the electronic ground state and the vibration frequencies of methylene remained, however, unsolved for a long time.* In connection with the lack of experimental data in literature a great number of works dealing with the theoretical calculation of the possible electronic configurations and the electronic states of the CH_2 molecule was published. A theoretical consideration made by Mulliken (see [4091]) showed that the assumption of a symmetric CH_2 molecule that is nonlinear with a singlet ground state is the most probable. This structure corresponds to the assumption that in the CH_2 molecule the carbon atom is in a state corresponding to the s^2p^2 electron configuration. A CH_2 molecule with a triplet ground state and linear structure corresponds to the sp^3 electron configuration of the carbon atom. Mulliken assumed that in reality the electron configuration of the carbon atom must lie between s^2p^2 and sp^3, but somewhat nearer to the first case, and, therefore, the CH_2 molecule must have a singlet ground state, and the HCH angle a value from 110 to 140°. Walsh [4139] also concluded that the HCH angle in CH_2 must be considerably smaller than 180°. Nira and Oohata [3096] applied the atomic orbital method and obtained the value 140° for the HCH angle in CH_2, but the authors of [3096] remarked that this result could not be regarded as a final one. A quantum mechanical calculation carried out by Gallup [1647] showed that the most probable value for the HCH angle lies close to 160°. Gray [1844], however, remarks in his work that Gallup's conclusions [1647] are erroneous* since he disregarded the lowest divalent state of the carbon atom connected with the electron configuration s^2p^2 without having any reason for doing so. The author of the work [1844] showed that the HCH angle in the CH_2 molecule corresponding to this state of the carbon atom must be somewhat greater than 90°. The calculations of Foster and Boys [1583a] carried out by the molecular orbital method with allowance for the configuration interaction showed that the electronic ground state of CH_2 is a triplet, and the CH_2 molecule has the following parameters in this state: $\angle HCH = 129°$ and $r_{C-H} = 1.12$ A. Searcy [3670] found the value $114.4 \pm 3°$, for the HCH angle, on the basis of calculations carried out by means of the electrostatic model.

We must emphasize the fact that all quantum mechanical calculations of CH_2 contain a great number of assumptions (in particular, on the value of the interatomic distance r_{C-H}) and, therefore, are more or less approximate [3000]. Consequently, we have to act cautiously in using the results of these calculations.

In the last few years numerous attempts were made to determine the spectrum of CH_2 experimentally. Many years investigations carried out in Herzberg's laboratory using the method of pulsed photolysis and carried out in order to discover the spectrum of CH_2 remained without success for a long time [2026]. Only in 1959 Herzberg and Shoosmith reported in a short note [2046] that in the photolysis of diazomethane they had succeeded, at last, in obtaining groups of CH_2 lines in the neighborhood of 1400 A, in the absirption spectrum. The study of the spectrum observed in the photolysis of ordinary, partially and totally deuterated diazomethane, but also an analysis of the fine structure of the bands observed in the photolysis of partially and totally deuterated dizomethane left no room for doubt that the CH_2, CHD and CD_2 molecules, respectively, emit the spectrum. The authors of the work [2046] came to the conclusion that in the lower state of the observed electron transition the molecule must have an HCH angle of 140 to 180° and, respectively, an interatomic distance r_{C-H} equal to 1.03 or 1.07 A. A study of the variable intensity of the lines in the CD_2 spectrum showed that the methylene molecule in the observed lower electronic state must have an incompletely symmetrical electronic structure, i.e., this state must be a state of the ${}^3\Sigma_g^-$ type. In fact, the authors of the work [2046] did not exclude the possibility that the observed lower state might not be the electronic ground state. Later on, McCarty and Robinson [2689] observed three distinct lines close to 2600 A in the absorption spectrum of the products of a condensed discharge through ethane in a krypton atmosphere that were frozen in liquid helium. Analogous lines appeared also in the absorption spectrum of the products of ketene and diazomethane photolysis frozen in krypton. On the basis of the magnitude of the observed isotopic shift, when working with partially and totally substituted ethane, the authors of [2689] concluded that the emission of the spectrum is due to the CH_2 radical. The experiments carried out, however, practically contributed nothing to the solution of the problem which type of ground state and which structure the CH_2 radical might have. They only corroborated the assumption that in one of the states connected with the observed electron transition the CH_2 molecule must be bent.

In the following works by Robinson and McCarty [3460a] and Goldfarb and Pimentel [1792a] the process of photodissociation of diazomethane and its deuteron substitution products located in nitrogen and krypton matrices was studied in detail, at temperatures of 20 to 4.2°K, respectively. In these works it was shown that in the process of photolysis, in fact, methylene is formed, but as to the problem of assigning the bands observed in the spectrum accompanying the photolysis the authors of the works [3460a, 1792a] obtained no unique solution. McCarty and Robinson [3460a] assign only the clear bands lying in the region of 3000 A to the CH_2 molecule whereas Goldfarb and Pimentel assume that with the methylene molecule bands in the visible and ultraviolet ranges with maxima at 4182 and 3968 A and absorption in the range from 3050-3300 A are connected. Robinson and McCarty carried out a theoretical consideration of the possible electron configurations and the electronic states of the CH_2 molecule corresponding to them and showed that if in the ground state the CH_2 molecule has a linear structure its ground state is a state of the $^3\Sigma_g^-$ type, in which case singlet states $^1\Delta$ and $^1\Sigma_g^+$ with very low excitation energies must exist. But if CH_2 has a nonlinear structure in the ground state its ground state is a singlet state of the $^1A_1$ type. A comparison of the obtained experimental data with the results of an analysis of the possible electron transitions permitted the authors of the work [3460a] to conclude that the bands observed in the region of 3000 A are connected with a transition between triplet states and, consequently, the CH_2 molecule is linear in the electronic ground state. Robinson and McCarty, however, remark that the identifying the ground state of molecules having incomplete electron shells one has to use certain precaution, and that in the given case the lower state of the transition observed in the solid phase at 4.2°K, in fact, cannot be the electronic ground state of the CH_2 molecule in the same way as this is the case for NH [2688] and C_2 [2688a].

In 1960, Anet, Bader and Van der Auwera [560a] studied the reaction of methylene obtained in the photolysis with cis or trans 2-butene in the gaseous and liquid phases with formation of cis or trans 1.2-dimethyl cyclopropane. Carrying out the photolysis of diazomethane under the conditions of nitrogen surplus the authors of [560a] found that the stereospecific properties of the reaction observed by Woodwoth and Skell with collaborators [4321a] are lost. This fact permitted them to draw the conclusion that under the conditions of nitrogen surplus (as had been supposed earlier by Herzberg) the methylene formed on dissociation of diazomethane is in a triplet state, and, consequently, the CH_2 molecule is linear in the electronic ground state.

In 1961, Herzberg presented more detailed data on the results of studies on the CH_2 spectrum carried out in his laboratory, in a review lecture dealing with the investigation of the spectra and structures of methyl and methylene [2026b]. Besides the ultraviolet bands whose structure was analyzed showing that they are connected with the electron transition $^3\Sigma_u^- - {^3\Sigma_g^-}$, under certain conditions of diazomethane photolysis groups of bands in the red range were observed in the absorption spectrum, whose structure is analogous to the α bands of NH_2 and which are assigned to the CH_2 molecule. An analysis of the very complex structure of these bands led to the conclusion that they are connected with the transition between singlet states $B_1 \leftarrow {^1A_1}$, where in the lower state ($^1A_1$) the molecule is bent and r_{C-H} = 1.12 A, and the H – C – H angle is equal to 103°, 2, whereas in the $^3\Sigma_g^-$ state the CH_2 molecule has a linear structure and $r_{C-H} = 1.03 \pm 0.01$ A. A comparison of the conditions under which ultraviolet and red bands appear in the CH_2 spectrum led to the conclusion that the lower state of the ultraviolet bands (the $^3\Sigma_g^-$ state) is lower than the lower state of the red bands ($^1A_1$), and that the energy difference between these states is not great. On the basis of these data Herzberg assumes that the $^3\Sigma_g^-$ state, close to which a singlet state of the $^1A_1$ type lies is the electronic ground state of the CH_2 molecule.

On the basis of the abovementioned experimental works we assume in the present Handbook that the CH_2 molecule in the ground state has a linear symmetric structure and belongs to the symmetry point group $D_{\infty h}$. According to Herzberg's [2026b] work the interatomic distance r_{C-H} is assumed equal to 1.03 ± 0.01 A. The product of the moments of inertia of the CH_2 molecule calculated on the basis of the adopted structural parameters is given in Table 178.

A triatomic molecule of $D_{\infty h}$ symmetry must have three fundamental frequencies_ the frequencies ν_1 and ν_3 corresponding to the symmetric and antisymmetric valency vibrations of the C-H bands, and the frequency ν_2 connected with a doubly degenerate deformation vibration of the molecule.

The vibration frequencies of the CH_2 molecule were estimated by the authors of the works [3905, 4338, 4310a, 168, 56]. Sutherland and Dennison [3905], Wu [4338] and A. Gurvich and Frost [168] approximately estimated the frequencies of CH_2 on the basis of the force constants and frequencies of the C_2H_4 and H_2CO molecules, assuming values from 110 to 142°.5 for the angle between the C-H bands. Tatevskiy and Tyulin [56] calculated the vibration frequencies of CH_2 on the basis of the force constants of methane: $f_d = 8.34 \cdot 10^6$, $f_\alpha = 0.71 \cdot 10^6$, $f_{dd} = 0.05 \cdot \cdot 10^6$, $f_{d\alpha} = 0.35 \cdot 10^6$ cm^{-2} ([128], page 352) for different values of the angle between the C-H bonds: 110, 115, 120, 140, and 160°. In 1960, Wolfsberg [4310a] adopted the vibration frequencies of methylene equal to $\nu_1 = 3396.7$, $\nu_2 = 1484.6$ and $\nu_3 = 3287.8$ cm^{-1} ($\angle HCH = 120°$). The values of the CH_2 frequencies found in the works [3905, 4338, 56, 128, 4310a] are given in Table 177.

TABLE 177

Fundamental Frequencies of CH_2 Calculated for Different Values of the HCH angle by Various Authors

Авторы 1	∠HCH	ν_1	ν_2	ν_3
	град 2	см⁻¹ 3		
Ву [4338] 4	115	2990	1440	3100
Сезерленд и Деннисон [3905] 5	120	2970	1440	3000
А. Гурвич и Фрост [168] . 6	142,5	2990	1440	3110
Татевский и Тюлин [56] 7	110	3070	1300	3160
	115	3060	1300	3160
	120	3050	1310	3170
	140	3030	1310	3210
	160	3020	1310	3230
Вольфсберг [4310a] . 8	120	3396,7	1484,6	3287,8

1) Authors
2) degree;
3) cm^{-1};
4) Wu;
5) Sutherland and Dennison;
6) A. Gurvich and Frost;
7) Tatevskiy and Tyulin;
8) Wolfsberg.

As can be seen from the table, the values of the frequencies of CH_2 calculated for a nonlinear molecule are slightly dependent on the value of the HCH angle and agree with each other within the limits of 10%. The calculation of the frequency of the deformation vibration of the linear CH_2 molecule on the basis of the force constant of the angle between the bonds in the nonlinear molecules may lead to great errors since the variation of the angle between the bonds in the transition from CH_4 and C_2H_4 to CH_2 is connected with a change of the valency state of the carbon atom.

In 1958, Mulligan and Pimentel [2918] studied the products of diazomethane photolysis by the method of matrix isolation. On the basis of an analysis of the experimental conditions and the relative intensity of the bands observed in the absorption spectrum in the range from 700 to 3200 cm^{-1} the authors of [2918] came to the conclusion that one of the bands: 1114 or 1362 cm^{-1} must be connected with the deformation vibration of the CH_2 molecule. Since on the basis of the existing data an accurate estimation of the force constant of the deformation vibration of the CH_2 molecule cannot be made, it is, at present, not possible to make a wellfounded choice between these values of the frequencies.* In the present Handbook the value of $\nu_2 = 1100 \pm 200$ cm^{-1} is adopted for the frequency of the deformation vibration of CH_2. The frequencies of the valency vibrations of the linear CH_2 molecule not observed in the spectrum may be estimated relatively reliably on the basis of a calculation with the help of Eqs. (P4.32) since the force constant of the C-H bonds varies slightly in the various hydrocarbon compounds (ethane: $5.3 \cdot 10^5$ dyne·cm^{-1}, ethylene: $5.1 \cdot 10^5$ dyn·cm^{-1}. methane: $5.4 \cdot 10^5$ dyn·cm^{-1}).

The values 3000 ± 100 cm^{-1} and 3200 ± 100 cm^{-1} corresponding to $f_d = (5.1 \pm 0.2)\ 10^5$ dyn·cm^{-1} are adopted in the Handbook for the frequencies ν_1 and ν_3. According to the work of Herzberg and Shoosmith [2046] it is assumed in the present Handbook that the electronic ground state of CH_2 is a triplet state of the $^3\Sigma$ type. The adopted molecular constants of CH_2 are given in Table 178.

We must note that according to the results of theoretical calculations [1583a] and experimental investigations [2026b] we may expect that there are stable electronic states with low excitation energies with the CH_2 molecule; the state $^1A_1$ is the first excited state with an energy close to zero.

TABLE 178

Adopted Values of the Molecular Constants of CH_2, CHF, CF_2 and CCl_2

1 Молекула	ν_1	ν_2	ν_3	$I_A I_B I_C$	σ
	$см^{-1}$			$10^{-117}(г \cdot см^2)^3$	
CH_2	3000	1100(2)	3200	3,55[a]	2
CHF	3000	1200	1600	0,86	1
CF_2	1162	666,5	1480	48,20	2
CCl_2	730	340	1000	1115	2

[a] The value of $1 \cdot 10^{-39}$ $g \cdot cm^2$ is given.
1) Molecule.

CF_2. Venkateswarlu [4091] was the first to obtain the emission spectrum of the carbon difluoride molecule in an electrodeless discharge through CF_4 vapors. The spectrum was photographed with a spectrograph having a dispersion of 2.6 A/mm at 2500 A. An analysis of the vibrational structure of the observed band system lying in the range from 2400 to 3250 A showed that the band edges are described very well by the equation

$$\nu = 39195 + 750v_1' + (495{,}5v_2' - 0{,}5v_2'^2) - (1162v_1'' - 0{,}2v_1''^2 - 0{,}008v_1''^3) - (666{,}5v_2'' - 1{,}0v_2''^2 - 0{,}5v_1''v_2''),$$

where v_1 and v_2 are the quantum numbers of the symmetric valency and deformation vibrationa and, consequently, the fundamental frequencies of the corresponding in the lower state are equal* to $\nu_1'' = 1162$ and $\nu_2'' = 666.5$ cm^{-1} and in the upper state: $\nu_1' = 750$ and $\nu_2' = 495.5$ cm^{-1}.

A theoretical consideration of the possible electron configurations of various states of the CF_2 molecule carried out by Mulliken (see [4091]) under the assumption that the molecule belongs to the symmetry point group C_{2v} ($\angle$FCF ~ 110-130°) showed that the observed system of bands in the emission spectrum of CF_2 may be interpreted as a system connected with the transition $^1B_2 \rightarrow {}^1A_1$.

Laird, Andrews and Barrow [2543] studied the absorption spectrum of the CF_2 molecule and in the range from 2340-2660 A found bands that are completely identical with the emission bands observed in the work [4091]. This fact served to corroborate the assumption that the lower state $^1A_1$ of Venkateswarlu's band system is the electronic ground state of the CF_2 molecule.

Since from studying the ultraviolet spectrum of CF_2 [2543, 4091] only two frequencies ν_1 and ν_2 were found, Duchesne and Burnelle [1429] calculated the force constants of CF_2 in order to estimate the frequency of the antisymmetric valency vibration ν_3, on the basis of the values $\nu_1 = 1162$ and $\nu_2 = 666.5$ cm^{-1} found in the work [4091]. Since the value of the force constant of the C – F bond obtained in this way proved to be considerably higher than in the CH_3F, CH_2F_2 and CHF_3 molecules, the authors of [1429] chose the lower value $\nu_2 = 344$ cm^{-1} for the frequency of the deformation vibration. The conclusion drawn on the value of ν_2 in the work [1429] must, however, not be considered justified since for $\nu_1 = 1162$ and $\nu_2 = 344$ cm^{-1} and an FCF angle equal to 110° $f_d = 7.6 \cdot 10^5$ dyn·cm^{-1}, which seems to be too low for the C – F bond.*

Tatevskiy and Tyulin [56] showed by comparing the values of the deformation vibration frequencies of the $SiCl_4$, $SiCl_2$ and CF_2 molecules that the deformation frequency of CF_2 must be greater than that of CF_4 (437 cm^{-1}), i.e., the value of ν_2 equal to 666.5 cm^{-1} is better founded than the value of 344 cm^{-1}. Assuming that the relationships between the force constants of CF_2 remain the same as in the CH_nF_m molecules Tatevskiy and Tyulin [56] calculated the force constant $f_d = (13.2 \pm 0.8) \cdot 10^6$ cm^{-2} and $\angle FCF = 109.5 \pm 4°$ from the values of $\nu_1 = 1162$ and $\nu_2 = 666.5$ cm^{-1}. This permitted them to find the frequency of the antisymmetric vibration $\nu_3 = 1480 \pm 60$ cm^{-1}. The authors of [56] also remark that if f_d in CF_2 is assumed equal to k_e in the CF molecule and ∠FCF within the limits of 110 to 130°(as recommended by Walsh [4139], then $\nu_3 = 1530 \pm 50$ cm^{-1}, which is in good agreement with the aforeindicated value.*

On the basis of these facts, values of the frequencies of CF_2 as given in Table 178 are adopted in the present Handbook. The possible error in the value of ν_3 is 10%.

As was noted above, the results of the study on the spectrum of CF_2 [4091] and the theoretical analysis of the electron configuration of CF_2 carried out by Mulliken lead to the conclusion that the CF_2 molecule in the electronic ground state belongs to the symmetry point group C_{2v} and must have an ∠FCF angle equal to 110-130°. A calculation carried out by Tatevskiy and Tyulin [56] on the basis of the values of the CF_2 frequencies found in the work [4091] showed that ∠FCF = = 109.5 ± 4° . An estimate of Searcy [3670] carried as a result of a calculation for the electrostatic molecular model yielded the value ∠FCF = 108 ± 3°.5, which is in good agreement with the value found in the work [56].

In the present Handbook we assume that in the CF_2 molecule ∠FCF = 110 ± 5°. The interatomic distance r_{C-F} in CF_2 is assumed equal to the average of the values of r_{C-F} in the CF radical and in the CF_4 molecule: 1.30 ± 0.05 A. Table 178 gives the value of the product of the moments of inertia of the CF_2 molecule corresponding to these structural parameters. According to the assumed structure of CF_2 it is assumed in the handbook that the ground state of CF_2 is a singlet.

CHF. There are no experimental data on the spectrum and the structure of the CHF molecule in literature. In connection with the fact that the CH_2 and CF_2 molecules have different ground states and a different structure the estimation of the structure of CHF is not unique. In the present Handbook it is assumed that the CHF molecule has a nonlinear structure with an angle HCF = 110 ± 10°, belong to the symmetry point group C_{1v}, and its ground state is the state $^1A_1$. The interatomic distance r_{C-F} is assumed to be equal to the interatomic distance r_{C-H} in the methane molecule $r_{C-H} = 1.09 \pm 0.03$ A,* and the distance between the carbon atom and the fluroine atome is assumed to be equal to the mean value of r_{C-F} in the CF radical and the CF_4 molecule: 1.30 ± 0.05 A. Table 178 gives the value of the product of the moments of inertia of CHF calculated for the adopted structural parameters.

A nonlinear asymmetric triatomic molecule belonging to the symmetry point group C_{1v} must have three fundamental frequencies corresponding to valency vibrations of the C-H and C-F bonds and to a deformation vibration of the molecule.

The fundamental frequencies of the CHF molecule were estimated in the present Handbook on the basis of a calculation with the help of equations derived by Lechner [2579] for nonlinear XYZ molecules and a valency-force field model without allowance for the interaction of bonds and angles. The calculation was carried out on the assumption that the force constants of the C-H and C-F bonds are equal to the corresponding constants in the CH_2 and CF_2 molecules calculated from Eqs. (P4.30) and the fundamental frequencies of CH_2 and CF_2 adopted in the Handbook: $f_{C-H} = 9.0 \cdot 10^6$, $f_{C-F} = 11.0 \cdot 10^6$ cm^{-2}, and f_α/d^2 - the deformation constant in CHF - equal to the average of the values of f_α/d^2 for the CH_2 nd CF_2 molecules, or $2.5 \cdot 10^6$ cm^{-2}. The value $f_\alpha/d^2 = 2.5 \cdot 10^6$ cm^{-2} is also the average of the values of the corresponding deformation constants in the CH_3F, CH_2F_2 and CHF_3 molecules [128]. The following fundamental frequencies of CHF correspond to the force constants estimated in this way: $\nu_1 = 3140$, $\nu_2 = 1180$ and $\nu_3 =$

= 1600 cm^{-1}. The calculation carried out on the assumption that the force constants of the CH and CF bonds in the CHF molecule are equal to the corresponding constants in the diatomic radicals CH and CF (f_{C-H} = $= 7.7 \cdot 10^6$ and $f_{C-F} = 13.0 \cdot 10^6$ cm^{-2}), yields the frequencies $\nu_1 = 2900$, $\nu_2 = 1250$ and $\nu_3 = 1650$ cm^{-1}. Practically the same values of the frequencies of CHF ($\nu_1 = 2970$, $\nu_2 = 1210$ and $\nu_3 = 1680$ cm^{-1}) result from a calculation with the help of Eqs. (P4.25) if we assume that the force constants in CHF are equal to the constants of the C-H and C-F in the CH_4 and CF_4 molecules ($f_{C-H} = 8.34 \cdot 10^6$ and $f_{C-F} = 12.3 \cdot 10^6$ cm^{-2}).

We must also note that the values of the fundamental frequencies of CHF do not vary by more than 5-7% if the value of the deformation constant f_α/d^2 varies within the limits of 50%.

On the basis of the aforementioned facts the values $\nu_1 = 3000 \pm 200$, $\nu_2 = 1200 \pm 100$, $\nu_3 = 1600 \pm 150$ cm^{-1} given in Table 178 are adopted in the present Handbook for the fundamental frequencies of CHF.

$\underline{CCl_2}$. There are no experimental data on the spectrum and the structure of CCl_2 in literature. In analogy to CF_2, but also to $SiCl_2$ we may assume that CCl_2 has an angular symmetric structure and belongs to the symmetry point group C_{2v}. The interatomic distance r_{C-Cl} in CCl_2 is assumed in the Handbook to be equal to this distance in the CCL_4 molecule: 1.76 ± 0.05 A*, and the angle between the bonds, as in the carbon difluoride molecule, equal to 110 ± 10°. We must note that the calculation carried out by Searcy [3670] yields the similar value of $\angle ClCCl = 112.4 \pm 3°.5$. On the basis of the adopted structural parameters the product of the moments of inertia of CCl_2 which is given in Table 178 was calculated.

The vibrations frequencies of the CCl_2 molecule were calculated by Tatevskiy and Tyulin [56] with the help of Eqs. (P4.28). The calculation carried out for CF_2 showed that the calculated values of the frequencies of the fully symmetric vibrations ν_1 and ν_2 are in good agreement with those observed edperimentally only in the case where the force constant of the C – F bond is assumed equal to 1.20 $f_d(CH_2F_2)$ or 1.05 $k_e(CF)$. The authors of the work [56], therefore, adopted the value $7.0 \cdot 10^6$ cm^{-2} for $f_d(CH_2Cl_2)$ which is the average of the value of $f_d(CH_2Cl_2) = 5.9 \cdot 10^6$ cm^{-2} [128], multiplied by 1.20 and the value of $k_e(CCl) = 6.5 \cdot 10^6$ cm^{-2}, multiplied by 1.05.* The force constant of the interaction of the C – Cl bonds between one another $f_{dd} = 0.52 \cdot 10^6$ cm^{-2}, the constant of the angle between the bonds $f_\alpha d^2 = 1.77 \cdot 10^6$ cm^{-2} and the force constant of the interaction of the ClCCl angle with the C – Cl bond $f_{d\alpha} = 1.18 \cdot 10^6$ cm^{-2} were estimated on the basis of the adopted value of $f_d(CCl_2)$ on the assumption that between the force constants of CCl_2 the same relationships remain valid as between the force constants of the CCl_4, $CHCl_3$ and CH_2Cl_2 molecules. The values of the fundamental frequencies of CCl_2 recommended in the work [56] are given in Table 178 and are adopted in the Handbook. The possible error in the values of the frequencies is 10%.

In analogy to CF_2 it is assumed in the present Handbook that the electronic ground state of CCl_2 is a singlet.

$\underline{CH_3}$. Until a short time ago, there had been no experimental data on the spectrum and the structure of CH_3. The structural parameters and the vibration frequencies of the methyl molecule could, therefore, be estimated only approximately.

On the basis of qualitative considerations and quantum mechanical calculations two alternative models of the CH_3 molecule - a plane and a pyramidal one - were discussed in literature. Some considerations in favor of a plane structure of methyl were expressed by Van Vleck [4065, 4066, 4067], Voge [4118], Walsh [4136], and Lennard-Jones and

Pople [2594]. The most detailed works, in which the choice of the plane structure of methyl is founded, are the works by Penney [3216] and Mamotenko [291]. The authors of the works [291, 3216] used the Heitler-London-Slater-Pauling [HLSP] method of localized electron pairs and calculated the total bond energy of the CH_3 molecule for the plane and the pyramidally tetrahedral model. According to the calculations carried out by Penney and Mamotenko the bond energy for the plane model of CH_3 is greater than for the tetrahedral one, by 15.6 and 21 kcal/mole, respectively. Especially on the basis of the results obtained by Penney and Mamotenko a plane model was adopted for methyl in the works [146, 168, 370].

In following works by Linnett and Poe [2622], Walsh [4139] and Itoh, Ohno and Kotani [2194] it was, however, shown that the methyl molecule must have a pyramidal form.

The considerations set forth by Linnett and Poe [2622] had, above all, a qualitative character. The authors of [2622] assumed that methyl has a pyramidal structure, the angle between the C – H bonds having a value between 109°.5 and 116°.5.

Walsh [4139] came to the general conclusion that if an AH_3 molecule has not more than six valency electrons in the ground state its structure must be plane, but if it contains seven or eight valency electrons its structure must be pyramidal. Consequently, Walsh [4139] assumed that the structure of the CH_3 molecule having seven valency electrons must be bypramidal. According to Walsh [4139] the HCH angle in methyl must lie between 120° (plane model) and the valency angle HNH in NH_3, equal to 107°.

In contrast to the aforementioned works, Itoh, Ohno and Kotani [2194] carried out a quantum mechanical calculation of the total bond energy in the CH_3 molecule for the electronic ground state. Using a method which they called a generalized Heitler-London method (OGL), Itoh, Ohno and Kotani [2194] calculated the total bond energy in the CH_3 molecule for angles β between the C – H bond and the axis of symmetry equal to 45; 54.7; 60; 70.5; 80 and 90°. The corresponding values of the angles between the C – H bonds are equal to 75, 90° (rectangular model), 97, 109°.5 (tetrahedral model), 117 and 120° (plane model). On the basis of the obtained dependence of the bond energy in CH_3 on the angle between the bonds the authors of [2194] concluded that the most stable shape of the CH_3 molecule is pyramidal with an angle between the C – H bonds equal to 117°. In their calculations Itoh, Ohno and Kotani [2194] as well as Penney and Mamotenko assumed that the interatomic distance of C – H in methyl is the same and equal to 1.09 Å for arbitrary HCH angles. This assumption as well as a number of other assumptions simplifying the calculations could, obviously alter the value of the optimum angle in an essential way since the difference between the bond energies for the angles 109.5, 117 and 120° is not great and amounts only to 2-3 kcal/mole. Consequently, until reliable experimental data were obtained, the conclusions of the work [2194] as well as those of calculations carried out earlier [3216, 291] could not be considered wellfounded, and the problem of the structure of the CH_3 molecule remained unsolved.

Using the method of pulsed photolysis, Herzberg and Shoosmith [2045] in 1956 for the first time obtained the absorption spectrum of the CH_3 molecule. The spectrum was recorded by a trimetric vacuum spectrograph with grating. In the photolysis of $Hg(CH_3)_2$ (pressure 0.04 mm, length of the absorbing vessel 50 cm) four narrow groups of diffuse bands in vacuum ultraviolet were obtained in the absorption spectrum in the range from 1300-1510Å. Analogous, but somewhat shifted bands were obtained in the photolysis of $H_g(CD_3)_2$. Besides, additional bands were observed in the region of 2160 A in the photolysis of $H_g(CH_3)_2$ and in the region of 2140 A in the photolysis of $H_g(CD_3)_2$. The same bands appeared in the photolysis of CH_3CHO, $(CH_3)_2N_2$, $(CH_3)_2CO$, CH_3J and CH_3Br, and, consequently, they are connected with the methyl radicals since photochemical dissociation of all aforementioned molecules must lead to the formation of a CH_3 molecule.*

The main bands in the vacuum range of the spectrum form sharp Rydberg series, which can be described by the following formulas:

$$\left.\begin{aligned} &\text{for } \mathbf{CH_3} \quad \nu = 79380 - \frac{R}{(n-0{,}077)^2}; \\ &\text{for } \mathbf{CD_3} \quad \nu = 79305 - \frac{R}{(n-0{,}077)^2}. \end{aligned}\right\} \quad n = 3, 4, 5, 6, 7\ldots$$

The constant terms in these formulas yield values of the ionization potentials for CH_3 equal to 9.840 ± 0.002 ev and for CD_3 9.832 ± 0.002 ev, which are in very good agreement with the value of 9.90 ± 0.1 ev obtained by various authors [2559, 2660] from mass-spectrometric measurements. This agreement shows once more that the bands really belong to CH_3. Except for the 2140 A band of CD_3, all bands are diffuse, evidently owing to predissociation. The sole resolved band at 2140 A is of variable intensity. The variable intensity of the band may be explained by the fact that this band is parallel. The parallel band can be observed in the spectrum of CH_3 only if the molecule has a plane configuration, at least, in one of the electronic states between which the transition is observed. If the molecule has no plane configuration the variable intensity may be due to the great inversion splitting which is possible only in cases where the deviations of the molecule from the plane structure are small. As a result of the investigations carried out the authors of the work [2045] concluded that in the ground state the CH_3 molecule slightly deviates from the plane configuration and is plane in all excited states forming the

Rydberg series. The latter agrees with the theoretical predictions that the CH_3^+ molecule should be plane [2026].

Thus, a preliminary investigation of the CH_3 and CD_3 spectra [2045] shows that the CH_3 molecule has a plane structure or a nearly plane structure in the ground state. This conclusion agrees with the theoretical calculations [2194, 2622, 4139].

On the basis of the results of theoretical calculations [2194, 2622, 4139] and an experimental investigation of the CH_3 and CD_3 spectra [2045] it is assumed in the present Handbook that the CH_3 molecule belongs to the symmetry point group C_{3v} and has $\angle HCH = 117 \pm 3°$. The interatomic distance r_{C-H} is assumed to be equal to the interatomic distance r_{C-H} in the methane molecule $r_{C-H} = 1.09 \pm 0.03$ A. On the basis of these structural parameters the product of the moments of inertia of CH_3 which is given in Table 180 was calculated.*

The normal vibration frequencies of the CH_3 molecule may be estimated approximately on the basis of a calculation with the help of the equations for the field of valency forces (P4.37) with force constants of CH_3 assumed equal to the force constants of methane (see page 1247). Such a calculation, however, cannot be carried out exactly enough for the pyramidal model with an HCH angle equal to 117° (i.e., almost for a plane molecule) since for a molecular model close to the plane one an additional force constant characterizing the vibration analogous to the extraplanar vibration ν_2 of the plane molecule XY_3 must be introduced. Consequently, besides the calculation for the angle of 117° corresponding calculations for a tetrahedral angle and for a plane molecule with an HCH angle equal to 120° were carried out [Eqs. (P.4.41)]. In the latter case, the calculation was carried with the help of the force constants of methane calculated by Herzberg for a field of valency forces without taking account of the interaction of bonds and angles (see [152] page 200) and on the assumption that the force constant of the nonplane vibrations f_γ/d^2 is equal to 0.1 f_d.* The values of the frequencies of CH_3 calculated in this way are given in Table 179.

As may be seen from Table 179, the frequencies connected with the vibrations of the C — H bonds are practically independent of the chosen value of the HCH angle and similar to the corresponding characteristic frequencies of the C — H angles] The discrepancies between the values of the frequencies ν_2 and ν_4 calculated for the angle HCH = 117° and for the angles of 110 and 120° are considerably greater and amount to ~ 500 for ν_2 and to ~ 200-300 cm^{-1} for ν_4. This is due to the aforementioned unreliability of the calculation of the frequencies of the pyramidal molecule with an angle close to 120° with the help of Eqs. (P4.37)-(P4.39).

An estimate of the vibration frequencies of the CH_3 molecule on the basis of a frequency extrapolation in the molecule series $CH_3J \rightarrow \rightarrow CH_3Br \rightarrow CH_3Cl \rightarrow CH_3F \rightarrow CH_3H$ yields the values $\nu_1 = 2920$, $\nu_2 = 1300$, $\nu_3 = 3040$ and $\nu_4 = 1600$ cm^{-1}, which, except for ν_2, agree with the values calculated from Eqs. (P4.39) and (P4.41) for HCH angles equal to 110° and 120°, within the limits of an error of 10%.

On the basis of the estimates carried out values equal to 3000 ± ± 100 and 3100 ± 100 cm^{-1}, respectively, are adopted in the present Handbook for the frequencies ν_1 and ν_3, the frequency ν_4 is assumed to be equal to 1650 cm^{-1} with an error not exceeding 150 cm^{-1}. The value of the frequency ν_2 is the least determined. In the Handbook the value of $\nu_2 = 1000$ cm^{-1} is adopted and it is assumed that the error in this value is 25%. The adopted values of the frequencies of CH_3 are given in Table 180.

TABLE 179

Values of the Fundamental Frequencies and the Product of the Moments of Inertia for Different Models of the CH_3 Molecule

Метод расчета и автор 1	∠ HCH	ν_1	ν_2	ν_3 (2)	ν_4 (2)	$I_A I_B I_C$
	град 2	см⁻¹ 3				4 $10^{-118}(г \cdot см^2)^3$
5 Расчет по уравнениям (П4.37) и силовым постоянным метана	109,5	3053	875	3143	1712	53,64
	117	3034	512	3157	1949	53,34
6 Расчет по уравнениям (П4.41) и силовым постоянным метана[a] с $f_\gamma/d^2=0,1f_d$	120	2915	1030	3100	1620	53,06
Экстраполяция. 7		2920	1300	3040	1600	—
8 Оценка Халфорда, Андерсона и Киссина [1932]	109,5	2895	1465	2987	1445	—
9 Оценка А. Гурвича и Фроста [168]	120	2923	—[b]	3025	1602	—

[a] A calculation with the help of the force constants of ethane yields values of the CH_3 frequencies practically coinciding (±50 cm^{-1}) with the frequencies as calculated with the help of the methane constants.

[b] In the work [168] the value of the frequency ν_2 is not given.

1) Method of calculation and author;
2) degree;
3) cm^{-1};
4) $(g \cdot cm^2)^3$;
5) calculation with the help of Eqs. (P4.37) and the force constants of methane;
6) calculation with the help of Eqs. (P4.41) and the force constants of methane with $f_y/d^2 = 0.1f_d$;
7) extrapolation;
8) estimate by Halford, Anderson and Kissen [1932];
9) estimate by Gurvich and Frost [168].

Earlier an approximate estimate of the fundamental frequencies of the CH_3 molecule was carried out on the basis of a comparison of the characteristic frequencies of the CH_3 group in various compounds by Gurvich and Frost [168] for the plane model of CH_3 and by Halford, Anderson and Kissin [1932] for the pyramidal model with a tetrahedral HCH angle. Table 179 gives the values obtained by these authors.

Since there is one free electron in the CH_3 molecule, it is assumed in the Handbook in accordance with the works [2592, 2990, 2026] that its ground state is a doublet $^2A_2''$. The first excited state $^2E'$ must lie by about 53,000 cm^{-1} higher than the ground state as was shown by a quantum mechanical calculation carried out by Higuchi [2069]. The experimental data considered above attest to the fact that the energy of the first excited state has a value of about 46,700 cm^{-1}.

CF_3 and CCl_3. There are no informations whatsoever in literature as to experimental studies on the spectrum or the structure of carbon trifluoride or trichloride.

In the present Handbook it is, according to a recommendation of Tatevskiy and Tyulin [56], assumed that the CF_3 and CCl_3 molecules have a pyramidal structure and belong to the symmetry point group C_{3v}. The authors of the work [56] assume that the most probable value of the angle between the bonds is the angle XCX equal to 110°. As was remarked above, theoretical considerations [2622, 4139, 2194] and the results of an investigation of the spectra of CH_3 and CD_3 [2026, 2045] show that the CH_3 molecule must have a structure similar to a plane one. It is, therefore, quite probable that the XCX angle in the CF_3 and CCl_3 molecules, similar to the CH_3 molecule, should have values within the limits from 110 to 120°. Until experimental data on the structure of these molecules are obtained it is assumed, however, in the Handbook, in accordance with the recommendation of Tatevskiy and Tyulin, that the FCF and ClCCl angles are equal to 110 ± 10°.

A preliminary study on the structure of the 2140 A absorption band in the spectrum of CD_3 showed that the interatomic distance in this molecule must be smaller than in the methane molecule [2026]. It is, therefore, assumed in the Handbook that in the CF_3 molecule $r_{C-F} = 1.30 \pm 0.05$ A (the bond length in CF_4 is equal to 1.322 A). The interatomic distance in CCl_3 is assumed equal to 1.76 ± 0.05 A, as in CCl_4.* The products of the principal moments of inertia of CF_3 and CCl_3 calculated on the basis of these structural parameters are given in Table 180.

TABLE 180

Adopted Values of the Molecular Constants of CH_3, CH_2F, CHF_2, CF_3 and CCl_3

1 Молекула	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	$I_AI_BI_C$	σ
	$см^{-1}$ 2						10^{-117} $(г \cdot см^2)^3$ 3	
CH_3	3000	1000	3100(2)	1650(2)	—	—	$53{,}34 \cdot 10^{-8}$	3
CH_2F	3000	3000	1100	1200	1500	1400	0,73	1
CHF_2	3000	1150	1200	600	1350	1400	52,7	1
CF_3	925	630	1210(2)	550(2)	—	—	793,8	3
CCl_3	615	345	830(2)	275(2)	—	—	$307{,}30 \cdot 10^{2}$	3

1) Molecule; 2) cm^{-1}; 3) $(g \cdot cm^2)^3$.

An approximate estimate of the fundamental frequencies of the CF_3 and CCl_3 molecules was carried out by Tatevskiy and Tyulin [56]. The fundamental frequencies of CF_3 were estimated on the basis of a comparison of the frequencies in the CF_3Cl, CF_3F and CF_3H series, but were calculated with the help of Eqs. (P4.37), as well. The calculation was carried out for different values of the FCF angle (110, 115 and 120°) using the force constants of the CH_2F_2, CHF_3 and CF_4 molecules.* Tatevskiy and Tyulin [56] recommend the values that are mean values of those calculated for the angle 110° and those obtained by an extrapolation in the CF_3Cl, CF_3F and CF_3H series, as the most probable values of the fundamental frequencies of carbon trifluoride.

Kohlrausch [236] was the first to carry out an estimate of the fundamental frequencies of the CCl_3 molecule by extrapolating the frequencies in the CCl_3Br, CCl_3Cl, CCl_3F, CCl_3D and CCl_3H molecule series. Tatevskiy and Tyulin [56] calculated the fundamental frequencies of CCl_3 with the help of Eqs. (P4.37) for different values of the ClCCl angle. In doing so, they assumed that the force constants of CCl_3 are equal to the corresponding force constants of $CHCl_3$.* The authors of the work [56], as in the case of CF_3, recommend the values of the CCl_3 frequencies which are the average values of those calculated from Eqs. (P4. 37) for an angle ClCCl = 110° amd those found by Kohlrausch [236] by extrapolation, as the most probable values.

The values of the frequencies of CF_3 and CCl_3 recommended in the work [56] are given in Table 180 and adopted in the present Handbook. The possible error of these values is about 10%.**

Since in the CF_3 and CCl_3 molecules there is one free atom the electronic ground state of these molecules should be a doublet as in the CH_3 molecule.

CH_2F and CHF_2. The spectrum and the structure of the CH_2F and CHF_2 molecules were not determined experimentally. Consequently, their fundamental frequencies and structural parameters are adopted in the present Handbook on the basis of approximate estimates.

We may assume that if the hydrogen atoms in CH_3 are replaced by fluorine atoms the structure of the CH_2F and CHF_2 molecules remains pyramidal. Since the CH_2F and CHF_2 molecules have one symmetry plane, they belong to the symmetry point group C_s. The C – H and C – F bond lengths in CH_2F and CHF_2 were assumed to be the same as in CH_3 and CF_3, in the present Handbook: $r_{C-H} = 1.09 \pm 0.05$ and $r_{C-F} = 1.30 \pm 0.05$ A, and the angles equal to 110 ± 10°. On the basis of the adopted values of the structural parameters the products of the principal moments of inertia given in Table 180 were calculated.

A tetratomic molecule of C_s symmetry must have six nondegenerate frequencies, three of which are connected with valency vibrations of the bonds and three with deformation vibrations.

A comparison of the fundamental frequencies in the molecule series

$$CH_2FCl \rightarrow CH_2FF \rightarrow CH_2FH \rightarrow CH_2F$$

and

$$CHF_2Cl \rightarrow CHF_2F \rightarrow CHF_2H \rightarrow CHF_2$$

permits an estimate of the values of the corresponding frequencies of the CH_2F and CHF_2 molecules which, of course, should be considered to be only roughly approximate.

These values are adopted in the present Handbook and given in Table 180. The errors in the frequencies corresponding to vibrations of the C – H bonds, obviously, do not exceed ± 200 cm^{-1}, as is shown by a comparison of the vibration frequencies of these bonds in various molecules. The values of the frequencies connected with valency vibrations of the C – F bonds and given in Table 180 are similar to the frequencies of the fluorine substitution products of methane, ethylene, ethane, and, obviously, also their error does not exceed ± 200 cm^{-1}. Estimating the error in the values of the deformation vibration frequencies is more complex. It is assumed in the Handbook that the errors in the corresponding frequencies are 20-30%. In order to verify the correctness of the chosen values the fundamental frequencies of CH_2F and CHF_2 were calculated from Eqs. (P4.33). In doing so, it was assumed that the force constants are equal to the corresponding constants of the molecules of the fluorine substitution products of methane [128]*: $f_{C-H} = 8{,}5 \cdot 10^6$, $f_{C-F} = 10{,}6 \cdot 10^6$, $f_{FCF} = 1{,}5 \cdot 10^6$, $f_{HCH} = 0.75 \cdot 10^6$, $f_{HCF} = 1.0 \cdot 10^6$ cm^{-2}. The values of the frequencies calculated in this way are equal to: for CH_2F $\nu_1 = 3150$, $\nu_2 = 3090$, $\nu_3 = 1350$, $\nu_4 = 650$, $\nu_5 = 1400$ and $\nu_6 = 1130$ cm^{-1}, for CF_2H $\nu_1 = 3000$, $\nu_2 = 1000$, $\nu_3 = 1220$, $\nu_4 = 250$, $\nu_5 = 1170$, $\nu_6 = 1420$ cm^{-1}. Except for the frequencies ν_4 which correspond to deformation vibrations they agree with the frequencies given in Table 180, within the limits of 10-20%.

The too low values of the deformation vibration frequencies ν_4

are, obviously, connected with the fact that the chosen approximation describes the force field of the pyramidal molecules XY_2Z only with insufficient accuracy.

In analogy to CH_3 it is assumed in the present Handbook that the electronic ground states of CH_2F and CHF_2 are doublets.

C_2H and C_2F. There are no informations whatsoever in literature as to the spectra and structural parameters of the C_2H and C_2F molecules. Investigations of the absorption spectra in the pulsed photolysis of propiolaldehyde (HC_2CHO) carried out in Herzberg's laboratory [2026] showed that irrespective of the presence of C_2H in the absorption cell as a result of propiolaldehyde photolysis,* no discrete bands connected with the C_2H radical are observed in the spectrum.

We may assume that in the electronic ground states C_2H and C_2F must have a linear structure with a triple bond between the carbon atoms $C \equiv C - X$. The molecules of this type belong to the point group $C_{\infty v}$ and are characterized by three vibration frequencies (one of which is doubly degenerate). The fundamental frequencies and the structural parameters of the C_2H and C_2F molecules may be estimated with sufficient accuracy on the basis of the corresponding data for the molecules of acetylene and its halogen substitution products.

The $C \equiv C$ triple bond length in the molecules of acetylene and its halogen substitution products varies slightly if we pass over from one substituting element to another. It is, therefore, natural to assume that the $C \equiv C$ bond length in the C_2H radical is equal to $r_{C \equiv C}$ in acetylene. On this basis it is assumed in the Handbook that $r_{C \equiv C}$ (C_2H) = 1.21 ± 0.02 A. The C – H bond length also changes slightly in the different substitution products of acetylene**; within the limits of an error of ±0.005 A it is assumed equal to 1.055 A. The $C \equiv C$ bond length in C_2F was estimated on the basis of a comparison of the interatomic distances in the C_2H_6, C_2H_4, C_2H_2, C_2F_6 and C_2F_4 molecules as equal to 1.20 ± 0.03 A. The interatomic distance r_{C-F} in the C_2F molecule was assumed equal to the interatomic distance r_{C-F} in the molecules C_2FH, C_2F_2 and FCN (see pages 1219 and 1323): r_{C-F} = 1.28 ± 0.05 A. On the basis of the structural parameters of C_2F and C_2H estimated in this way the moments of inertia of these molecules given in Table 181 were calculated.

TABLE 181

Adopted Values of the Molecular Constants of C_2H and C_2F

1 Молекула	ν_1	ν_2 (2)	ν_3	I	σ
	$см^{-1}$ 2			10^{-39} г · $см^2$ 3	
C_2H	3300	600	2030	1,90	1
C_2F	2480	360	1090	7,66	1

1) Molecule; 2) cm^{-1}; 3) $g \cdot cm^2$.

The fundamental frequencies of C_2H and C_2F were calculated on the basis of the estimated force constants of these molecules. The calculation was carried out with the help of Eqs. (P4.27). The force constants of the C_2H molecule were assumed to be equal to the force constants of the acetylene molecule $f_{d_1} = 5.92 \cdot 10^5$, $f_{d_2} = 15.80 \cdot 10^5$ dyn$\cdot$ $\cdot cm^{-1}$, $f_\alpha = 0.15 \cdot 10^{-11}$ dyn·cm rad^{-1}. The estimate of the force constants of the C – F(f_{d_2}) and C ≡ C(f_{d_1}) bonds was carried out for C_2F by comparing the force constants of the C ≡ C, C – F and C – H bonds in the C_2H_6, C_2H_4, C_2H_2, C_2F_6, C_2F_4, molecules, and the estimate of the deformation constant f_α was carried out with the help of the value of this constant in the C_2H_2 and C_2N_2 molecules. The adopted values of the force constants of C_2F are equal to: $f_{d_1} = 8.5 \cdot 10^5$, $f_{d_2} = 19.00 \cdot 10^5$ dyn$\cdot cm^{-1}$, $f_\alpha = 0.25 \cdot 10^{-11}$ dyn·cm/rad^{-1}. The fundamental frequencies of

C_2H calculated with the help of Eqs. (P4.27) $\nu_1 = 3330$, $\nu_2(2) = 560$ and $\nu_3 = 2045$ cm^{-1} are similar to the characteristic frequencies of the corresponding vibrations given in Herzberg's monograph [152] (3300 700 and 2050, respectively).* In the Handbook it is assumed: $\nu_1 = 3300 \pm 100$, $\nu_2(2) = 600 \pm 100$, $\nu_3 = 2050 \pm 100$ cm^{-1}. For the frequencies of the C_2F molecule the calculation with the help of Eqs. (P4.27) led to the values $\nu_1 = 2480$, $\nu_2(2) = 360$ and $\nu_3 = 1090$ cm^{-1} which are given in Table 181; the possible error of these values is 15%.**

Since there is one free electron in the C_2H and C_2F molecules and they are isoelectronic with the CN and CP molecules, it is assumed in the Handbook that their ground states are $^2\Sigma$ doublet states.

§82. THERMODYNAMIC FUNCTIONS OF THE GASES

The thermodynamic functions of the substances considered in the present chapter were calculated for the perfect gas state in the temperature interval from 293.15 to 6000°K with the help of the molecular constants adopted in the preceding section. The calculated values of the thermodynamic functions are given in Tables 138, 139, 140, 144, 145, 146, 150, 151, 153, 157, 158, 159, 211 and 214 Volume II of the Handbook.

In the calculation of the thermodynamic functions of these gases the difference in the constants of the isotopic modifications of their molecules was not aken into account.

CH, CF and CCl. The thermodynamic functions of methine, carbon monofluoride and monochloride given in Tables 138 (II), 144 (II) and 157 (II) were calculated with the help of Eqs. (II.161) and (II.162) on the basis of the molecular constants presented in Table 176. The values of $\ln \Sigma$ and $T\, d/\partial T \ln\Sigma$ in these equations were calculated by the method of Gordon and Barnes [relations (II.137) and (II.138)] without introducing corrections for the limitation of the number of rotational levels of the electronic ground state. The CH, CF and CCl molecules have electronic ground states $^2\Pi_r$. According to the adopted molecular constants the ratio A/B_0 has a value of the order of 1.95 for CH and, consequently, the type of bond in this molecule is similar to the Hund case b. In accordance with this fact, in the calculation of the thermodynamic functions of methine the quantities $\ln \Delta$ and $T \partial/\partial T \ln \Delta$ in Eqs. (II.161) and (II.162) were calculated with the help of Eqs. (II.153) and (II.154). For the CF and CCl molecules the ratio A/B has a value of the order of ~ 55 and ~ 190, respectively. Consequently, the values of $\ln \Delta$ and $T \partial/\partial T \ln \Delta$ were calculated with the help of Eqs. (II.151) and (II.152) in the calculation of the thermodynamic functions of these gases.

TABLE 182

Values of the Constants for the Calculation of Thermodynamic Functions of CH, CF and CCl

Вещество 1	θ	$x \cdot 10^3$	$\beta_1 \cdot 10^2$	$\beta_2 \cdot 10^4$	$\frac{q_0}{T}$	$\frac{d_0 \cdot 10^6}{T}$	$\frac{f_0}{T} \cdot 10^{10}$	C_Φ	C_S
	град 2	—	—	—	град⁻¹ 3		град⁻² 4	кал/моль·град 5	
CH	4127,2	22,4508	3,7369	13,96	0,0490043	9,79	−1,13	−2,8717	4,0838
CF	1882,1	8,3002	1,3475	1,90	0,493201	4,66	—	2,9274	9,8824
CCl	1256,9	8,0128	0,9680	0,937	1,00264	5,44	—	5,6055	12,5610

1) substance; 2) degree; 3) degree^{-1}; 4) degree $^{-2}$; 5) cal/mol·degree.

Table 182 shows the values of the constants C_Φ and C_S for the calculation of the components of the rigid rotator and translatory motion in Eqs. (II.161) and (II.162), the values of the quantities θ and x, and also the values of the coefficients in Eqs. (II.137) and (II.138). The excited electronic states of the CF and CCl molecules were not taken into account in the calculation of the thermodynamic functions of both gases since at 6000°K the contribution of these states to the values of Φ_T^* does not exceed 0.005 cal/mol·degree. The contributions of the $A^2\Delta$, $B^2\Sigma$ and $C^2\Sigma$ states of the CH molecule were calculated from Eqs. (II.127), i.e., taking into account the difference of the vibration frequencies and rotational constants of CH in the ground state and in the excited states.

The main errors in the calculated values of the thermodynamic functions of methine, carbon monofluoride and monochloride are connected with the lack of experimental data on the energy of their high vibrational levels in the electronic ground state. In connection with the fact, however, that the dissociation energies of CH, CF and CCl are close to the values obtained by linear extrapolation with the help of the constants adopted in the Handbook (see pages 1278, 1285 and 1291), the corresponding errors must be unimportant and do not exceed 0.1 cal/mol·degree in the values of Φ^*_{6000}. The errors due to the neglect of the necessity of limiting the number of rotational levels of the electronic ground states of the gas molecules do not exceed 0.05 cal/mol·degree in the values of Φ^*_{6000}. The total errors in the values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} for CH, CF and CCl are given in Table 184.

The thermodynamic functions of CH were calculated by Zeise [4382], A. Gurvich and Frost [168] ($T \leq 5000°K$), Ward and Hussey [4149] ($2000 \leq T \leq 5000°K$), Ribaud [3426] ($T \leq 3500°K$), Kroepelin, Neumann and Winter [2489] (Φ^*_T for $T \leq 6000°K$). All these calculations were carried out in the approximation of the rigid rotator-harmonic oscillator model, and the multiplet structure of the $X^2\Pi$ state was taken into account by the term R ln 4. The application of an approximate method of calculation and inaccurate values of the molecular constants of CH led to the result that the thermodynamic functions of methine calculated in these works contain considerable errors, particularly at high temperatures. The results of the calculation by Ward and Hussey (discrepancies within the limits from 0.04 cal/mol·degree in Φ^*_{2000} to 0.6

cal/mol·degree in S°_{6000}) and of that by Zeise (discrepancies within the limits of 0.2 cal/mol·degree) are those which agree best with the data of the present Handbook. In Ribaud's work, obviously, rough errors were committed, for which reason his values differ from those in Table 138 (II) by 3-4 cal/mol·degree. The thermodynamic functions of CH calculated by Zeise are presented in this book [4384].

The thermodynamic functions of CF were not published in the periodic literature, in American literature there are reference to tables of the thermodynamic functions of CF calculated in the US National Bureau of Standards which, however, have remained unknown to the authors of the present Handbook. In the book [2775] Margrave presents values of Φ^*_T of carbon monofluoride for $2000 \leq T \leq 5000$°K, which are in good agreement with the data of Table 144 (II).

The thermodynamic functions of CCl were calculated in a work by J. Gordon [1816] $T \leq 6000$°K with the help of the vibrational constants found by Venkateswarlu (see page 1238) and the rotational constants $B_e = 0.616$ and $\alpha_1 = 0.001$ cm^{-1}. The discrepancies between the results of this calculation and the values given in Table 157 (II) are 0.1--0.5 cal/mol·degree. They are due to the difference of the constants of CCl adopted in the calculations (in the work [1816] the method of calculation is not indicated).

The thermodynamic functions of CF given in the first and in the present edition of the Handbook are identical. The discrepancies between the corresponding data for CH and CCl attaining 0.05 and 0.62 cal/mol·degree in the values of S°_{6000} are due to the fact that the accuracy of the molecular constants of these gases has been increased.

The thermodynamic functions of methylene given in Table 139 (II) were calculated from Eqs. (II.241) and (II.242). The calculation was carried out in the approximation of the rigid rotator-harmonic oscillator model on the basis of the molecular constants adopted in Table 178. Table 183 shows the values of the constants C'_Φ and C'_S in Eqs. (II.241) and (II.242) calculated with the help of the adopted molecular constants of CH_2, but also the values of the quantities θ_n used calculate the vibrational constants in the values of Φ^*_T and S°_T. Since it was assumed above that CH_2 has a $^3\Sigma$ ground state (see page 1245) the terms R ln 3 are included in the values of C_Φ and C_S.

TABLE 183

Values of the Constants for Calculating the Thermodynamic Functions of CH_2, CH_3, C_2H and Their Fluorine and Chlorine Substitution Products

Вещество	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	C'_Φ	C'_S
1	2 град						3 кал/моль·град	
CH_2	4316,4	1582,7 (2)	4604,1	—	—	—	—3,2809[a]	3,6746[a]
CH_3	4316,4	1438,8	4460,3 (2)	2374,0 (2)	—	—	—5,9373	2,0118
C_2H	4748,0	863,27 (2)	2920,7	—	—	—	2,1998[a]	9,1553[a]
CF_2	1671,9	958,95	2129,4	—	—	—	3,8366	11,7857
CF_3	1330,9	906,44	1740,9 (2)	791,34 (2)	—	—	8,1519	16,1010
C_2F	3568,2	517,96 (2)	1568,3	—	—	—	6,5850[a]	13,5405[a]
CHF	4316,4	1726,6	2302,1	—	—	—	—0,2915	7,6576
CH_2F	4316,4	4316,4	1582,7	1726,6	2158,2	2014,3	4,1914	9,1405
CHF_2	4316,4	1654,6	1726,6	863,27	1942,4	2014,3	6,7454	14,6945
CCl_2	1050,3	489,2	1438,8	—	—	—	8,4659	16,4146
CCl_3	884,86	496,38	1194,2 (2)	395,67 (2)	—	—	13,3945	21,3432

[a] The values of C_Φ and C_S are given. 1) Substance; 2) degree; 3) cal/mol·degree.

The main errors in the calculated values of the thermodynamic functions of methylene are due to the fact that there are no experimental data on the vibrational constants of CH_2 (up to 0.5-0.8 cal/mcl·degree) in the values of Φ^*_T), but also to the fact that there are no data which are needed to take account of the deviations of the CH_2 molecule from the rigid rotator-harmonic oscillator model (up to 0.5

cal/mol·degree in the values of Φ^*_T). According to Herzberg's data (see page 1246) the CH_2 molecule has a singlet electronic state $^1A_1$ with low excitation energy whose value has remained unknown, as yet. In the calculation of the thermodynamic functions of CH_2 the components of this state were not allowed for since there are no data on its excitation energy. The errors in the calculated values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} due to this fact are 2, 2.5 and 3 cal/mol·degree if the energy of the $^1A_1$ state is equal to zero, and 0, 2 and 2.5 cal/mol··degree if it is equal to 2000 cm^{-1}. Table 184 shows the total errors of the calculated values of Φ^*_T of methylene at 298.15, 3000 and 6000°K.

TABLE 184

Errors in the Calculated Values of Φ^*_T of CH_2, CH_3, C_2H and Their Fluorine and Chlorine Substitution Products

Вещество 1	$\delta\Phi^*_{298.15}$	$\delta\Phi^*_{3000}$	$\delta\Phi^*_{6000}$	Вещество 2	$\delta\Phi^*_{298.15}$	$\delta\Phi^*_{3000}$	$\delta\Phi^*_{6000}$
CH	0,02	0,1	0,2	CF	0,02	0,1	0,2
CH_2	0,2	1,2	2,0	CF_2	0,2	0,8	1,2
CH_3	0,3	1,3	2,0	CF_3	0,8	3,0	4,0
C_2H	0,1	1,0	1,7	C_2F	0,3	2,0	3,0
CHF	0,2	1,5	2,5	CCl	0,02	0,1	0,2
CH_2F	1,0	2,8	4,0	CCl_2	0,3	1,5	2,0
CHF_2	1,0	3,0	4,0	CCl_3	1,0	3,5	5,0

1) Substance; 2) substance.

The thermodynamic functions of methylene were calculated in the works by Zeise [4382] (T ≤ 1500°K), A. Gurvich and Frost [168] (T ≤ ≤ 5000°K), Ribaud [3426] (T ≤ 3500°K), and Kroepelin, Neumann and Winter [2489] (Φ^*_T for T ≤ 6000°K). All these calculations were carried out on the assumption that the CH_2 molecule has a nonlinear structure and a singlet electronic ground state. A difference in the type of the electronic ground state and in the structure of CH_2 gives rise to considerable discrepancies between the results of these calculations and the data of Table 139 (II).

The discrepancies between the results of the calculations [2489, 3426] and the data of the present Handbook are about 1 cal/mol·degree at 1000°K and are reduced if the temperature rises. The results of the calculation of A. Gurvich and Frost differ from those given in Table 139 (II) by values up to 0.3 cal/mol·degree in the values of Φ_T^* and up to 1 cal/mol·degree in the values of S_T°. If the temperature rises the differences change their sign.

The differences between the values of the thermodynamic functions of CH_2 calculated in the first and in the present editions of the Handbook are due to the same reasons. In the values of Φ_T^* they attain their maximum at 1000°K (about 1.3 cal/mol·degree), in the values of S_T° they decrease from 1.6 cal/mol·degree at 298.15°K, pass through zero at about 4000°K and increase anew up to 0.3 cal/mol·degree at 6000°K.

CHF, CF_2 and CCl_2 . The thermodynamic functions of the three gases under consideration presented in the Tables 150, 145, 158 of Volume II of the Handbook were calculated with the help of Eqs. (II.243) and (II.244) in the approximation of the rigid rotator-harmonic oscillator model. The calculation was carried using the molecular constants given in Table 178. Table 183 shows the values of the constants C'_Φ and C'_S used to calculate the rotational-translational components in the values of the thermodynamic functions of these gases, and alsθ θ_n used to obtain the vibrational components of Φ_T^* and S_T° with the help of harmonic oscillator tables.

The main errors in the calculated values of the thermodynamic functions of CHF, CF_2 and CCl_2 at low temperatures are due to the fact that there are no experimental data on the rotational constants and geometric parameters of these molecules*; at high temperatures there are additional errors due to the lack of experimental data on the vibration frequencies, the application of an approximate method of calculation and disregarding the excited electronic states of these molecules. The values of the errors in the calculated values of Φ_T^* for CHF, CF_2 and CCl_2 at 298.15, 3000 and 6000°K are given in Table 184.

Calculations of tables of the thermodynamic properties of CF_2 were not published in literature, although there are indications of the fact that such calculations were carried out in the U. S. National Bureau of Standards. Margrave (see [2775]) presents values of Φ_T^* for carbon difluoride for $T \leq 5000$°K without indicating the way in which they calculated and which constants of CF_2 were adopted. The corresponding values agree with those presented in Table 145 (II) within the limits of 0.1 cal/mol·degree.

The discrepancies between the values of the thermodynamic functions of CF_2 given in the first and in the present editions of the Handbook are connected with the fact that the accuracy of the adopted values of the fundamental frequencies and structural parameters has been increased to some extent; they do not exceed 0.03 and 0.14 cal//mol·degree in the values of Φ_T^* and S_T°. The thermodynamic functions of CCl_2 in the first and in the present editions of the Handbook are identical. No other calculations of the thermodynamic functions of CCl_2 are known in literature.

The thermodynamic functions of CHF are published for the first time.

CH_3, CF_3, CH_2F, CHF_2.CCl_3. The thermodynamic functions of methyl and the four other gases under consideration given in the Tables 140, 146, 151, 153, and 159 of Volume II of the Handbook were calculated from

Eqs. (II.243) and (II.244) in the approximation of the rigid rotator-harmonic oscillator model. The calculation was carried out with the help of the molecular constants given in Table 180. Table 183 shows the values of the constants C'_{Φ} and C'_{S} for the calculation of the rotational-translatory components in the values of the thermodynamic functions, and also the values of θ_n for the calculation of the vibrational components with the help of the harmonic oscillator tables. Since the molecules of these gases must have doublet ground states the terms R ln 2 are included in the values of C'_{Φ} and C'_{S}.

The main errors in the calculated values of the thermodynamic functions of methyl and the rest of the gases are connected with the fact that there are no experimental data on the structure of the molecules, their vibration frequencies and rotational constants; the values of the errors in the calculated values of Φ^*_T at 298.15, 3000 and 6000°K are given in Table 184.

The thermodynamic functions of methyl were calculated in the works by A. Gurvich and Frost [168] ($T \leq 5000$°K), Zeise [4382] ($T \leq 1600$°K), Ribaud [3426] ($T \leq 3500$°K) and Kroepelin, Neumann and Winter [2489] (Φ^*_T for $T \leq 6000$°K). The discrepancies between the results of the calculation [168] and the data of the Handbook attain 1.5-1.7 cal/mol· degree and are, in the first place, due to the fact that for the plane model of CH_3 the symmetry number is equal to 6, whereas for the pyramidal model it is equal to three, and, in the second place, to some difference in the adopted values of the molecular constants. The discrepancies between the data of the Handbook and Ribaud's calculation also have a magnitude of the order 1.5 cal/mole·deg, and are, obviously, connected with the difference of the adopted models of the CH_3 molecule or the neglect of the statistical weight of the ground state of this molecule in the work [3426]. The data of Zeise and Kroepelin et al differ from the values given in the Handbook by 0.1-0.2 cal/ /mol·degree, evidently owing to some difference in the adopted values of the molecular constants.

Calculations of the thermodynamic functions of CF_3 were not published in the periodic literature. The values of Φ^*_T of carbon trifluoride recommended by Margrave in the book [2775] and based on unknown calculations, differ from those given in Table 146 (II) by 0.7 to 0.9 cal/mol·degree.

The thermodynamic functions of CCl_3 given in the first and in the present editions of the Handbook are identical. The discrepancies between the corresponding data for CH_3 and CF_3, due to some variations of the values of the molecular constants, adopted for the calculations attain 0.2 and 0.08 cal/mol·degree, respectively. No other calculations of the thermodynamic functions of CCl_3 are known in literature; the thermodynamic functions of CH_2F and CHF_2 are published for the first time.

C_2H and C_2F. The thermodynamic functions of C_2H and C_2F given in Tables 211 (II) and 214 (II) were calculated from Eqs. (II.241) and (II.242) in the approximation of the rigid rotator-harmonic oscillator model. The calculation was carried out with the help of the molecular constants given in Table 181. Table 183 presents the values of C_Φ and C_S for the calculation of the rotational-translatory components in the thermodynamic functions of these gases, and also θ_n needed to obtain the vibrational components from the harmonic oscillator tables. Since the C_2H and C_2F molecules have doublet electronic ground states $^2\Sigma$ the terms R ln 2 are included in the values of C_Φ and C_S.

The errors in the calculated values of the functions of C_2H and C_2F are connected with the fact that there are no experimental data on the constants of these molecules and that an approximate method of calculation was used. The estimated magnitudes of the errors in the values of Φ_T^* at 298.15; 3000 and 6000°K are given in Table 184.

The thermodynamic functions of C_2H were calculated recently in a work by Plooster and Reed [3266] from the estimated values of the molecular constants (see page 1267) for $T \leq 3500$°K. The discrepancies between the data of these authors and the values given in Table 211 (II) have a value of the order of 1.5 cal/mol·degree. They are, above all, due to the fact that in the work [3266] the statistical weight of the ground state of the C_2H molecule is chosen equal to 1.

There are no data in literature on other calculations of the thermodynamic functions of C_2H, nor are there any data on those of C_2F.

§83. THERMODYNAMIC QUANTITIES

CH (gas). In the spectrum of CH (as well as in that of CD) in the states $A^2\Delta$, $B^2\Sigma$ and $C^2\Sigma$ predissociation takes place [1694]. The most accurate value of the dissociation energy of CH equal to about 28,000 cm^{-1} was found by Gero [1694] from the limiting curve of the rotational levels of the $B^2\Sigma$ states of the CH and CD molecules, with which dissociation takes place on rotation on the levels $v = 0$ and $v = 1$. The results of studies on the predissociation in the $A^2\Delta$ and $C^2\Sigma$ states, according to which the dissociation energy of CH is equal to 29,500 and 28,800 cm^{-1}, respectively, are in good agreement with this value.

On the basis of the data obtained by Gero in the work [1694], Gaydon [1668] and Herzberg [2020] recommend for the dissociation energy of CH 28,000 cm^{-1} or 80 kcal/mol.

A linear extrapolation of the vibrational levels of the ground state $X^2\Pi$ with the help of the constants obtained in the work of Kiess and Broida [2394] (see page 1235) yields $D_0(CH) = 30,500$ cm^{-1} (of the order of 87.2 kcal/mol). A shorter and, consequently, more accurate linear extrapolation of the vibrational levels $B^2\Sigma$ yields the value

$D_0(CH) = 29{,}000\ cm^{-1}$ (of the order of 82.9 kcal/mol) if account of the excitation energy of this state is taken. This value is in good agreement with the values obtained by a study on the predissociations in the spectrum of CH although it proves to be less accurate.

In the present Handbook we assume

$$\mathbf{D_0(CH) = 80 \pm 1} \text{ kcal/mole.}$$

To this value corresponds

$$\mathbf{\Delta H^\circ f_0 (CH,\ ^{gas}) = 141{,}217 \pm 1} \text{ kcal/mole.}$$

CH_2 (gas). The value needed to remove a hydrogen atom from the CH_3 molecule and the value of the formation heat of CH_2 can be calculated from the results of investigating the kinetics of several reactions and determining the potentials of ion occurrence on bombarding methane and methyl with electrons.

Kistiackowsky and Rosenberg [2419] investigated the kinetics of photochemical dissociation of ketene in the presence of ethylene and determined the activation energy of the reaction $CH_2 + C_2H_4 \rightarrow CH_2CH_2CH_2$. On the basis of this value and a number of assumptions on the dissociation mechanism the authors found that the lower limit of the energy needed to remove a hydrogen atom from the CH_3 radical is given by the inequality $D(CH_2 - H) \geq 71$ kcal/mol. Using the results of several other measurements the authors of the work [2419] came to the conclusion that $D(CH_2 - H)$ is about 80 kcal/mol ($\Delta H^\circ f_0\ (CH_2) \approx 62$ kcal/mol). The error of the obtained value of the dissociation energy may be about ± 10 kcal/mol, according to an estimate [255].

Frey and Kistiakowsky [1608] discovered that the CH_2 radicals obtained by photochemical dissociation of ketene enter the reaction with ethylene, propane, cyclopropane and butane. Gesser and Steacie [1703] ascertained the fact that the CH_2 radicals also react with hydrogen, thereby forming CH_3. According to a remark made by Trotman-Dickenson

[4021] $D(CH_2 - H)$ must be greater than or equal to 101 kcal/mol in order to make these reactions possible. This conclusion is, however, not uncontradicted since the CH_2 radicals formed by the photochemical dissociation of ketene, obviously, possess excess energy, which explains their elevated reactivity.

The upper limit of the dissociation energy of methyl $D(CH_2 - H)$ was calculated by Laidler and Casey [2541] on the basis of the results of studying the chemiluminescence arising if methylene chloride reacts with sodium vapors [693]. In this work the limit of the heat effect of the reaction

$$2Na_{(gas)} + CH_2Cl_{2(gas)} = 2NaCl_{(gas)} + CH_{2(gas)}, \qquad (XX.1)$$

was found, exceeding 48.3 kcal/mol, to which $\Delta H°f_0 (CH_2) \leq 69$ kcal/mol and $D(CH_2 - H) \leq 87$ kcal/mol correspond.

Using data on the kinetics of cyclobutane dissociation [1678a], Reed [3411a] calculated $\Delta H°f_0 (CH_2, gas) = 64$ kcal/mol. This work gave rise to several critical remarks made by Trotman-Dickenson [4021] who assumes that **D**$(CH_2 - H)$ must be greater than 101 kcal/mol (or $\Delta H°f_0 (CH_2) \geq 82$ kcal/mol). In the work [3411b] Reed proved the correctness of the value he had proposed in the work [3411a].

On the basis of numerous data on the dissociation kinetics of methane, the reactions of the methyl radicals and the continuous spectrum of the CH_2CO molecule, Long [2642] recommends a value of 70 ± 15 kcal/mol for the heat of formation of CH_2.

McDowell and Warren [2702] measured the potential of CH_2^+ ion occurrence from methane and calculated $D_{500}(CH_2 - H) \leq 80 \pm 5$ kcal/mol. In doing so, they assumed that in the dissociation ionization of CH_4, a hydrogen molecule is formed, besides CH_2^+. To this value of the dissociation energy corresponds a value of $\Delta H°f_0 (CH_2) = 60$ kcal/mol. As is shown by Cottrell [255] the potential of CH_2^+ ion occurrence, is, ob-

obviously, too low and, accordingly, the heat of formation of CH_2 calculated from these data is too low. An analysis of the data of McDowell and Warren [2702] permitted Cottrell [255] to make the following estimate: $D_{500}(CH_2 - H) = 86$ kcal/mol ($\Delta H^\circ f_0(CH_2) = 66$ kcal/mol).

The measurements of the potentials of the CH_2^+ ion occurrence from methane permitted Branson and Smith [904] to determine the lower limit of the dissociation energy: $D(CH_2 - H) \geq 88$ kcal/mol, or $\Delta H^\circ f_0(CH_2) \geq$ ≥ 61 kcal/mol. This estimate may, however, have a great error.

Langer, Hipple and Stevenson [2559] determined the potentials of the occurrence CH_4^+, CH_3^+, CH_2^+, CH^+ and C^+ ion from methane, methyl and methylene and the ionization potential of CH_2. By combining these potentials $D_{500}(CH_2 - H) = 3.7 \pm 0.3$ ev $= 86 \pm 7$ kcal/mol, or $D_0(CH_2 - H)$ $= 83.4$ kcal/mol and $\Delta H^\circ f_0(CH_2) = 65.6$ kcal/mol, were obtained.* In a work by Waldron [4129] the potential of the occurrence of the CH_2^+ ion from CH_3 was measured, and the value of $D(CH_2 - H) = 3.39 \pm 0.22$ ev or 78 ± 5 kcal/mol was found, coinciding with the values found by Langer et al [2559] within the error limits.

The values of the dissociation energy $D(CH_2 - H)$ calculated with the help of the potential of the occurrence of CH_2^+ from CH_3 [2559, 4129] are more reliable than the results of calculations based on the potential of the occurrence of CH_2^+ from CH_4 [2702, 904] since in the latter case the process of dissociation ionization involves the rupture of several bonds and may be interpreted in various ways.

The most comprehensive study on the potentials of the occurrence of the CH_2^+ ion was carried out in a work by Langer, Hipple and Stevenson [2559]. In the same work the ionization potential of CH_2 was measured.

On the basis of the data of this work it is assumed in the Handbook

$$\Delta H^\circ f_0(\mathrm{CH_2},\text{ газ}) = 66 \pm 15 \text{ kcal/mole}^*$$

This value is in good agreement with the results of calculations based on kinetic measurements [2419, 4129, 3411a]; a value of

$$D_0(\mathrm{CH_2}) = 206{,}849 \pm 15 \text{ kcal/mole.}$$

corresponds to it.

CH$_3$ (gas). The heat of formation of methyl may be calculated on the basis of a measurement of the energy needed to break off a hydrogen atom from methane. The latter value was determined by different methods.

When investigating the kinetics of $\mathrm{CH_3I}$ pyrolysis Butler and Polanyi [1036] found $D(\mathrm{CH_3 - I}) = 54.0 \pm 0.5$ kcal/mol. To this value corresponds $\Delta H^\circ f_0(\mathrm{CH_3}) = 35.3$ kcal/mol and $D_0(\mathrm{CH_3 - H}) = 102.9$ kcal//mol. Further studies, however, showed that the mechanism of $\mathrm{CH_3I}$ pyrolysis is more complex than Butler and Polanyi had assumed [1036].

The most accurate determination of the energy needed to break off a hydrogen atom from the methane molecule was carried out by Kistiakowsky, Artsdalen and Andersen [548, 571, 547, 2413]. These authors studied the kinetics of photobromination of methane. The reaction velocity was determined by photometric measurement of the bromine concentration. As a result of the investigation the activation energy of the reaction

$$\mathrm{CH_4 + Br = CH_3 + HBr}, \qquad \text{(XX.2)}$$

was determined equal to $E_{453} = 17.8$ kcal/mol. For the inverse reaction the activation energy proved to be equal to 2 kcal/mol [2413]. The heat effect of the bromination reaction (XX.2) is equal to $\Delta H_{453} = 15.8$ kcal/mol, in this case. On the basis of this value and the enthalpies and heats of formation of the reaction components $\Delta H^\circ f_0(\mathrm{CH_3}) = 33.9$ kcal/mol and $D_0(\mathrm{CH_3 - H}) = 101.6$ kcal/mole.

Surveys of the numerous measurements of the energy needed to break off a hydrogen atom from the methane molecule carried out by the electron impact method are given in the works by Stevenson [3854], McDowell and Warren [2702] and Cottrell [255]. The mean value of $D_{500}(CH_3 - H)$ obtained by this method is 102 ± 1 kcal/mol, or $D_0(CH_3 - H) = 99.6$ kcal/mol and $\Delta H°f_0(CH_3) = 32 \pm 1$ kcal/mol. In following works by Branson and Smith [904], Lossing, Ingold and Henderson [2661], Stevenson [3855] and Langer, Hipple and Stevenson [2559] this value of $D_{500}(CH_3 - - H)$ was corroborated.

The heat of formation of methyl may also be calculated with the help of the bond dissociation energies of a number of compounds of the CH_3X type, where X is a halogen, as measured by Lossing, Ingold and Henderson [2661]. The investigation was carried out by the electron impact method. Recalculation of the results obtained by these authors by taking account of the heats of formation of the corresponding compounds adopted in the Handbook yields $\Delta H°f_0(CH_3) \approx 31$ kcal/mol.

Szwarc [3912] studied the kinetics of the thermal dissociation of CH_3Br in a toluene stream and found $D(CH_3 - Br) = 68$ kcal/mol. To this value $\Delta H°f_0(CH_3) = 34.9$ kcal/mol corresponds.

In the Handbook, the value of

$$\Delta H°f_0(CH_3,\ \text{gas}) = 33{,}9 \pm 2 \text{ kcal/mole},$$

which is found in the works by Kistiakowsky, Artsdalen and Andersen [548, 571, 547, 2413] is adopted. The works of these authors are the most accurate. The rather high error of the adopted value was estimated taking account of the results of mass spectrometric measurements. To the adopted value corresponds

$$D_0(CH_3) = 290{,}581 \pm 2 \text{ kcal/mole}.$$

C_2H (gas). Cherton [1095] studied the process of diacetylene formation from acetylene under the action of ultraviolet radiation. Assuming that the primary act is the detachment of a hydrogen atom Cherton found from the longwave limit of the radiation initiating this reaction that $D(C_2H - H) \leq 121$ kcal/mol. On the basis of the empirical dependence of the dissociation energy of the carbon-carbon bond in various compounds on the length of the corresponding bond, the same author obtained a similar value in the work [1096].

When investigating the polymerization of acetylene under the action of photosensitized mercury atoms Le Roy and Steacie [2595] found the values of 112.2 and 120.7 kcal/mol for the upper limit of $D(C_2H - H)$, depending on the adopted reaction mechanism.

Using a method they had worked out Frankevich and Tal'rose [429] studied the collisions of several ions and molecules in a special mass spectrometer. Frankevich and Tal'rose found that the reactions

$$C_2H_2^+ + H_2O = H_3O^+ + C_2H \qquad (XX.3)$$

and

$$CH_3OH^+ + C_2H_2 = CH_3OH_2^+ + C_2H \qquad (XX.4)$$

do not take place under these conditions. This attests to the fact that the corresponding reactions cannot be exothermic [406]. On the basis of this observation Frankevich and Tal'rose concluded that $D(C_2H - H)$ must be greater than 117 kcal/mol, or $\Delta H°f_0(C_2H) > 120$ kcal/mol.

A detailed investigation of the potentials of the occurrence of various ions from acetylene and its homologs was carried out by Coats and Anderson [1138]. As a result of the investigation carried out the authors of the work [1138] calculated the values of the heat of formation of the C_2H radical lying in the interval from 110 to 153 kcal/ /mol (this corresponds to dissociation energies from 107 to 150 kcal/ /mol), depending on the initial substance. It was discovered that the dissociation ionization products of some substances, e.g., of acetylene, have an excess of kinetic energy. The most accurate measurement was carried out in the case of 1-butyne. On the basis of the obtained data the authors of the work [1138] recommend $\Delta H°f_0(C_2H) = 112 \pm 3$ kcal/mole and $D_0(C_2H - H) = 109$ kcal/mole corresponds.

It is, at present, not possible to choose the value of the heat of formation of C_2H in a sufficiently wellfounded way. In the Handbook the value of the heat of formation of the C_2H radical is assumed to be

$$\Delta H°f_0(\mathrm{C_2H,\ gas}) = 116 \pm 10 \text{ kcal/mole};$$

this value is the mean of the results obtained in the works [429, 1138]. To this value corresponds

$$D_0(C_2H) = 274,\ 802 \pm 10 \text{ kcal/mole}.$$

CF (gas). A linear extrapolation of the vibrational levels of the ground state $X^2\Pi$ of the CF molecule with the help of the constants adopted in the Handbook (see Table 176) leads to a value of $D_0(CF) = 39{,}000$ cm^{-1} = 111.5 kcal/mol. A shorter extrapolation of the vibrational levels of the excited state $B^2\Sigma$ with the help of the constants given in Table 176 yields the value of 61,700 cm^{-1} for the dissociation limit of this state relative to the v = 0 level of the $X^2\Pi$ state. On the assumption that the $B^2\Sigma$ state of the CF molecule is correlated to the atomic states $\mathrm{C}(^1S_0) + \mathrm{F}(^2P_{3/2})$, this dissociation limit corresponds to a value of the dissociation energy of $D_0(CF) = 40\,050$ cm^{-1} = 114 kcal/mole, which is in good agreement with the value obtained by a linear extrapolation for the ground state. Gaydon [1668] reduces the value of the dissociation limit of the $B^2\Sigma$ state found by Andrews and Barrow [557] by 2800 cm^{-1} and assumes a value of $37{,}250 \pm 2400$ cm^{-1}, or 106.5 ± 6.9 kcal/mol for the dissociation energy of CF. An analysis of the diagrams showing the dependence of $\Delta G(v + 1/2)$ on v and of $\Delta G(v + 1/2)$ on $G(v)$ shows that the value recommended by Gaydon [1668] requires a too fast convergence of the levels of the $B^2\Sigma$ state of the CF molecule. A somewhat greater value of the dissociation limit of the $B^2\Sigma$ state (39,500 cm^{-1}) is, therefore, adopted in the Handbook, or

$$D_0(C_2F) = 108 \pm 5 \text{ kcal/mole},$$

to which a value of

$$\Delta H^\circ f_0(CF, \text{gas}) = 80{,}085 \pm 5 \text{ kcal/mole}.$$

corresponds.

CF_2 (gas). Atkinson [586] studied the kinetics of the photodissociation of tetrafluoro ethylene and on the assumption that the disruption of the double bond is the first state of the process found that $D(CF_2 = CF_2) < 112$ kcal/mol, to which a value of the heat of formation of CF_2 greater than -25 kcal/mol and $D(CF_2 - F) < 113$ kcal//mol correspond.

Reed and Rabinovitch [3410] studied the reaction kinetics of the interaction of sodium vapors with the halogen substitution products of methane and concluded that the activation energy of the secondary reaction $CF_3 + Na \rightarrow CF_2 + NaF$ must not exceed 3.5 kcal/mol. Hence the authors of the work [3410] found that the heat of formation of CF_2 must be greater than -18 kcal/mol and that $D(CF_2 - F) \leq 120$ kcal/mol.

Reed and Snedden [3412] measured the energies of the successive removal of atoms from the CF_4 molecule. The investigation was carried out by the electron impact method and yielded $D_{500}(CF_2 - F) \leq 125 \pm 7$ kcal/mol (the heat of formation of CF_2 is greater than -14 kcal//mol).

Margrave [2774] determined the potential of the occurrence of the CF_2^+ molecule in the dissociation ionization of C_2F_4 and using an estimated value of the ionization potential $I(CF_2) = 11 \pm 1$ ev calculated the value of the dissociation energy $D(F_2C = CF_2) = 93 \pm 20$ kcal/mol,* and the heat of formation of $\Delta H^\circ f_0(CF_2, \text{gas}) = -30 \pm 20$ kcal/mol.

Since the distance between the carbon atoms in C_2F_4 is smaller than in C_2H_4 we may assume that $D(F_2C = CF_2)$ is greater than $D(H_2C =$

$= CH_2) = 117.6$ kcal/mol and, accordingly, that $\Delta H^\circ f(CF_2)$ must be smaller than -17 kcal/mol. The energies of the successive removal of atoms from the CH_4 and CCl_4 molecules are equal to (in kcal/mol):

	$D(CX_3-X)$	$D(CX_2-X)$	$D(CX-X)$	$D(C-X)$,
X = H	101,5	83,7	126,8	80
X = Cl	65,8	61,6	100,7	80

Hence it is evident that the CX-X bond which amounts to about 32.5% of the energy of atomization is the strongest. If we assume that D(CF - F) is the same portion of the energy of atomization, this yields the values $\Delta H^\circ f_0(CF_2) \approx -50$ kcal/mol and $D_0(F_2C = CF_2) \approx 51$ kcal/mol. The latter, low value seems to be unjustified. Obviously, it is more correct to assume: $D_0(CF - F) > D_0(CH - H) = 126.8$ kcal/mol. This leads to a value of $\Delta H^\circ f_0(CF_2$, gas) greater than -29 kcal/mol.

Thus, a comparison of the dissociation energies and the interatomic distances in the C_2F_4 and C_2H_4 molecules, as well as a comparison of the energies of the successive removal of the fluorine atoms from the CF_4 molecule leads to contradictory results.

In the Handbook the value of

$$\Delta H^\circ f_0(CF_2,\ \text{gas}) = -30 \pm 20 \text{ kcal/mole.}$$

is adopted, as obtained by Margrave [2774]. To this value corresponds

$$D_0(CF_2) = 236{,}585 \pm 20 \text{ kcal/mole.}$$

The accuracy of the adopted value will have to be increased.

CF_3 (gas). The heat of formation of CF_3 may be calculated on the basis of measurements of the $CF_3 - X$ bond dissociation energy, where X is a hydrogen or halogen atom.

Sehon and Szwarc [3676, 3913, 3912, 3914] studied the kinetics of CF_3Br pyrolysis in a toluene stream and found that $D(CF_3 - Br) = 64.5$ kcal/mol. Investigating the kinetics of fluoroform pyrolysis in the presence of deuteroacetylene, G. Pritchard, H. Pritchard, Schiff and Trotman-Dickenson [3328] found that the difference between $D(CH_3 - H)$

and $D(CF_3 - H)$ is 0.5 kcal/mol. Hence $D(CF_3 - H) = 101.1$ kcal/mol is obtained on the basis of thermodynamic data adopted in the Handbook. Later on, the same authors investigated the reaction kinetics of the interaction of the CF_3 radical with methane in the work [3329] and on the basis of the activation energy of the forward and back reactions verified the difference between the values of $D(CH_3 - H)$ and $D(CF_3 - H)$ obtained earlier. The results of these investigations, however, cannot be used to determine the heat of formation of the CF_3 radical since in the present Handbook values of the heats of formation of CF_3Br and CF_3H based on the afore-indicated values of $D(CF_3 - Br)$ and $D(CF_3 - H)$ are adopted.

The interaction kinetics of gaseous sodium with various halogen substitution products of methane was studied by Hodgins and Haines [2092] and, particularly in detail, by Reed and Rabinovitch [3410, 3347]. Using the relationship between the activation energies and the dissociation energies of the bonds prepared by Ogg and Polanyi [3117] and choosing $D(CH_3 - Cl) = 81.2$ kcal/mol for the basis, which coincides with the value adopted in the present Handbook, Reed and Rabinovitch found that $D(CF_3 - Cl) = 80\text{-}81$ kcal/mol, to which a value of $\Delta H°f_0(CF_3) = -118\text{-}119$ kcal/mol corresponds.

Dibeler, Reese and Mohler [1330] carried out a detailed mass spectrometric investigation of the dissociation ionization of CF_4, CF_3Cl, CF_3Br and CF_3I. In particular, the excess kinetic energies of the dissociation ionization products were measured experimentally in this work. The fact, however, that there is no reliable value of the ionization potential of CF_3 did not permit the obtained results to be used to calculate the heat of formation of CF_3.

Farmer, Henderson, Lossing and Marsden [1530] measured the ionization potential of CF_3 and the potential of the occurrence of the CF_3^+

ion and other ions in the dissociation ionization of CF_3H, CF_4, CF_3Cl, CF_3Br, CF_3I, CF_3CH_3 and C_2F_6. In particular, the authors of [1530] found that $D_{500}(CF_3 - I) = 57 \pm 4$, $D_{500}(CF_3 - F) = 123 \pm 2$ and $D_{500}(CF_3 - H) = 102 \pm 2$ kcal/mol. Heats of formation of carbon trifluoride amounting to -112, -116 and -118 kcal/mol correspond to these dissociation energies. In the work by Farmer et al [1530] the kinetic energy of the dissociation ionization products was not taken into account. Consequently, the obtained values of $\Delta H°f_0(CF_3)$ must be considered to be only lower limits, particularly as in an analogous work by Dibeler, Reese and Mohler [1330] it was found out that in many cases the dissociation products have considerable kinetic energies.

Reed and Snedden [3412] determined the energies of the successive removal of fluorine atoms from the CF_4 molecule by the electron impact method. For $D_{500}(CF_3 - F)$ these authors found a value lower than or equal to 121 ± 3 kcal/mol, to which a value of $\Delta H°f_0(CF_3) \geq 118$ kcal/mol corresponds.

The most accurate value of the heat of formation of CF_3 was obtained by Reed and Rabinovitch [3410, 3347]. The results of mass spectrometric investigations lead to less accurate values that are not in good agreement with each other. In the Handbook the value

$$\Delta H°f_0(CF_3, \text{gas}) = -119 \pm 1 \text{ kcal/mole.}$$

of the heat of formation of carbon trifluoride was adopted. To this value corresponds

$$D_0(CF_3) = 344{,}085 \pm 2{,}5 \text{ kcal/mole.}$$

C_2F (gas). The value of the dissociation energy of the C_2F radical

$$D_0(C_2F) = 293 \pm 10 \text{ kcal/mole,}$$

adopted in the Handbook was estimated using the bond energies in the C_2H_2, C_2HF, C_2F_2, C_2H and C_2 molecules. To this value corresponds

$$\Delta H^\circ f_0(C_2F,\ \text{gas}) = 64{,}67 \pm 10 \text{ kcal/mole.}$$

CHF (gas). The value of the heat of formation of the CHF radical adopted in the Handbook

$$\Delta H^\circ f_0(CHF,\ \text{gas}) = 8 \pm 20 \text{ kcal/mole}$$

was estimated with the help of the mean bond energies in the CH_2 and CF_2 radicals. An analogous calculation of the heats of formation of CHF_2 and CH_2F showed a good agreement with the experimental data. The error of the adopted value depends, above all, on the error of the heat of formation of the CF_2 radical. The value of

$$D_0(CHF) = 231{,}717 \pm 20 \text{ kcal/mole.}$$

corresponds to the adopted value of the heat of formation.

CHF_2 (gas) and CH_2F (gas). Reed and Rabinovitch [3410] studied the diffusion flames of sodium with CHF_2Cl, CH_2FCl_2 and other compounds and found the activation energies of reactions of the type

$$CHF_2Cl + Na \rightarrow CHF_2 + NaCl. \qquad (XX.5)$$

Using the relationship between the activation energies and the bond dissociation energies proposed by Ogg and Polanyi [3117], Reed and Rabinovitch found that $D(CHF_2 - Cl)$ and $D(CH_2F - Cl)$ are equal to 81-82 kcal/mol. Heats of formation of CHF_2 and CH_2F equal to −67 and −17 kcal/ /mol correspond to these values. A calculation of the heats of formation of CHF_2 and CH_2F based on the mean bond energies in the CF_3 and CH_3 radicals leads to the values of −68 and −17 kcal/mol, respectively.

The following values of the heats of formation are adopted in the Handbook

$$\Delta H^\circ f_0(CHF_2,\ \text{gas}) = -67 \pm 5 \text{ kcal/mole,}$$
$$\Delta H^\circ f_0(CH_2F,\ \text{gas}) = -17 \pm 5 \text{ kcal/mole,}$$

to which correspond

$$D_0(CHF_2) = 325{,}217 \pm 5{,}1 \text{ kcal/mole,}$$
$$D_0(CH_2F) = 308{,}349 \pm 5 \text{ kcal/mole.}$$

CCl (gas). A linear extrapolation of the vibrational energy levels of the $X^2\Pi$ ground state of the CCl molecule carried out with the help of constants found by Kuzyakov and Tatevskiy [269] yields a value of $D_0(\mathrm{CCl}) \cong 104$ kcal/mol, and with the help of constants found by Gordon and King [1819] and adopted in Table 176, a value of about 78 kcal/mol. An estimate of the dissociation energy of CCl with the help of a relation proposed by Lippincott and Schroeder [2625] yields a value of $D_0(\mathrm{CCl}) = 80.5$ kcal/mol. A similar value results from an estimate on the basis of the data on the dissociation energies of diatomic compounds of elements of the 4th and 7th groups, as given in the monograph by Gaydon [1668].

Reed and Snedden [3412] found that $D_0(\mathrm{CCl}) = 130 \pm 20$ kcal/mol by the electron impact method. This value seems to be too high since the mean bond energy in the $\mathrm{CCl_4}$ molecule is equal to 77 kcal/mol.*

We must note that the value of $D_0(\mathrm{CCl})$ obtained by Reed and Snedden [3412] is based on a certain interpretation of several processes whose correctness cannot be established reliably enough. The calculation of $D_0(\mathrm{CCl})$ by the graphical method of Karapet'yants with the help of the data on $\mathrm{CCl_4}$, $\mathrm{CCl_3}$, $\mathrm{CCl_2}$, $\mathrm{CH_4}$, $\mathrm{CH_3}$, $\mathrm{CH_2}$ and CH yields values from 73 to 103 kcal/mol (the scatter is, above all, explained by the fact that the extrapolation abruptly decreases the accuracy of the estimate).

It is assumed in the Handbook that

$$\mathbf{D_0(CCl) = 80 \pm 10}\ \text{kcal/mole.}$$

The ratio of the adopted value of $D_0(\mathrm{CCl})$ to the mean bond energy in $\mathrm{CCl_4}$ is in good agreement with the analogous rations in the case of CF and CH.

A heat of formation equal to

$$\Delta H^\circ f_0(\mathrm{CCl},\ \text{gas}) = 118{,}135 \pm 10\ \text{kcal/mole.}$$

corresponds to the adopted value.

CCl_2 (gas). Blanchard and Le Goff [839] studied the potentials of the occurrence of various dissociation products of carbon tetrachloride passing through a chamber in which a tungsten tape heated up to 1300-1800°K was located. An analysis of the possible mechanisms of the CCl^+ and CCl_2^+ ion formation permitted the authors to calculate two possible values of the dissociation energy at 1700°K: $D(CCl_2 - Cl) = 62 \pm 7$ and 93 ± 7 kcal/mol. The authors assume the lower value to be correct. The reduction of these values to 0°K yields $D_0(CCl_2 - Cl) = 61.7$ and 92.7 kcal/mol, or respectively, $\Delta H°f_0(CCl_2) = 46$ and 77 kcal/mol. A comparative estimate of these two values by the method of Karapet'yants making use of the corresponding data on the halogen substitution products of methane and their dissociation products confirm the lower value.

In the Handbook the value of

$$\Delta H°f_0(CCl_2,\ \text{gas}) = 46 \pm 10 \text{ kcal/mole,}$$

is adopted; a value of

$$D_0(CCl_3) = 180,\ 685 \pm 10 \text{ kcal/mole.}$$

corresponds to it.

CCl_3 (gas). When studying the kinetics of CCl_3Br pyrolysis in a toluene stream Szwarc and Sehon [3914, 3913] found that $D_0(CCl_3 - Br) = 49$ kcal/mol. The value found by Szwarc and Sehon is confirmed by the results of studying the exchange reaction between bromine and CCl_3Br [255]. To this value of the dissociation energy corresponds a value of $\Delta H°f_0(CCl_3) = 12.7$ kcal/mol. On the basis of data obtained from studying the photobromination of chloroform [982], Szwarc [3912] found that $D_0(CCl_3 - H) = 89 \pm 2$ kcal/mol, to which a value of $\Delta H°f_0(CCl_3) = 13.6$ kcal/mol corresponds. The error of these values is, evidently, somewhat greater than is assumed by Szwarc (see [255]).

In the work by Farmer, Henderson, Lassing and Marsden [1530] the potentials of the occurrence of CCl_3^+ ions formed in the dissociation ionization of CCl_4 and CCl_3Br and the ionization potential of CCl_3 were determined (8.78 ± 0.05 ev). The potential of CCl_3^+ occurrence from CCl_4 equal to 11.67 ± 0.1 ev, proved to be in good agreement with the corresponding value 11.83 ± 0.05 ev, obtained by Warren and Craggs [4151], and the value of 11.7 ± 0.3 ev, obtained by Blanchard and Le Goff [839] Farmer et al [1530] recommend a mean value of the potential of the CCl_3^+ ion occurrence, equal to 11.75 ± 0.1 ev; to this value corresponds $D_{500}(CCl_3 - Cl) = 68.5 \pm 3$ kcal/mol, or $D_0(CCl_3 - Cl) = 67.7 \pm 3$ kcal/ /mol, and $\Delta H°f_0(CCl_3) = 15 \pm 3$ kcal/mol. The results of the measurements [1530] of the potential of the occurrence of the CCl_3^+ ion from the CCl_3Br molecule (10.90 ± 0.1 ev) yield $D_0(CCl_3 - Br) = 48.5 \pm$ ± 3 kcal/mol.*

The values of the heat of formation of CCl_3 calculated from the data of Szwarc and Sehon [3912, 3914] are, obviously, the most accurate. It is assumed in the Handbook that

$$\Delta H°f_0(CCl_3,\ \text{gas}) = 13 \pm 2 \text{ kcal/mole},$$

to which a value of

$$D_0(CCl_3) = 242{,}235 \pm 2 \text{ kcal/mole}.$$

corresponds.

TABLE 185

Adopted Values (in cal/mol) of the Thermodynamic Quantities of the Simplest Free Radicals of Hydrocarbons and Their Fluorine and Chlorine Substitution Products in the Gaseous State.

Вещество 1	D_0	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{293.15} - H^\circ_0$	$H^\circ_{298.15} - H^\circ_0$
CH	80 000	141 217	142 026	142 035	2026	2061
CH_2	206 849	66 000	65 859	65 853	2068	2106
CH_3	290 581	33 900	33 053	33 034	2354	2396
C_2H	274 802	116 000	116 788	116 798	2230	2275
CF	108 000	80 085	80 955	80 963	2131	2167
CF_2	236 585	− 30 000	− 29 878	− 29 880	2420	2465
CF_3	344 085	−119 000	−119 645	−119 651	2690	2750
C_2F	293 000	64 670	65 662	65 677	2478	2530
CHF	231 717	8 000	8 089	8 084	2342	2383
CH_2F	308 349	− 17 000	− 17 885	− 17 905	2361	2404
CHF_2	325 217	− 67 000	− 67 834	− 67 851	2456	2504
CCl	80 000	118 135	119 040	119 048	2206	2244
CCl_2	180 685	46 000	46 259	46 263	2637	2691
CCl_3	242 235	13 000	12 822	12 827	3276	3352

1) Substance.

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1234	Until the works by Porter [3300] and Norrish, Porter and Thrush [3103a, 3104], in which the absorption spectrum of CH was obtained for the first time, was published, several authors expressed the opinion that the $^4\Sigma$ state is the ground state of the CH radical.
1238	In a following work published in 1959 Kuzyakov and Tatevskiy [268] applied harder conditions of the electric discharge through the flow of CF_4 vapors and thus reduced the intensity of the CF_2 bands. This permitted them to measure nine more bands in the system $A^2\Sigma - X^2\Pi$, besides the four bands of CF observed by Andrews and Barrow [557]: 0–2, 0–3, 0–4, 0–5, 0–6, 1–4, 1–5, 1–6 and 1-7. The values of the zero lines of these bands calculated with the help of the vibrational constants of CF proposed by Andrews and Barrow [557] are in good agreement with the observed values (in the work [268] the values of the vibrational constants of CF are not given). We must note that in the work [268] the values $B_2'' = 1{,}360$ and $B_3'' = 1{,}341$ $см^{-1}$, obtained as a result of analyzing the fine structure of the 0-2 and 0-3 bands are presented. These values are only in poor

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agreement with the values of B_e and α_1 given in Table 176.

1239 The extrapolation of the vibrational levels of the ground states with the help of the constants found by Venkateswarlu leads to an extraordinarily high values of the dissociation limit (177,453 cm^{-1}).

1240 The linear extrapolation of the vibrational levels of the $X^2\Pi_r$ state with the help of the constants found in the works [55, 296, 296b] yields a value of the dissociation energy D_0 (CCl) = 36 297 см$^{-1}$ (104 kcal/mol^{-1}) which essentially exceeds the mean bond energy in the CCl_4 molecule.

1241 As to the absorption spectrum of CCl the authors of the work [4102a] refer to a private communication by Herzberg.

1242 It was proposed in literature during a number of years that the angle between the C-H bonds in CH_2 should be equal to 140°. This value was obtained in 1942 by Herzberg from an analysis of the structure of the λ 4050 A band, which he observed in the spectra of coments and in the spectrum of an electrodeless discharge in methane vapors [2018, 2017]. Herzberg assumed that this band belongs to the CH_2 molecule. In 1949, however, this assignment was refused by Monfils and Rosen [2939] who did not find an isotopic shift when replacing the hydrogen in the excitation source by deuterium. Later on, Douglas [1368] and Clusius and Douglas [1133] proved unambiguously that the λ 4050 A band belongs to the triatomic molecule C_3.

1243 We must note that Gallup's objection [1648] to the note by Gray [1844] is incompetent since he refers to the agreement of the conclusions of his own work [1647] with the experimental data obtained by Herzberg in the works [2017, 2018] where the band λ 4050 A was ascribed to the CH_2 molecule.

1249 To the frequency $\nu_2 = 1114$ см$^{-1}$ corresponds a deformation vibration force constant $f_\alpha/d^2 = 0{,}32 \cdot 10^5$ dyn•cm^{-1}, to the frequency of 1362 cm^{-1} a force constant of $-f_\alpha/d^2 = 0{,}47 \cdot 10^5$ dyn•cm^{-1}.

1250 Venkateswarlu [4091] remarks that the observed bands are also described well by the equation given above if 344 is chosen instead of 66.5 cm^{-1} for the deformation vibration frequency in the lower state. In the general case, however, the calculated values of the band edge wave numbers are in better agreement with the experimental ones if $\nu''_3 = 666{,}5$ см$^{-1}$.

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1251 After the text of the present Division had been finished a work by Mann and Thrush [2761a] was published, who investigated the absorption spectrum of CF_2 in the ultraviolet range. An analysis of the vibrational structure of the observed bands carried out by Mann and Thrush showed that the frequencies of the deformation vibrations of CF_2 are, respectively, equal to 660 and 500 cm^{-1} in the ground and excited electronic states.

1252 Besides the calculation of the frequencies of the SiF_2 molecule carried out in order to cooroborate the assignment of the bands observed in the spectrum to the SiF_2 molecule (see page 1375), Johns, Chantry and Barrow [2259] also calculated the fundamental frequencies of the CF_2 molecule by Barrow's method applying values estimated on the basis of the well known frequencies of CF and CF_4 for the force constants of CF_2. The values of the frequencies $\nu_1 = 1178$ and $\nu_2 = 630$ $см^{-1}$ obtained as a result of the calculation are in good agreement with those observed experimentally.

1253 In the $^1A_1$ state of the CH_2 molecule CH_2: $r_{C-H} = 1,12$ Å (see page 1246).

1254 Since in the CCl molecule $r_{C-Cl} = 1,654$ Å, the value $r_{C-Cl} = 1,70 \pm 0,05$ Å. is more probable for CCl_2.

1255 The value of $\omega_e(CCl) = 875$ $см^{-1}$, corresponds to the value $k_e = 6,79 \cdot 10^6$ $см^{-2}$. adopted in the present Handbook and found in the work [1819].

1258 In 1960, Gaydon, Spokes and Suchtelen [1670a] reported that they had succeeded in observing CH_3 bands in the region of 2157 A in the absorption spectra of flames rich in methyl ether, acetaldehyde, acetone and methane. In a work by Nelson and Kuebler [3038a] the absorption spectra of CH_3 and CD_3 formed immediately as a result of the pyrolysis of methane and deuteromethane were observed.

1259 We must note that during the last few years papers dealing with the study of the paramagnetic resonance spectrum of CH_3 at low temperatures in different matrices [1152, 2329, 3768, 3845] were published. In particular, an investigation of the paramagnetic resonance in a mixture of $C^{12}H_3$ and $C^{13}H_3$ obtained by X-ray irradiation of CH_3I at a temperature of 77°

carried out by Cole, Pritchard, Davidson and McConnell [1152] showed that the CH_3 molecule must have a plane structure or a structure that is very similar to a plane one. Karplus [2329] who studied the paramagnetic resonance spectrum of CH_3 draws the same conclusion. Thus, we may assume that the results of studying the paramagnetic resonance spectrum of CH_3 are not in contradiction to the structure of the methyl adopted in the present Handbook.

In the work [2026] published in April 1959 Herzberg reported on additional results obtained from a study on the spectra of CH_3 and CD_3 in his laboratory. An analysis of the fine structure of the CD_3 band at 2144 A permitted an approximate value of the moment of inertia of CD_3 relative to an axis perpendicular to the axis of symmetry of the molecule ($I \doteq 5{,}769 \cdot 10^{-40}$ $g \cdot cm^2$) to be obtained. The fact that there is no fine structure in the CH_3 band makes it impossible to obtain the value of the second moment of inertia of the CH_3 molecule needed to determine the structural parameters in a unique way. In the work [2026], however, two values of $r_0(CD)$ corresponding to two different assumptions on the value of the angle β between the C-D bond and the axis of symmetry are presented: $\beta_0 = 90°$, $r_0(C-D) = 1{,}072$ Å and $\beta = 75°$, $r_0(C-D) = 1{,}061$ Å. Since the value of $r_0(C-D)$ corresponding to an angle $\beta = 75°$ proved to be too small compared to this distance in other molecules, Herzberg [2026] concluded that the angle β should be greater than 75°. It is evident from the given figures that even for the plane model of the CD_3 molecule the value of $r_0(C-D)$ is smaller than in methane. The smaller value of the interatomic distance of C-D in CD_3 compared to the distance compared to the distance in CD_4 is explained by Herzberg by a corresponding increase of the carbon-hydrogen bond energy in methyl compared to methane. In the following works [2026a, 2026b] Herzberg presents the values 1.0699 and 1.079 A, respectively, for the interatomic distance of C-H in CH_3.

1260 The calculation of the vibration frequencies of CH_3 for the plane model ($\angle HCH = 120°$) with the help of the force constants of ethylene [128] practically yields the same values of the frequencies of CH_3 as the calculation with the help of the constants of methane.

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1262 Since in the CCl molecule $r_{C-Cl} = 1{,}654\,\text{Å}$, the value of $r_{C-Cl} = 1{,}70 \pm 0{,}05\,\text{Å}$ is more probable for CCl_3.

1263 The following force constants were chosen in the work [56] for calculating the frequencies of CF_3: $f_d = 10{,}9 \cdot 10^6$, $f_{dd} = 0{,}65 \cdot 10^6$, $f_\alpha = 2{,}28 \cdot 10^6$, $f_{d\alpha} = 1{,}70 \cdot 10^6$, $f_{\alpha\alpha} = 0{,}23 \cdot 10^6\ \text{см}^{-2}$. The calculation of the fundamental frequencies for the plane model of the CF_3 molecule with the help of the force constants of cinyl fluoride taken from a work by Monfils and Duchesne [2938] yields frequency values which differ slightly from the frequencies calculated with the help of the constants of the fluorine substitution products of methane presented above. We must note that, in contrast to CH_3, the values of the frequencies ν_2 for the plane model of CF_3 and CCl_3 differ from the adopted values only by 30 and 80 cm^{-1}, respectively (if $\frac{f_\gamma}{d^2} = 0{,}1 f_d$).

1264 * $f_d = 6{,}1 \cdot 10^6$, $f_{dd} = 0{,}45 \cdot 10^6$, $f_\alpha = 1{,}62 \cdot 10^6$, $f_{d\alpha} = 1{,}00 \cdot 10^6$, $f_{\alpha\alpha} = 0{,}14 \cdot 10^6\ \text{см}^{-2}$.

1264 In the Handbook by Landoldt-Boernstein [2555] the frequencies of CF_3 are given: $\nu_1 = 937$, $\nu_2 = 697$, $\nu_3 = 1116$ and $\nu_4 = 503\ \text{см}^{-1}$, and those of CCl_3: $\nu_1 = 668$, $\nu_2 = 367$, $\nu_3 = 760$ and $\nu_4 = 262\ \text{см}^{-1}$, assumed equal to the corresponding frequencies of CF_3H and CCl_3H. Venkateswarlu and Sundaram [4087] calculated the following values of the force constants of CF_3 using Wilson's method and the aforementional values of the frequencies of CF_3 for an angle FCF = 109°: $f_d = 3{,}846 \cdot 10^5$, $f_{dd} = 0{,}2203 \cdot 10^5$, $f_\alpha = 1{,}6970 \cdot 10^5$ and $f_{d\alpha} = -0{,}509 \cdot 10^5$ dyn·cm^{-1}.

1265 The values of the frequencies of CH_2F and CHF_2 calculated from Eqs. (P4.33) with the help of the force constants of the fluorine substitution products of methane obtained in the work [3277] differ slightly from the frequencies calculated with the help of the force constants of the work [128].

1266 The existence of C_2H under these conditions was established in an indirect way by the fact that absorption bands of diacetylene (C_4H_2) are present in the spectrum of the residual gases. Recombination of two C_2H radicals formed in the photolysis [2026] is the only way in which diacetylene is formed in the photolysis of propiolaldehyde.

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1266 $r_{C-H}(C_2H_2) = 1{,}0585$ Å [1101], $r_{C-H}(C_2HCl) = 1{,}052$ Å [4220], $r_{C-H}(C_2HCN) = 1{,}056$ Å [164], $r_{C-H}(C_2HCH_3 \text{ и } C_2HCF_3) = 1{,}056$ Å [164].

1268 The calculation from Eqs. (P4.27) with force constants of C_2H adopted equal to the force constants of C_2H_2 (see page 1223) yields $\nu_1 = 3320, \nu_2\,(2) = 610, \nu_3 = 2015\ см^{-1}$, which within the error limits coincides with the frequencies calculated above.

1268 The structural parameters and the vibration frequencies of the C_2H radical were estimated recently by Plooster and Reed [3266]. The authors of [3266] started from the assumption that the C_2H molecule is linear, belongs to the symmetry point group $C_{\infty v}$ and has the following values of interatomic distances: $r_{C\equiv C} = 1{,}220$ and $r_{C-H} = 1{,}062$ Å. Since the $-C\equiv C-H$ and $-C\equiv N$ groups are isoelectronic, and the CN radical corresponding to the C_2H radical has been studied in a very detailed manner the authors of the work [3266] estimated the force constant and the vibration frequency of the $C\equiv C$ bond in the C_2H radical on the basis of a comparison of the force constants of the $C\equiv C$ and $C\equiv N$ bonds in various compounds containing such groups with triple bonds. The force constant of the C-H bond in C_2H was assumed equal to the corresponding constant in C_2H_2, and the constant of the deformation vibrations $f_\alpha = 0{,}210\, r_{C-H}$. On the basis of the estimated force constants the authors calculated the vibration frequencies of C_2H: $\nu_1 = 3216{,}7, \nu_2 = 639{,}4$ and $\nu_3 = 1923{,}4\ см^{-1}$. The values of the fundamental frequencies and interatomic distances $r_{C\equiv C}$ and r_{C-H} obtained in this way agree satisfactorily with the values recommended in the present Handbook.

1275 The errors in the values of Φ_T^* and S_T of the CCl_2 and CCl_3 molecules are about 0.2 cal/mole·degree since r_{C-Cl} is assumed equal to 1.76 A rather than to 1.70 A (see pages 1255 and 1262).

1281 In the work [1125a] a value of the ionization potential of CH_2 which proved to be in very good agreement with that found by Langer et al [2559] was obtained. This agreement is an indirect proof of the correctness of the value $D(CH_2 - H)$ obtained in the work [2559].

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1282 In the lecture theses of Chupka, Meshi and Berkowitz [113a] published after the work with the present division of the Handbook had been finished the results of mass-spectrometric determinations of the composition of the reaction products of graphite with hydrogen are given. Using the ratio of the measured C^+ and CH_2^+ ion current strengths and the thermodynamic functions of CH_2, Chupka et al calculated the value of $\Delta H°f_{298.15}(CH_2, \text{gas}) = 80$ kcal/mole. From the CH^+, CH_2^+ and CH_3^+ ion current strengths the authors of [113a] found the value of the equilibrium constant of the reaction

$$2CH_2\,(\text{газ}) = CH\,(\text{газ}) + CH_3\,(\text{газ})$$

and that of its heat effect. The value of $\Delta H°f_{298.15}(CH_2, \text{gas})$ calculated on the basis of these measurements is equal to 86 kcal/mol. Thus, the values of $\Delta H°f(CH_2, \text{gas})$ found in the work by Chupka et al [113a] proved to be considerably greater than those obtained in the preceding works.

1285 We must note that Kuzyakov and Tatevskiy [268] did not discover bands connected with transitions from the level v' = 2 when studying the system $A^2\Sigma - X^2\Pi$. The authors of the work [268] assumed that between the levels v' = 1 and v' = 2 of the $A^2\Sigma$ state predissociation takes place, and on this basis they estimated the upper limit of the dissociation energy of CF equal to 5.8 ev (133 kcal/mole).

1286 In order to confirm the value of $D(F_2C = CF_2)$ he has adopted Margrave refers to the results of the calculations of Patrick [3197] who calculated $D(H_2C{=}CH_2) = 142$, $D(Cl_2C{=}CCl_2) = 149$ and $D(F_2C{=}CF_2) = 105$ kcal/mole, on the assumption that the C-H, C-Cl and C-F bond energies in these molecules are equal to the mean bond energies in CH_4, CCl_4 and CF_4. This assumption is very rough. A more accurate calculation making use of the heats of formation of CH_2 and CCl_2 leads to the values $D(H_2C{=}CH_2) = 117.6$ and $D(Cl_2C{=}CCl_2) = 96$ kcal/mole.

1291 The dissociation energies of CF and CH are lower than the mean bond energies in CF_4 and CH_4.

1293 In an article [1590a] published after the work with the present chapter had been completed the value of the potential Cl^- ion occurrence from CCl_4 was found, to which a value of

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$D(CCl_3{-}Cl) = 76{,}1 \pm 1{,}6$ kcal/mole corresponds, which considerably exceeds the values found in the works [1530, 4151, [illegible].

Chapter 21

COMPOUNDS OF CARBON WITH SULFUR, NITROGEN AND PHOSPHORUS

The present chapter deals with some of the simplest compounds of carbon with sulfur, nitrogen and phosphorus.

The carbon - sulfur compounds (CS, CS_2 and COS) discussed in the Handbook are the most important compounds of this class which are thermodynamically stable at high temperatures. Such compounds as CH_3SH, HCNS, CH_4N_2S, etc., decompose readily when heated, especially in the presence of oxidizers.

Only a number of the simplest carbon - nitrogen compounds, CN, C_2N_2, HCN and FCN, are discussed in the Handbook. A great number of other compounds of this class are known (for example, CNHS, CN_2H_2, CN_2H_4, HNCO, CN_4O_8, ClCN, etc.). The majority of them are unstable at high temperatures, with the exception, perhaps, of HNCO, NCO and a few others.

The carbon - phosphorus compounds are represented in the Handbook by the simplest CP molecule. Other more complex carbon - phosphorus compounds are thermodynamically unstable at high temperatures.

§84. MOLECULAR CONSTANTS

CS. The $^1\Sigma^+$ state is the ground electron state of the CS molecule. The CS spectrum was investigated in both emission [2537, 2790, 2249, 1217, 238, 328, 237] and absorption [237, 239, 1042a, 1435, 1436, 2543, 3302]. In contrast to the thoroughly investigated spectrum of the CO molecule, the great number of developed bands of which made it possible to determine the constants of this molecule in a great deal of electron states (see page 870), only one band system ($A^1\Pi - X^1\Sigma$), lying in ultraviolet, has - up to the present - been thoroughly investigated in the spectrum of the CS molecule. Furthermore, bands have been observed in the 2500-2700 A region of the CS spectrum, the assignment of which remains undertermined.

The band spectrum of CS, first obtained by Fowler and Strutt [1585a], was subsequently investigated by Martin [2790] and Jevons [2249]. A minute analysis of the CS spectrum was carried out by Crawford and Shurcliff [1217], who photographed the CS spectrum with devices of various dispersion. The spectrograms used for the analysis of the vibrational structure of the spectrum were obtained with a prism spectrograph having a dispersion from 7 A/mm at 2400 A to 18 A/mm at 3200 A. The use of devices with diffraction gratings (with a dispersion in the order of 0.28 A/mm) enabled these authors to obtain spectra with a well resolved rotational structure of the bands. Crawford and Shurcliff [1217] analyzed 65 bands ($v' \leq 11$, $v'' \leq 16$) degrated toward to red and composed by P-, Q- and R- branches. On the basis of the investigation of the fine structure of two bands and the analogy with the fourth positive system of CO, the authors of the paper [1217] assigned the observed system to the transition from the excited $^1\Pi$ state into the $^1\Sigma^+$ electron ground state, and explained the observed intense perturbation of the vibrational and rotational levels of the $^1\Pi$ state by the interaction with the neighbouring $^3\Pi$ state. The molecular constants of CS, determined in the paper [1217], are recommended in Herzberg's monograph [2020] and in the Handbook [649].

It should be noted that Howell [2138], comparing the ω_e''/ω_e' values of the basic band systems of diatomic oxide, sulfide, selenide and telluride molecules of the elements of the IVth Periodic system group,* came to the conclusion that the analysis of the rotational structure, carried out in paper [1217], is incomplete, and that the basic band system in the CS spectrum refers not to the $^1\Pi - {}^1\Sigma$ transition but to the $^3\Pi - {}^1\Sigma$ transition analogous to the Cameron system in the CO spectrum (in the Cameron system, $\omega_e''/\omega_e' = 1.24$ is valid, which conforms well with the value $\omega_e''/\omega_e' = 1.20$ in the CS system). Howell also assumed that the perturbations observed in the CS spectrum, as well as the perturbations of the Cameron bands in CO, are connected with the perturbing effect of the $^1\Pi$ state. However, a minute analysis of the rotational band structure of the basic CS system, carried out by Bowen [878] and Laird [2542], based on the spectrograms obtained by Crawford and Shurcliff, did not confirm Howell's assumptions [2138].

The final solution of the problem of the type of excited electron state, connected with the basic system of the CS spectrum, and of the nature of the disturbing states became possible only after the thorough analysis of the rotational structure of the bands in a wide range of the v' values, carried out by Lagerqvist, Westerlund, Wright and Barrow [2537], to specify more precisely the type of the upper electron state of this system. The CS spectrum was excited by discharge in a CS_2 flow and photographed in the first and second order of a 21-feet grating. In the paper [2537], an analysis of the rotational structure of 24 bands ($v' \leq 5$, $v'' \leq 7$) was carried out. The values found by Mockler and Bird [2930] by investigating the microwave spectrum of various isotopic CS modifications ($B_e'' = 0.82005$, $\alpha_1'' = 0.00592$ and $D'' = 1.34 \cdot 10^{-6}$ cm^{-1}) (calculated by Eq. (1.36)) were used for the analysis of the rotational constants of CS in the ground state. The vibrational and rotational constants of CS in the $X^1\Sigma$ and $A^1\Pi$ states, found in paper [2537], are accepted in the present Handbook and quoted in Table 186. The investigation of the perturbations in the $A^1\Pi$ state enabled the authors of paper [2537] to ascertain that they are caused by interaction with the $a'^3\Sigma^+$ and $e^3\Sigma^-$ states, and to evaluate the excitation energy and the molecular constants of CS in these states; the results are also cited in Table 186.

TABLE 186

Accepted Values of the Molecular Constants of CS, CN and CP

1 Молекула	2 Состояние	T_e	ω_e	$\omega_e x_e$	B_e	$\alpha_1\cdot10^3$	$D_0\cdot10^6$	r_e
		3. $см^{-1}$						Å
CS	$X^1\Sigma^+$	0	1285,08	6,46	0,82005	5,92	1,34	1,535
	$a'^3\Sigma^+$	38858[а]	760	7	0,585	8	—	1,82
	$A^1\Pi$	38898[б] b	1081,20	11,1	0,77995	6,29	1,62	1,574
	$e^3\Sigma^-$	39155[а]	750	5	0,610	6	—	1,78
CN	$X^2\Sigma$	0	2068,616	13,111[в] c	1,8989	17,17[г] d	6,395[д] e	1,172
	$A^2\Pi_i$	9246,04[в] c	1812,316	12,588[ж]	1,7166	17,16[з] h	6,246[д] e	1,233
	$B^2\Sigma$	25752,0	2163,9	20,2	1,985	23	6,574[д] e	1,146
CP	$X^2\Sigma^+$	0[и] i	1239,67	6,86	0,79863	5,97	1,326	1,5583
	$A^2\Pi_i$	6974,07[к]	1061,99	6,035	0,6980	7,7	—	1,667
	$B^2\Sigma^+$	29100,35[л] l	836,32	5,917	0,68289	6,26	1,821	1,6852

a) The T_0 values are given.

b) The existence of another two $^3\Pi$ states with an excitation energy of the order of 35,000-38,000 cm^{-1} is possible.

c) $\omega_e y_e$ = 0.91 cm^{-1}

d) $\alpha_2 = 4.73\cdot10^{-5}$ cm^{-1}

e) calculated by Eq. (1.36)

f) A = -52.2 cm^{-1}

g) $\omega_e y_e$ = -0.012 cm^{-1}

h) $\alpha_2 = -4.14\cdot10^{-5}$ cm^{-1}

i) γ = -0.017 cm^{-1}

k) the averaged value is given; $T_e(A^2\Pi_{1/2})$ = 6894.93, $T_e(A^2\Pi_{3/2})$ = 7053.20 cm^{-1}.

1) Molecule
2) state
3) cm^{-1}.

The analysis of the possible electron configurations of CS, carried out by Lagerqvist et al [2537], proved that besides the states quoted in Table 186, the CS molecule must have yet another four states ($^3\Pi$, $^1\Sigma^+$, $^1\Sigma^-$, $^3\Delta$) with relatively low excitation energies. By analogy with the CO molecule, one may expect that another two states $^3\Pi$ with excitation energies of the order of 35,000-38,000 cm^{-1} are situated between the basic and the first excited singlet $A^1\Pi$ state of CS.

As was mentioned above, Crawford and Shurcliff [1217] observed in the CS spectrum besides the basic $A^1\Pi - X^1\Sigma$ system another four bands in the 2500-2710 A region, degrated toward to red and possessing only P- and R- branches. Crawford and Shurcliff assigned these bands hypothetically to the $C^1\Sigma - B^1\Sigma$ system. Kondrat'yev [239] and, subsequently, Porter [3302] proved, however, that the ground state $X^1\Sigma^+$ of the CS molecule must be the lower state of this system. Later on, Lagerqvist et al [2537] suggested that the bands in question do not in fact refer to any new electron transition, but are groups of lines caused by transitions from the v' = 1level of the ground system.*

<u>CN</u>. The $X^2\Sigma$ state is the basic ground electron state of the CN molecule. The thorough analysis of the possible electron configurations and of the corresponding electron states, which may be anticipated for the CN molecule, was carried out by Douglas and Routly [1382], Band systems, caused by transitions between eight electron states, and reaching from the near infrared region to the far vacuum ultraviolet, have been observed in the CN spectrum.

Two systems, a red, caused by the $A^2\Pi - X^2\Sigma$ transition, and a violet, caused by the $B^2\Sigma - X^2\Sigma$ electron transition, are the most characteristic ones in the CN spectrum.

The $A^2\Pi - X^2\Sigma$ system was investigated by Jenkins, Roots and Mulliken [2236]. The authors of paper [2236] obtained by means of a spectograph with a 21-feet grating a spectrum in the 3500-8000 A region containing 24 bands ($v' \leq 12$, $v'' \leq 12$) of this system. The analysis of the rotational structure was carried out for seven bands. The analysis of the vibrational structure was carried out, based on the edges of the R_2- band branches, and taking into account corrections for the difference in the wavelengths of the R_2- branch edges and the band heads. As a result of the analysis, the vibrational and rotational constants of CN in the $X^2\Sigma$ and $A^2\Pi$ states were determined.

In 1948, however, Herzberg and Phillips [2038] proved that an error was committed in paper [2236] when analysing the vibrational structure of the $A^2\Pi - X^2\Sigma$ system. This error was caused by the fact that the band λ = 9140 A was assumed as the 0-0 band of the $^2\Sigma - {}^2\Pi$ system. Herzberg and Phillips proved that this band is a 0-1 band and that the head of the 0-0 band has λ = 10,550 A. Based on the analysis of spectrograms obtained in paper [2038] and in earlier investigations [2236, 2237], Herzberg and Phillips determined precisely the values of the CN constants in the $A^2\Pi$ state.

The violet system of CN bands, caused by the $B^2\Sigma - X^2\Sigma$ transition and reaching from the visible to the near ultraviolet region, was observed in both the emission and absorption spectra [2414, 4[illegible], 4242, 3104]. The bands of this system have been measured by Uhler and Patterson [4034], Kayser and Runge [2340] and Heurlinger [2060]. Later on, these measurements were repeated by Jevons [2248], Jenkins [2227], and Jenkins and Wooldridge [2237]. In 1955 Weinard [4194] and Douglas and Routly [1382] measured and analyzed anew a series of bands of the red and violet systems of CN.

Apart from the bands of the violet system, identified earlier, Douglas and Routly [1382] obtained the bands 16-13, 19-15, 18-17, 18--18 and 19-18 in the CN spectrum excited by discharge in C_2N_2 vapor in the presence of helium. In order to determine precisely the vibrational and rotational constants of CN on the low levels of the $X^2\Sigma$ and B states, the bands of the $\Delta v = 1$ sequence were measured up to the 5-6 band in the paper [1382]. Douglas and Routly [1382] also investigated the red band system of CN. The results of their own measurements (the bands up to $v' = 19$ were investigated) and the data obtained by Jenkins, Roots and Mulliken [2236] enabled Douglas and Routly to find the equation expressing $\Delta G_{v+1/2}$ as a function of v for the $^2\Pi_{1/2}$ component of the $A^2\Pi$ state.

The extrapolation by means of this equation gives the dissociation limit of the $X^2\Sigma$ state equal to 77,717 cm^{-1} (9.64 ev). The linear extrapolation gives $D_0(CN) = 80{,}542$ cm^{-1} (9.99 ev). The accepted value of $D_0(CN)$ is equal to 8.41 ev (see page 1350). Using also the data of Jenkins, Roots and Mulliken [2236] and Parker [3184] and the results of the analysis of the rotational structure of the 15-8 band, Douglas and Routly found the rotational constants of CN in the $A^2\Pi$ state. The values of the molecular constants of CN in the $X^2\Sigma$, $A^2\Pi$ and $B^2\Sigma$ states, found by Douglas and Routly [1382], are accepted in the present Handbook and quoted in Table 186. These constants differ only insignificantly from the constants found earlier in papers [2236, 2038, 2237, 2248, 2227] and recommended in the Handbook [649] and in Herzberg's monograph [2020].

Weinard [4194] obtained the CN spectrum in diverse orders of the diffraction grating with a dispersion varying from 0.88 to 2.14 A/mm. Only the $B^2\Sigma - X^2\Sigma$ system was thoroughly investigated in paper [4194]. The wave numbers of the band heads and the values of the rotational constants B_v for the $B^2\Sigma$ and $X^2\Sigma$ states, found for nine measured bands ($v' \leq 3$, $v'' \leq 3$), are excellently described by the vibrational and rotational constants accepted in the present Handbook. It should be noted that the difference between the values of ν_{00}, listed in paper [4194], and the values calculated by these constants, does not exceed

1 cm^{-1}. The corresponding difference for the B_v constants does not exceed 0.003 cm^{-1}.

In order to obtain supplementary data on the dissociation energy of CN, investigations of the CN spectrum in the short wave region up to 1650 A have been recently carried out [1380, 1381, 1382, 1063]. Besides the $X^2\Sigma$, $A^2\Pi$ and $B^2\Sigma$ states, which were already known, Douglas and Routly [1380, 1381, 1382] discovered the following electron states of CN:$D^2\Pi$, $F^2\Delta$ and $H^2\Pi$, which give rise to foud band systems in the near ultraviolet region: $D^2\Pi \rightarrow X^2\Sigma$, $D^2\Pi \rightarrow A^2\Pi$, $F^2\Delta \rightarrow A^2\Pi$ and $H^2\Pi \rightarrow B^2\Sigma$. Carroll [1063] found another two excited states of CN, unknown earlier: $E^2\Sigma$ and $J^2\Delta$, involving the band systems $E^2\Sigma \rightarrow X^2\Sigma$, $E^2\Sigma \rightarrow A^2\Pi$ and $J^2\Delta \rightarrow A^2\Pi$, which are situated in the 1650-2100 A region. The values of the molecular constants of CN in the $X^2\Sigma$, $A^2\Pi$ and $B^2\Sigma$ states, found by analysis of the vibrational and rotational structure of the ultraviolet band systems [3182, 1063], nearly concur with the constants found by analysis of the red and violet systems. The vibrational and rotational constants of CN in the $D^2\Pi$, $E^2\Sigma$, $F^2\Delta$, $H^2\Pi$, $J^2\Delta$ states, recommended in papers [1382, 1063], are not listed in Table 186 because the excitation energies of these states exceed 50,000 cm^{-1}.

It should be noted that, by analogy with the SiN molecule (see Table 198), a stable $C^2\Pi$ electron state of the CN molecule with an excitation energy of about 35,000 ± 3000 cm^{-1} most probably exists.

<u>CP</u>. Two band systems are known in the spectrum of the CP molecule: the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system, situated in the near ultraviolet region (4400-2900 A), and the $B^2\Sigma^+ \rightarrow A^2\Pi_i$ system, situated in the visible region (5000-4400 A).

The spectrum of the CP molecule was obtained for the first time by Herzberg [2014] in the first order of a two-meter diffraction grating (8.7 A/mm dispersion). The band system $B^2\Sigma^+ \rightarrow X^2\Sigma^+$, with a partially resolved fine structure, was observed in paper [2014], and a preliminary analysis of the vibrational structure of the bands of this system was carried out.

Later on, Barwald, G. Herzberg and L. Herzberg [673] obtained the CP spectrum with a resolved fine structure of the bands in the 2900--5000 A region by the second order of a three-meter diffraction grating (2.8 A/mm dispersion). The CP bands, however, were superposed by CN bands, and only four CP bands of the $^2\Sigma - {}^2\Sigma$ (3-0, 2-0, 0-1 and 0-3) were free from superposition by CN bands. The band edges of the $^2\Sigma - {}^2\Sigma$ system, corresponding to $v' \leq 10$, $v'' \leq 9$, and of the $^2\Sigma - {}^2\Pi$ system, corresponding to v', $v'' \leq 4$, were measured in paper [673], and the analysis of the vibrational structure was carried out. The values of the vibrational constants of the CP molecule in the $X^2\Sigma^+$, $A^2\Pi_i$ and $B^2\Sigma^+$ states as well as of the excitation energies of these states, resulting from this analysis, are accepted in the present Handbook and quoted in Table 186. In paper [673], the rotational structure of the 3-0, 2-0, 0-1, 0-3 bands has also been analyzed, thus making it possible to determine the rotational constants B_e, α_e, D_e and the constants of the multiplet splitting of the $^2\Sigma$ states (the γ constants) of the CP molecule. The values of the rotational constants of CP, recommended in paper [673], are accepted in the present Handbook and listed in Table 186.

$\underline{CS_2}$. The molecule of carbon bisulfide has a lineary symmetric structure and belongs to the symmetry point group $D_{\infty h}$.

The results of investigations of CS_2 spectra, carried out up to 1944, are thoroughly discussed by Herzberg [152]. It should be noted that the majority of papers published before 1944 dealt with the investigation of the Raman spectra of liquid, solid and gaseous carbon bisulfide [4081, 4082, 2562, 2168, 3751, 1882, 4321], and only in the papers by Bailey and Cassie [609, 614], Dennisson and Wright [1316], and Sanderson [3578], was the infrared absorption spectrum of CS_2 investigated by devices with a low dispersion. Based on the analysis of the data obtained in these papers, Herzberg [152] recommended the following values of the fundamental frequencies of CS_2: $\nu_1 = 656.5$, $\nu_2 = 396.7$ and $\nu_3 = 1523$ cm^{-1}, found by Bailey and Cassie [614], Dennisson and Wright [1316] and Langseth, Srensen and Nielsen [2562].

Subsequently, the infrared absorption spectrum of gaseous CS_2 was investigated by Gailar and Plyler [1639, 1640] (the $3\nu_3$ band), Allen, Plyler and Blaine [512] (the $\nu_1 + \nu_3$, $2\nu_1 + \nu_3$, $\nu_1 + 2\nu_2 + \nu_3$ bands), Plyler and Acquista [3272], and Lord and McCubbin [2650] (the ν_2 band), Guenther [1873, 1873a, 1873b], Guenther, Wiggins and Rank [1874] (the bands $3\nu_3$ and $\nu_2 + 3\nu_3 - \nu_2$), Hadni [1919, 1920] (the ν_2 band), and Wentink [4205] (the $\nu_3 - \nu_1$ band). The Raman spectrum of CS_2 was investigated by Stoicheff [3877] and Evans and Bernstein [1511].

The most accurate values of vibrational constants of the CS_2 molecule have been stated in Stoicheff's work [3877]. Stoicheff [3877] photographed the Raman spectrum of gaseous CS_2 in the second order of the grating with a dispersion of 1.25 A/mm. The intense ν_1 and $2\nu_2$ bands, three bands of isotopic CS_2 modifications: $(\nu_1 + \nu_2 - \nu_2)\ CS^{32}S^{34}$, $\nu_1\ CS^{32}S^{34}$ and $\nu_1\ CS^{32}S^{33}$ and ten "hot" bands: $(\nu_1 + 3\nu_2^1) - 3\nu_2^1$, $(\nu_1 + 2\nu_2^2) - 2\nu_2^2$, $(\nu_1 + 2\nu_2^0 - 2\nu_2^0)$, $(2\nu_2 - \nu_2^1)$, $(\nu_1 + \nu_2^1)$, $(\nu_1 + \nu_2^1) - \nu_2$, $(2\nu_1 - \nu_1)$, $(3\nu_1^1 - \nu_2^1)$, $(4\nu_2^0 - 2\nu_2^0)$ and $(4\nu_2^2 - 2\nu_2^2)$, were measured.

The results of his own measurements and the data obtained by investigation of infrared bands enabled Stoicheff to determine the vibrational constants of CS_2 quoted in Table 187 and accepted in the present Handbook. These constants are calculated taking into account the resonance interaction between the energy levels. Although the Fermi resonance in the CS_2 molecule is considerably weaker than in the CO_2 molecule, Stoicheff [3877] showed that the regard for this interaction noticeably influences the value of the vibrational constants.*

The pure rotational Raman spectrum of CS_2 was also obtained in Stoicheff's work [3877], and Stoicheff succeeded in measuring the Stokes and anti-Stokes branches up to lines with $J = 94$. The analysis of this spectrum enabled Stoicheff to find the following rotational constants of CS_2 in the ground state: $B_{000} = 0.10910 \pm 0.0005$, $D_{000} = 1.0\cdot10^{-8}$ cm^{-1}, $r_0 = 1.5545 \pm 0.0003$ A. Using the value $\alpha_1 + 2\alpha_2 + \alpha_3 = 0.000460$ cm^{-1}, obtained by Allen, Plyler and Blaine [512] by analysis of the $\nu_2 + 2\nu_2 + \nu_3$ band in the infrared spectrum, Stoicheff found $B_e = (0.10933 \pm 0.00008)$ cm^{-1} and $r_e = (1.5529 \pm 0.0005)$ A, which excellently conforms with the results of the investigation of the fine structure of the bands $3\nu_3$ and $\nu_2 + 3\nu_3 - \nu_2$, carried out by Guenther [1873, 1873a, 1873b] and Guenther, Wiggins and Rank [1874, 1875]. About 275 lines of the 003-000 and 01^13-01^10 bands were measured in the papers [1874, 1875]. The values of the rotational constants, recommended in these papers, are quoted in Table 187 and accepted in the present Handbook. The value of α_1, listed in the Table, was calculated by means of the value of α_3, found in the papers [1874, 1875], and of the value of $B' - B''$, obtained by Allen, Plyler and Blaine [512] for the 201_000 band. It should be mentioned that the values of the rotational constants found in papers [1874, 1875, 3877] are more accurate, than the values obtained by Allen, Plyler and Blaine [512]. These authors found the value $4.34\cdot10^{-8}$ cm^{-1} for D_{000}, which is too high in comparison with the value $B_{000} = 0.10927$ cm^{-1}, found by the same authors, and which indicates an error in the measurements or calculations carried out in paper [512].

The ultraviolet spectrum of CS_2 was investigated in papers [4286, 2228, 4186, 3324, 2503, 2612, 3353, 2434, 1373, 3358, 3717a].

TABLE 187

Accepted Values of the CS_2 Molecular Constants[a] (in cm^{-1})

1 Постоянная	2 Значение постоянной	1 Постоянная	2 Значение постоянной	1 Постоянная	2 Значение постоянной
ω_1	671,36	x_{12}	0,861	B_{000}	0,109099
ω_2 (2)	398,62	x_{23}	—6,67	α_1	0,000156
ω_3	1551,92	x_{13}	—4,95	α_2	—0,000256
x_{11}	—1,054	g_{22}	0,671	α_3	+0,000711
x_{22}	0,126	W	36,05	D_{000}	$1,05 \cdot 10^{-8}$
x_{33}	—5,135			q_1	$6,6 \cdot 10^{-5}$

[a] The fundamental frequencies of the CS_2 molecule found by the band heads in the Raman spectrum ν_1) and the infrared absorption spectrum (ν_2 and ν_3) are equal to: $\nu_1 = 657.98$, $\nu_2 = 396.8$ and $\nu_3 = 1532.5$ cm^{-1}.

1) Constant; 2) value of the constant.

The attempts at analyzing the structure and interpreting the ultraviolet bands in the absorption spectrum of CS_2, made in papers [4286, 2228, 4186, 3324] were unsuccessful because the spectral devices used for recording the spectrum did not give a resolution necessary for the analysis of the fine structure. Only in Liebermann's paper [2612], were the absorption bands of CS_2 in the 3050-3700 Å region photographed for the first time by a device with a resolving power of 300,000. Liebermann succeeded in the analysis of the rotational structure of six bands not overlapped by neighboring bands, out of the great number of bands observed in the region from 3050 to 3700 A. The analysis showed that the ultraviolet bands refer to the ${}^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ transition and that the CS_2 molecule is bent in the excited state, which lies about 27,000 cm^{-1} higher than the electron ground state (the angle between the C-S bonds is nearly 125° and $r_{C-S} \cong 1.735$ A). The value of the excitation energy found in paper [2612] conforms with the value suggested by Mulliken [2992] on the basis of a theoretical analysis, and is corroborated by the papers by Ramasastry [3353] and Kleman [2434].

Investigating the ultraviolet bands, Ramasastry [3352] found that two band systems of CS_2 are situated in the 2900-3800 A region. In the more intense system, occupying the 2900-3300 A region, an evolved progression with an interval of 450 cm^{-1} was observed, which Ramasastry attributed to the fully symmetrical valence vibration in the excited state of CS_2. Assuming that the intense system refers to the transition between the ground state and the excited state of CS_2 in which the molecule is bent, and based on the selection rules suggested by Mulliken [2999] for such transitions, Ramasastry recommended the following values for the fundamental frequencies in excited state: $\nu_1 =$ $= 450$, $\nu_2 = 226$, $\nu_3 = 1050$ cm^{-1}. The second system, observed by Ramasastry, obviously refers to the excited $^1\Pi_u$ state, the existence of which was reported by Liebermann [2612] on the basis of an investigation of perturbations in the bands λλ 3501 and 3601 A.

It should be mentioned that Douglas [1373] observed a change in the shape of the bands in the ultraviolet CS_2 spectrum when a magnetic field was superposed. A preliminary investigation showed that the observed Zeeman effect is only explicable when assuming that the first excited electron state of the CS_2 is not a singlet state, as was earlier supposed, but a triplet one. The final solution of this problem is possible only by investigation of the Zeeman splitting of the rotational CS_2 levels in excited state.

COS. The COS molecule is linear, as well as the CO_2 and CS_2 molecules, but it belongs to the symmetry point group $C_{\infty h}$. Such a molecule must have three fundamental frequencies active in the infrared and the Raman spectrum (symmetric and antisymmetric valence vibrations and a doubly degenerated deformation vibration).

The infrared spectrum of COS was first obtained by Bailey and Cassie [610, 614]. The analysis of the observed bands, the fine structure of which could not be resolved, resulted in the following values of fundamental frequencies: $\nu_1 = 859$, $\nu_2 = 527$, $\nu_3 = 2079$ cm^{-1}. The interpretation of the infrared spectrum of COS, obtained by Bartunek and Barker [672], gave somewhat different frequency values: $\nu_1 = 859.2$, $\nu_2 = 521.5$, $\nu_3 = 2050.5$ cm^{-1}.

Simultaneously with the investigation of the infrared COS spectrum in 1930-1940, papers were also published dealing with the study of the Raman spectrum of carbon oxysulfide [1242, 4125]. The values of frequencies, found in these works, conform excellently – within the error limits of the experiment – with the results of measurements in the infrared region of the spectrum.

In 1951 Callomon, MacKean and Thompson [1045] investigated anew the infrared absorption spectrum of COS in the region from 500 to 5000 cm^{-1}. The analysis of 20 bands, observed in the investigated range, enabled the authors of paper [1045] to recommend the following values of fundamental frequencies: $\nu_1 = 859$, $\nu_2 = 524$ and $\nu_3 = 2064$ cm^{-1}, which conform with the values found earlier.

The rotational structure of the bands of the carbon oxysulfide spectrum was first resolved in the infrared spectrum by Callomon and Thompson [1046].* Analyzing four bands in the COS absorption spectrum, Callomon and Thompson found: $\nu_1 = 859.1$, $\nu_2 = 524$ and $\nu_3 = 2062.22$ cm^{-1}. Supposing a Fermi resonance between the $4\nu_2$ and ν_3 and ν_1 and $2\nu_2$ levels, the authors of [1046] calculated the interaction energies of the resonating levels as equal to 12.00 and 33.1 cm^{-1}, respectively, and the values of the nondisplaced frequencies: $\nu_1 = 865.1$ and $\nu_3 = 2065.95$ cm^{-1}.

The most minute investigation of the infrared COS spectrum was carried out by Allen, Plyler and Blaine [513], who obtained the COS spectrum in the region from 1800 to 10,000 cm^{-1} (5.5-1 microns) by spectrometers with diffraction gratings. The analysis of the fine structure of eight bands, resolved in the best way, gave the values of the rotational constants $B_{000} = 0.20288 \pm 0.00002$ and $D_{000} = (4.08 \pm \pm 0.52) \cdot 10^{-8}$ cm^{-1}, conforming excellently with the investigation results of the COS microwave spectrum.

The authors of paper [513] came to the conclusion that the Fermi resonance and the Coriolis interaction do not affect the position of the 001 level, and that the value of the nondisplaced band centrum $\nu_3 = 2065.95$ cm^{-1}, suggested in paper [1046], is unreal.* On the other hand, it was shown in the paper by Allen et al [513] that the Fermi resonance between the ν_1 and $2\nu_2$ levels actually takes place. The existence of this interaction made it impossible to utilize the results of the analysis for the determination of all constants entering into the equation of vibrational energy. Only three anharmonicity constants were found: $x_{23} = -7.33$, $x_{13} = -1.86$ and $x_{33} = 11.50$ cm^{-1}.

Owing to the existence of resonance interaction between the vibrational states, the difficulties of the analysis of the carbon oxysulfide molecule spectrum hindered the determination of the nondisturbed values of fundamental frequences and of reliable values of the anharmonicity constants. In the present Handbook, the values of fundamental frequencies are accepted, obtained by investigations of the infrared and Raman spectra carried out without taking into account the resonance interaction of the levels. The accepted values of the fundamental frequencies of COS are listed in Table 188.

The microwave spectrum of the COS molecule was investigated in papers [2012, 1250, 1251, 4006, 4007, 4009, 3447, 3882, 2664, 4207, 2260, 3959, 2663, 3226, 3658, 2405], in which the lines corresponding to the various purely rotational transitions have been measured with high precision.

TABLE 188

Accepted Values of the Molecular Constants of COS

ν_1	ν_2 (2)	ν_3	B_{000}	σ
cm^{-1}				
859	524	2064	0,202867[a]	1

[a] $\alpha_1 = 6.858 \cdot 10^{-4}$; $\alpha_2 = -3.523 \cdot 10^{-4}$; $\alpha_3 = 1.75 \cdot 10^{-4}$; $D_{000} = 4.27 \cdot 10^{-8}$ cm^{-1}.

The values of the rotational constants of the COS molecule, quoted in Table 188, are found by Tetenbaum [3959] who investigated the rotational transition J = 3 → 4 in various vibrational states. In his calculations Tetenbaum used the value $D_{000} = (4.27 \pm 0.17) \cdot 10^{-8}$ cm^{-1} found by Johnson, Trambarulo and Gordy [2260]. The values of the constants α_1 and α_2 were found in paper [3959] from the data for excited states, taking into account the effect of the Fermi resonance; α_3 was found by investigation of the spectra of three isotopic modifications of COS. The value of the ℓ doubling constant ($q_\ell = 2.116 \cdot 10^{-4}$ cm^{-1}), found in paper [3959], conforms excellently with the value $q_\ell = 2.115 \cdot 10^{-4}$ cm^{-1}, calculated theoretically by Nielsen [3084].

The following values of structural parameters of the COS molecule correspond to the values of rotational constants determined by microwave spectra: $r_{C=O} = 1.1637 \pm 0.0013$ and $r_{C=S} = 1.5586 \pm 0.0010$ A. These values concur with the values of interatomic distances ($r_{C=O} = 1.16$ and $r_{C=S} = 1.56$ A) found by Cross and Broxkway [1228] by electron-diffraction measurements.

HCN. The HCN molecule possesses a linear structure and belongs to the symmetry point group $C_{\infty h}$. The vibrations of such a molecule are characterized by three fundamental frequencies: two frequencies (ν_1 and ν_3), referring to the valence vibrations of the C-H and C≡N bond, and the frequency ν_2 of the (doubly degenerated) deformation vibration.

The spectrum of the vapor of hydrocyanic acid was investigated by many authors. Based on the analysis of the results of investigations carried out up to 1944, Herzberg [152] accepts the values of vibrational and rotational constants of HCN, quoted in Table 189. A considerable number of papers dealing with the investigation of the spectra of various isotopic modifications of hydrocyanic acid were published in recent years; besides the infrared spectrum [2193, 3437, 2316, 3378, 1383, 3380, 3379, 4265, 3373, 3384, 3384a, 3384b, 3393a, 947a, 3385, 1243, 3830, 516, 3374] and the Raman spectrum [2316], the purely rotational spectrum [3728, 1821, 3048, 1708, 3716, 1823, 3729, 4188, 3084, 4189, 4354, 1947] and the ultraviolet spectrum of HCN [2035, 4139] have also been studied.

The minute investigation of the infrared HCN spectrum in the region from 0.5 to 2.5 microns was carried out by Douglas and Sharma [1383] by a device with a concave grating and a focal length of 6 m. Owing to the use of multipass cells, the length of the absorbing layer of hydrocyanic acid vapor reached 600 m. In order to increase the accuracy of determination of wavelengths of the observed lines, the interferometric system by Fabry and Perrot was used. Based on the frequencies of 27 bands, observed by them, and the ν_1 frequency, inactive in the infrared spectrum and determined by Stoicheff in the Raman spectrum,* Douglas and Sharma [1383] calculated the values of the vibrational constants of HCN listed in Table 189. As it is shown in this

Table, the values of the constants found in paper [1383] are close to the values accepted by Herzberg [152] with the exception of ω_i^0, x_{11} and x_{12}.

TABLE 189

Values (in cm^{-1}) of the Molecular Constants of HCN[a]

Постоянная 1	Герцберг [152] 2	3 Дуглас и Шарма [1383]	Аллен, Тидуэлл, Плайлер 4 [516]	Постоянная	Герцберг [152]	Дуглас и Шарма [1383]	Аллен, Тидуэлл, Плайлер [516] 6
ω_1^0	2041,2	2105,10	2107,66	y_{333}	0,768	0,527	—
ω_2^0	711,7	710,90	710,77	g_{22}	3,25	3,63	3,63
ω_3^0	3368,6	3364,39	3363,90	B_e	1,4878	1,4849	—
x_{11}	52,0	−9,0	−10,45	B_{000}	1,4784	1,47823	1,47791
x_{22}	−2,85	−2,47	−2,50	α_1	0,0093	0,00950	0,00991
x_{33}	−55,48	−54,20	−52,50	α_2	−0,0007	−0,00350	—
x_{12}	−4,2	−2,15	−2,90	α_3	0,0108	0,01079	—
x_{13}	−14,40	−16,8	−14,43	D_{000}	$3,3\cdot10^{-6}$	$2,85\cdot10^{-6}$	$2,59\cdot10^{-6}$
x_{23}	−19,53	−19,6	−19,19				

[a] After this Chapter had been written, the paper by Rank, Skorinko, Eastman and Wiggins [3384a] was published, in which the vibrational-rotational spectrum of HCN was investigated anew, and the structure of a number of HCN bands lying in this region from 2000 to 10,000 cm^{-1} (from 1 to 5 microns) was measured. Together with the results of foregoing investigations, these measurements made it possible to find the values of 21 vibrational constants necessary for the determination of the normal vibration frequencies, and also of 10 constants required for the calculation of the B_v values in various vibrational states (in cm^{-1}):

$$\omega_1 = 2119{,}8642,\ \omega_2 = 726{,}9950,\ \omega_3 = 3441{,}\ 2207,\ \omega_1^0 = 2104{,}2248,\ \omega_2^0 = 710{,}8955,\ \omega_3^0 = 3363{,}8737,\ x_{11} = -7{,}0741,\ x_{22} = -2{,}6533,\ x_{33} = -52{,}4901,\ x_{12} = -2{,}5265,\ x_{13} = -10{,}4434,\ x_{23} = -19{,}0055,\ g_{22} = 5{,}160,\ y_{111} = -0{,}1889,\ y_{222} = 0{,}0285,\ y_{333} = 0{,}27020,\ y_{112} = -0{,}0012,\ y_{113} = -0{,}7723,\ y_{122} = -0{,}0747,\ y_{133} = -1{,}1010,\ y_{123} = 0{,}1240,\ y_{223} = -0{,}0375,\ y_{233} = -0{,}1830,\ z_{3333} = 0{,}01943,\ B_e = 1{,}484514,\ \alpha_1 = 0{,}009673,\ \alpha_2 = -0{,}003988,\ \alpha_3 = 0{,}010441,\ \gamma_{11} = -0{,}000030,\ \gamma_{22} = 0{,}000065,\ \gamma_{33} = 0{,}000157,\ \gamma_{12} = 0{,}000595,\ \gamma_{13} = -0{,}000227.\ \gamma_{23} = -0{,}000223.$$

The listed vibrational constants describe excellently the position of the zero lines of $HC^{12}N$ bands observed experimentally (with an accuracy of ±0.2) up to 18,400 cm^{-1}. The following values of structural parameters of HCN are recommended in paper [3384a]: $r_e(C - H) = 1.06593 \pm 0.00010$ and $r_e(C \equiv N) = 1.15313 \pm 0.00002$ A.

[b] In paper [516], also the constants B = 9.30, a = -0.733 cm^{-1}, b = 0 and c = -0.1461 cm^{-1} are given, which enter into the equation for the interaction energy.

$$V_{kl} = A\,[v_2(v_2-1)(v_1-1)(v_1-3)]^{1/2},$$

where

$$A = B(1 + av_1 + bv_2 + cv_3).$$

1) Constant; 2) Herzberg; 3) Douglas and Sharma; 4) Allen, Tidwell, Plyler.

The difference between these constants is mainly cuased by the fact that Douglas and Sharma [1383] have essentially improved the value of the frequency of the $2\nu_1 + \nu_2$ band in comparison with the data by Adel and Barker [489] accepted by Herzberg. Moreover, the more precise value of the ν_1 frequency, found by Stoicheff, was taken.

In 1956, Allen, Tidwell and Plyler [516] obtained anew the infrared absorption spectrum of gaseous HCN in the region from 1.25 to 5.25 microns (8000-1900 cm^{-1}). Analyzing 22 HCN bands and taking into account the resonance interaction of third order between levels of the type $(\nu_1 \nu_2^{\ell} \nu_3)$ and $(\nu_1 + 3, \nu_2^{\ell}, \nu_3 - 2)$, the authors of [516] found the constants of HCN which are also quoted in Table 189. The values of the constants, found by Allen, Tidwell and Plyler [516], differ insignificantly from the values obtained in paper [1383]. Whereas, however, the constants found in paper [516] make it possible to calculate the energy of all levels below 12,000 cm^{-1} with an accuracy of ±0.2 cm^{-1}, the analogous calculation carried out with the constants obtained by Douglas and Sharma [1383] results in more significant differences between the calculated and measured magnitudes.* This permits us to assume that the constants found in paper [516] better describe the vibrational energy levels of the HCN molecule than the constants obtained by Douglas and Sharma [1383].

Douglas and Sharma [1383] also carried out the analysis of the rotational structure of 16 bands in the HCN spectrum, and, based on the found values of $B_{v_1 v_2 v_3}$ and the magnitude $B_{000} = 1.47828$ cm^{-1}, obtained by analysis of the microwave spectrum of HCN [3048], they calculated the value of B_e with an accuracy of ± 0.0003 cm^{-1} and the value of the interaction constants α_i quoted in Table 189. The values of the constants B_{000}, D_{000} and α_1, found by Allen, Tidwell and Plyler [516] are also listed in the same Table. In order to verify the values of the constants α_1, α_2 and α_3, found by Douglas and Sharma by analysis of bands lying the near infrared region, where the effect of the Fermi resonance is most intense, Dagg and Thompson [1243] analyzed the rotational structure of a series of HCN and DCN bands lying in the far infrared spectral region. The authors of paper [1243] found the values $B_{000} = 1.4782$, $B_e = 1.4846$, $\alpha_1 = 0.0103$, $\alpha_2 = -0.0037$ and $\alpha_3 = 0.0099$ cm^{-1}, which conform with the values obtained by Douglas and Sharma [1383]. This proves that the Fermi resonance affects but insignificantly the rotational constants of the HCN molecule. The small difference between the rotational constants found in papers [1383, 1243] does almost not affect the values of the interatomic distances $r_{C-H} = 1.0657$ and $r_{C\equiv N} = 1.1530$ A.

An analysis of the rotational structure of individual bands was also carried out with a high degree of accuracy in a series of papers by Rank and coworkers [3378, 3380, 3379, 4265, 3385, 3374]. The most accurate values $B_{000} = 1.478218$* and $D_{000} = 2.913 \cdot 10^{-6}$ cm^{-1}, found in the work [3374] by measuring 30 lines of the $2\nu_3$ band, conform excellently with the constants obtained by Douglas and Sharma [1383].

The results of investigations of the ultraviolet HCN spectrum, carried out up to 1953, are discussed in a review by Walsh [4139]. Later on, Herzberg and Innes [2035] carried out a thorough study of the ultraviolet HCN spectrum and showed that the first excited state ($\alpha^1\Delta$) of this molecule possesses an excitation energy equal to 52,277 cm^{-1}. The detailed analysis of the vibrational and rotational structure of bands of the $\alpha^1\Delta - X^1\Sigma^+$ system, situated in the region $\lambda < 2000$ A, led Herzberg and Innes [2035] to conclude that the HCN molecule is bent in the excited $\alpha^1\Delta$ state and possesses the following structural parameters: $r_{C-H} = 1.14$, $r_{C\equiv N} = 1.297$ A and $\angle HCN = 125°$. The two fundamental frequencies $\nu_1 = 1506$ and $\nu_2 = 949$ cm^{-1} were found in this state. The vibration frequency of the C-H bond was not found. The paper by Herzberg and Innes [2035] quotes also the vibrational and rotational constants of the subsequent $\beta^1\Sigma^-$ excited state of HCN, the energy of which is equal to 54,630 cm^{-1}.

FCN . Experimental data on the spectrum and structure of the FCN molecule were missing up to 1960. When preparing the present Handbook, the FCN constants necessary for the calculation of the thermodynamic functions were evaluated on the basis of the data on other cyanhalides and some other compounds. Subsequently, the results of these evaluations were corroborated by experimental data (see footnote to page 1326). Owing to the fact that the HCN, ClCN, BrCN and ICN molecules, the next analoga to FCN, are linear in the electron ground state, it is assumed in the present Handbook that the cyan fluoride possesses linear structure and belongs to the symmetry point group $C_{\infty h}$. Such a molecule is characterized by two interatomic distances (r_{C-F} and $r_{C\equiv N}$) and three fundamental frequencies (ν_1 and ν_3, the frequencies of the valence vibrations of the C-F and C≡N bonds, and the frequency ν_2 of the doubly degenerated deformation vibration).

The structural parameters, the force constants and the fundamental frequencies of the FCN molecule were formerly evaluated by Thomas [3965] and Luft [2673] who assumed a linear structure of the FCN molecule.

Based on the experimentally found fundamental frequencies of the HCN, ClCN, BrCN and ICN molecules, Thomas [3965] calculated the values of the force constants of these molecules and, using a number of semiempirical relationships between the force constants, bond lengths, atomic weights and ionization potentials of cyan halides, he evaluated the molecular constants of FCN: $r_{C \equiv N} = 1.1655$ A, $\nu_1 = 1052$ and $\nu_3 = 2294$ cm^{-1}.

Using analogous semiempirical relationships, Luft [2673] calculated the value of the frequency of the doubly degenerated deformation vibrations, $\nu_2 = 410$ cm^{-1}, and the interatomic distance $r_{C-F} = 1.30 \pm 0.03$ A.

It should be noted that the evaluation of the molecular constants of FCN was carried out by Thomas [3965] and Luft [2673] on the assumption that the observed relationships between the corresponding constants of cyan halide molecules remain when substituting F for I, Br and Cl. It is well known, however, that the extrapolation to fluor in the series of halogenized hydrocarbons results for the most part in erroneous values. Hence, such an evaluation must be treated cautiously, and it requires additional verification.

Based on conceptions of the length of the C-X bond on the bond type, developed by him, Tatevskiy [409, 410] obtained the value 1.30 A for the length of the $\equiv$C – F bond. This value was calculated using inaccurate values for the length of the C-F bond in various compounds. The calculation, based on new data of the interatomic distances of C-F in C_2F_6, C_2F_4 and C_6H_5F molecules, gives the value $r_{C-F} = 1.28$ A. The evaluation based on the assumption of a linear relationship between the length of the C-X bond in XCN molecules and the length of this bond in C_2X_4 molecules, where X = H, Cl, Br and I, results in the same value of the interatomic distance r_{C-F}. The value $r_{C-F} = 1.28 \pm 0.03$ A is accepted in the Handbook for the FCN molecule. The length of the $-C \equiv N$ bond changes insignificantly in the series of various cyan halides (from 1.153 for HCN to 1.163 A for ClCN A).* Therefore, the rounded off value 1.16 ± 0.01 A is accepted in the present Handbook for the interatomic distance $r_{C \equiv N}$. The value of the moment of inertia of the FCN molecule, quoted in Table 190, corresponds to the accepted structural parameters.

TABLE 190

Accepted Values of the Molecular Constants of FCN

ν_1	ν_2 (2)	ν_3	I	σ
1 . $см^{-1}$			$10^{-[illegible]}$ $г \cdot см^2$ 2	
1070	400	2260	8	1

1) cm^{-1}; 2) $g \cdot cm^2$.

It may be expected that the force constants of the C-F bond in the FCN molecule must be similar to the force constant of the corresponding bond in the C_2HF molecule: $f_{C-F} = 7.79 \cdot 10^5$ $dyne \cdot cm^{-1}$ (calculated by Eqs. (P4.34) on the grounds of the fundamental frequencies of the C_2HF molecule, found experimentally [1604]). The value $f_{C-F} = 8.3 \cdot 10^5$ $dyne \cdot cm^{-1}$, obtained by graphical extrapolation of the force constants of C-X bonds in the ClCN, BrCN and ICN molecules to the FCN molecule conforms well with this value.** The value $f_{C-F} = 8.0 \pm 0.5 \cdot 10^5$ $dyne \cdot cm^{-1}$, near to the mean value, is accepted in the present Handbook.

The values of the force constant of the C ≡ N bond in HCN, ClCN, BrCN, C_2N_2 molecules, calculated by various authors, change within the limits from 16 to $19 \cdot 10^5$ $dyne \cdot cm^{-1}$. Taking ClCN and BrCN as an example, it may be proved that the various methods of calculating force constants result in essentially different sets of force constants of these molecules. As an ocular demonstration, the values of force constants calculated by means of experimentally observed fundamental frequencies of ClCN and BrCN molecules are quoted in Table 191. In the first two columns the values are listed as calculated by Thomas [3965] according to the method developed by him, which makes it possible to evaluate the three force constants ($f_{C\equiv N}$, f_{C-X} and f_{dd}) by means of two frequency values (ν_1 and ν_3). In the third and fourth columns, the values of force constants are given as calculated by the authors of the Handbook using Eqs. (P4.26) and the frequencies of isotopic modifications of ClCN and BrCN found by Freitag and Nixon [1604]; and in the fifth and sixth columns, the values of force constants are listed as found by Johnson, Orville-Thomas and Opik [2305] using the Kivelson and Wilson method [2426, 2427] and taking into account the connection between the force constants and the constant of the centrifugal stretch of the molecules.

TABLE 191

Force Constants of ClCN and BrCN
(in 10^5 dyne·cm^{-1})

1 Постоянная	ClCN	BrCN	ClCN	BrCN	ClCN	BrCN
	2 Томас [3965]		3 вычислено по (П4. 26)		4 Джонс и др. [2305]	
$f_{C\equiv N}$	17,61	17,80	16,07	16,33	18,45 ± 0,10	17,76 ± 0,10
f_{C-X}	5,01	4,10	5,29	4,34	4,76 ± 0,02	4,00 ± 0,02
f_{dd}	0,50	0,70	−0,752	−0,629	1,33 ± 0,01	0,70 ± 0,01

1) Constant; 2) Thomas; 3) calculated by Eqs. (P4.26);
4) Jones et al.

The calculations, however, carried out with the various sets of force constants, quoted in Table 191, result in values of frequencies of ClCN and BrCN differing within 5-30 cm^{-1}. Therefore, it appears that the most correct procedure is to take the coincidence of the value of the centrifugal stretch constant, calculated by means of force constants, with the value, found experimentally from the microwave spectrum of the molecule in question, as a criterion to determine the selection of force constants most accurately describing the force field of the molecule [2305]. On these grounds, the value $f_{C\equiv N} = 18 \pm 2\cdot10^5$ dyne·cm^{-1} approximate to the values obtained by Jones et al [2305] for this constant in ClCN and BrCN molecules, is accepted in the Handbook.

The calculation of the frequencies of valence vibrations of FCN by Eqs. (P4.26) gives the values $\nu_1 = 1070$ and $\nu_3 = 2260$ cm^{-1}; their errors, caused by the errors in the values of the accepted force constants mentioned above, amount to ±40 and ±110 cm^{-1}, respectively. When using such a comparatively rough evaluation of the force constants, the constant of the bond interaction may be disregarded, because the equations (P4.26) describe satisfactorily the field of valence forces of linear three-atomic XYZ molecules (the errors of the frequencies caused by this fact are of the order of 1%).

The deformation constant of the HCN, ClCN, BrCN, and ICN molecules changes within the limits from $0.25\cdot10^{-11}$ to $0.35\cdot10^{-11}$ dyne·cm/rad. Assuming the mean value $0.30 \pm 0.05\cdot10^{-11}$ dyne·cm/rad for FCN, we obtain $\nu_2 = 400 \pm 40$ cm^{-1}.

The fundamental frequencies, calculated by this method, and also the moment of inertia of the FCN molecule, are quoted in Table 190. As a comparison shows, the divergences with the corresponding molecular constants of FCN, calculated by Thomas [3965] and Luft [2673] lie within the error limits of the evaluation of the corresponding values.*

$\underline{C_2N_2}$. Electron-diffraction measurements [3206, 2561] and also the results of investigation of the fine structure of infrared absorption bands [1220] and of the rotational Raman spectrum of dicyan [2397] lead to the unambiguous conclusion that the C_2N_2 molecule is a symmetric linear molecule and belongs to the symmetry point group $D_{\infty h}$. According to the vibration theory, such a molecule must possess three non-degenerated normal vibrations, from which two (with the frequencies ν_1 and ν_2) have the A_{1g} symmetry and one (ν_3) the A_{2u} symmetry, and two doubly degenerated vibrations, a symmetric E_{1g} (ν_4) one, and an antisymmetric one, E_{1u} (ν_5). All frequencies are present in the Raman spectrum, and the frequencies ν_3 and ν_5 of the antisymmetric vibrations also in the infrared spectrum.

A review of papers dealing with the investigation of the infrared and Raman spectrum of dicyan, carried out up to 1944, is given in Herzberg's monograph [152]. According to the interpretation of the vibrational spectrum suggested by Woo and Budger [4317], Herzberg recommends the values of fundamental frequencies, found by investigation of the infrared spectrum of gaseous C_2N_2 [608], and the Raman spectrum of liquid dicyan [3419, 3420]: $\nu_1 = 2322$, $\nu_2 = 848$, $\nu_3 = 2149$, $\nu_4(2) = 506$ and $\nu_5(2) = 226$ cm^{-1}.

Subsequent papers [2561, 1220, 2937, 2561a, 2928, 3659] corroborated the interpretation of the frequencies recommended by Herzberg.

In order to derive the function of the potential energy of the C_2N_2 molecule, Langseth and Moller [2561, 2561a] carried out a complex of investigations including electron-diffraction measurements (which proved that the C_2N_2 molecule has a linear structure) and the investigation of the Raman spectrum with simultaneous study of the degree of polarization of the strongest lines. The investigation of the Raman spectrum of gaseous C_2N_2 enabled Langseth and Moller [2561] to find the fundamental frequencies of C_2N_2: $\nu_1 = 2328.5$, $\nu_2 = 850.6$, $\nu_4 = 507.2$ and $\nu_5 = 240$ cm^{-1} which differ only insignificantly from the frequencies given in Herzberg's book [152].

Crein and Thompson [1220] investigated the infrared absorption spectrum of C_2N_2 in the 2000 to 3300 cm^{-1} (5-3 microns) region by a device with diffraction grating. In the investigated region of the C_2N_2 spectrum, three bands with λ 3.76, 3.90 and 4.63 microns were found and refer, respectively, to the vibrations $\nu_3 + \nu_4$, $\nu_1 + \nu_5$ and ν_3. Only the ν_3 band at $\lambda = 4.63$ microns was investigated in detail. The analysis of the rotational structure of this band, which possesses P- and R- branches, enabled the authors of [1220] to find the head of the ν_3 band at 2157.22 cm^{-1} and the values of the rotational constants $B_{000} = 0.1588 \pm 0.0001$ and $\alpha_3 = 5.32 \cdot 10^{-4}$ cm^{-1}. The value of D_{000} was not found in paper [1220] because the results of the analysis of the ν_3 band enabled the authors to conclude only that D_{000} must be smaller than $1 \cdot 10^{-7}$. It must be noted that, owing to the superposition of "hot" bands, the authors of [1220] failed to determine with certainty the centrum of the ν_3 band and, as it was proved later on [2937], the numbering of the rotational lines in this band, suggested in paper [1220], proved to be erroneous.

Moller and Stoicheff [2937] investigated the rotational Raman spectrum of gaseous C_2N_2, obtained in the second order of a concave 21-feet grating. The simple structure of the spectrum and the observed sequence of the intensity of the lines were an additional and indubitable argument in favor of the linear symmetric model of the C_2N_2 molecule. The analysis of the spectrum enabled the authors of [2937] to obtain the rotational constants of C_2N_2: $B_{000} = 0.15752 \pm 0.00015$ and $D_{000} = 4 \cdot 10^{-8}$ cm^{-1}. Assuming that $r_{C \equiv N}$ is equal to 1.157 A (by means of the data by Westenberg and Wilson concerning the investigation of the microwave spectrum of cyanacetylene [4221]) and based on the found value of B_{000}, the authors of paper [2937] calculated the value of $r_{C-C} = 1.380$ A, which conforms well with the results of the electron diffraction measurements ($r_{C \equiv N}$ = 1.15 ± 0.02, r_{C-C} = 1.38 ± 0.02 [2561] and $r_{C \equiv N}$ = 1.16 ± 0.02, r_{C-C} = 1.37 ± 0.02 A [3206]) within the accuracy limits of the latter method. As it is obvious from a comparion with the results of paper [1220], the value of the rotational constant B_{000}, found by Moller and Stoicheff [2937] is somewhat smaller than the value of B_{000} obtained formerly by Crein and Thompson [1220]. As was mentioned above, this discrepancy may be explained by the fact that the numbering of the rotational lines of the ν_3 band, suggested in paper [1220], was erroneous.

Schultz and Eggers [3659] obtained the infrared absorption spectrum of $C_2^{12}N_2^{14}$ and $C_2^{13}N_2^{14}$ by a split-beam spectrometer with CaF_2, KBr and NaCl prisms, and they found the value 2159 ± 2 cm^{-1} for ν_3, which, within the error limits of the measurement, almost concurs with the value of ν_3 found in the paper by Crein and Thompson [1220].

In Miyazawa's paper [2928],* dealing with the investigation of the infrared absorption spectrum of the two isotopic modifications of dicyan $C_2^{12}N_2^{14}$ and $C^{12}C^{13}N_2^{14}$, the ν_5 band with a maximum at 235 cm^{-1} was found for the $C_2^{12}N_2^{14}$ molecule in the investigated region from 400 to 180 cm^{-1} (corresponding band of the $C^{12}C^{13}N_2^{14}$ molecule has a maximum at 234 cm^{-1}).

In the present Handbook, the rotational constants of C_2N_2, found by Moller and Stoicheff [2937] by investigation of the rotational Raman spectrum of gaseous dicyan, are used for the calculation of the thermodynamic functions of C_2N_2. The following structural parameters of C_2N_2 correspond to these values of the rotational constants: $r_{C \equiv N}$ = = 1.157 and r_{C-C} = 1.38 A. The values of the ν_1, ν_2, ν_4 and ν_5 frequencies are adopted in the Handbook, corresponding to the data of Langseth's and Moller's paper [2561]. The value obtained by Crein and Thompson [1220] was adopted for the ν_3 frequency. It must be noted that the value of ν_5 may possess an error of ±5 cm^{-1} (see above). The adopted values of the molecular constants of C_2N_2 are quoted in Table 192.

TABLE 192

Adopted Values of the Molecular Constants of C_2N_2

ν_1	ν_2	ν_3	ν_4 (2)	ν_5 (2)	B_{000}	D_{000}	σ
1 см$^{-1}$							
2328,5	850,6	2157,22	507,2	240	0,15752	$4\cdot10^{-8}$	2

1) cm^{-1}.

§85. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of the substances, dealt with in the present Chapter, are quoted in the ideal gas state at temperatures from 293.15-6000°K in Tables 204-210 and 231 of the 2nd volume of the Handbook. The calculations were carried out without taking into account the difference of the molecular constants of isotopic modifications.

The data of the constants of the intermolecular potential of C_2N_2 are quoted in Supplement 5, and the values of this gas's virial coefficients and their derivatives are given in Table 240 (II).

CS. The thermodynamic functions of carbon monosulfide, calculated by Eqs. (II.161) and (II.162) for temperatures from 293.15 to 6000°K, are quoted in Table 204 (II). The calculation was carried out, based on the molecular constants of CS adopted above (see page), by means of the Gordon and Barnes method [Eqs. (II.137) and (II.138)] without limitation of the number of rotational states. The values of the constants C_Φ and C_S in Eqs. (II.161) and (II.162), of θ and x for the interpolation by means of the anharmonic oscillator tables, and also the coefficients of Eqs. (II.137) and (II.138) for the calculation of the functions of CS are quoted in Table 193.

TABLE 193

Values of the Constants for the Calculation of the Thermodynamic Functions of CS, CN and CP

1 Вещество	2 Состояние	θ	$x \cdot 10^3$	$\beta_1 \cdot 10^3$	$\beta_2 \cdot 10^4$	$\frac{q_0}{T}$	$\frac{d_0 \cdot 10^6}{T}$	A_Φ	A_S
		3 град	—	—	—	3 град⁻¹		4 кал/моль·град	
CS	$X\,^1\Sigma^+$	1848,96	5,0269	0,7245	0,525	0,85061	2,79	3,6804[a]	10,6359[a]
CN	$X\,^2\Sigma$	2975,8	6,3537	0,9176	0,87	0,36774	2,49	2,4315	7,3993
	$A\,^2\Pi$	2610,1	7,1003	1,0221	1,08	0,40706	2,93	—	—
CP	$X\,^2\Sigma$	1783,62	5,5337	0,7503	0,576	0,87354	2,91	3,9273	8,8954
	$A\,^2\Pi$	1527,98	5,6827	1,109	1,27	1,00013	—	—	—

[a] The values of C_Φ and C_S, respectively, are given.

1) Substance; 2) state; 3) degree; 4) cal/mole·degree

As was noted in §84, the CS molecule must have a series of electron states with low excitation energies in addition to the four electron state observed in its spectra and quoted in Table 186. When calculating the thermodynamic functions of CS, the components of the $a'\,^3\Sigma^+$, $A\,^1\Pi$ and $e\,^3\Sigma^-$ electron states were calculated by Eqs. (II.120) and (II.121), i.e., without taking into account the difference between the constants of the ground and the excited molecular states. The error caused by neglecting the other electron states of CS does not exceed 0.01 cal/mole·degree in the values of $\overset{*}{\Phi}_T$ at temperatures up to 6000°K.

Owing to the high dissociation energy of the CS molecule (see page 1342), the disregarding of the necessary limitation of the number of rotational ground state levels in the calculation also does not cause essential errors. The total errors of the calculated values of $\overset{*}{\Phi}_{298.15}$, $\overset{*}{\Phi}_{3000}$ and $\overset{*}{\Phi}_{6000}$ of the carbon monosulfide do not exceed 0.01, 0.03 and 0.06 cal/mole·degree.

The thermodynamic functions of CS were calculated earlier by Kelley [2364] using the rigid rotator-harmonic oscillator model approximation (Φ_T^* for $T \leq$ <000°). The differences between Kelley's data and that in the present Handbook, the latter changing from 0.02 cal/ /mole•degree at T = 298.15° to 0.09 cal/mole•degree at T = 2000°K, are caused by the approximate method of calculation used in paper [2364]. The results of the calculation carried out by Kelley are cited in Zeise's book [4384].

CN. The thermodynamic functions of cyan, quoted in Table 207 (II), were calculated by the Gordon-Barnes method, using the constants adopted in Table 186. Owing to the fact that the $A^2\Pi$ electron state of the CN molecule possesses a low excitation energy (see Table 186), the calculation of the values of Φ_T^* and S_T° was realized by means of Eqs. (II.131) and (II.132). The translational components were calculated by Eqs. (II.8) and (II.9), the components of the electron states $X^2\Sigma$ and $A^2\Pi$ by the quantities M_X, N_X, M_A, N_A using the equations (II.117) and (II.118).

When calculating the values of M_X and N_X, the multiplicity of the $X^2\Sigma$ state was taken into account by addition of the addend ln 2 to these quantities; the values of M_A and N_A were calculated by Eqs. (II.151) and (II.152). The values of A_Φ, A_S, θ and x, and also the coefficients of the Eqs. (II.137), (II.138), (II.151) and (II.152), used for the calculations of M_i and N_i, are quored in Table 193. No corrections were introduced by limiting the number of rotational levels in the $X^2\Sigma$ and $A^2\Pi$ states when calculating the M_i and N_i values, and the equations for the energy of the vibrational levels were not brought into accordance with the dissociation limits. The components of the second excited state were calculated by Eqs. (II.120) and (II.121), i.e., without taking into account the difference between the constants of CN in this and in the ground state; the components of higher electron states were not taken into account in the calculation of the thermodynamic functions of cyan.

The fundamental errors in the calculated values of the thermodynamic functions of cyan are caused by the lack of data about the energy of the high vibrational and rotational levels of the ground state of CN. However, due to the high magnitude of the dissociation energy of this molecule, the corresponding errors in the values of Φ_T^* and also the errors owing to the neglection of corrections for the limited number of rotational energy levels do not exceed 0.03 cal/mole·degree at $T \leq 3000°K$, and 0.1 cal/mole<degree at $T = 6000°K$.

The thermodynamic functions of cyan have been calculated by Kelley [2363] (S_T° at $T \leq 2000°K$) and Johnston, Belzer and Savedoff [2270] ($T < 6000°K$). Kelley's data are cited in Zeise's book [4383]. The differences between the data of [2363] and of the present Handbook do not exceed 0.1 cal/mole<degree; it may be assumed that they are caused mainly by the use of the results of calculations carried out for the present Handbook with those of Johnston and coworkers was impossible because the papers of these authors were not available to the libraries of the USSR.

Referring to literature data unknown to the authors of the Handbook, Margrave cites in the book [2775] values of thermodynamic functions of CN at temperatures from 2000-5000°K. These thermodynamic functions differ from those quoted in Table 207 (II) by 0.2-0.3 cal/ /mole·degree.

The tables of the thermodynamic functions of cyan adduced in the first and in the present edition of the Handbook are identical.

<u>CP</u>. The thermodynamic functions of the gaseous phosphorous carbide, quoted in Table 210 (II), are calculated by the Gordon and Barnes me-

thod. Owing to the fact that the CP molecule possesses excited electron states with low energies, the calculations were carried out by Eqs. (II.131) and (II.132). The translational components were calculated by Eqs. (II.8) and (II.9), using the values of A_{Φ} and A_S which are quoted in Table 193. The components of the $X^2\Sigma$ and $A^2\Pi$ states were found by the quantities M_X, N_X and M_A, N_A, calculated by Eqs. (II.117) and (II.118). When calculating these values, the multiplicity of the $X^2\Sigma$ and $A^2\Pi$ states has been taken into account by the addends ln 3 and ln 4. The components of the second excited state $B^2\Sigma$ were calculated by Eqs. (II.120) and (II.121). The values of θ and x, and also of the coefficients of the equations, used for the calculation of M_X, N_X, M_A, N_A, are given in Table 193.

The errors in the values of thermodynamic functions of CP which are quoted in Table 210 (II), are caused mainly by the inaccuracy of the molecular and physical constants adopted for the calculation. The errors of the values of Φ_T^* at 298.15; 3000 and 6000°K are estimated as 0.02; 0.05 and 0.1 cal/mole·degree, respectively.

The thermodynamic functions of gaseous phosphorous carbide have been calculated by Potter and Distefano [3314a] for T = 298.15-6000°K on the basis of the same constant values which are adopted in the present Handbook. Owing to this fact, the values of the thermodynamic functions of CP, quoted in paper [3314a] and in Table 210 (2), are almost identical.

$\underline{CS_2}$. The thermodynamic functions of carbon bisulfide, calculated by Eqs. (II.241) and (II.242) for temperatures from 293.15 to 6000°K, are quoted in Table 205 (II). The vibrational-rotational components were calculated by the Gordon method [Eqs. (II.195) and (II.196)] using the constants adopted in Table 197. Owing to the fact that the anharmonicity constant, according to the data of [3877], has the value

$x_{22} > 0$ (see Table 187), it was impossible to take into account in the applied method the anharmonicity of the double degenerated vibration of this molecule and also of all terms in Eqs. (II.195) and (II.196), related to those vibration (for example, $x_{12} \cdot \bar{v}_1 \bar{v}_2$, etc.). Hence, the corresponding terms in Eqs. (II.195) and (II.196) were taken as equal to zero; the errors caused by this simplification are relatively small owing to the small value of $x_2 = -\frac{x_{22}}{\omega_2} \approx -0{,}003$.

The values of C_Φ and C_S for the calculation of the components of the rigid rotation and the translational movement, and also the values of θ_n and x_n are quoted in Table 194. As was mentioned above (see page 1311), a resonance perturbation of the vibrational states $2\nu_2$ and ν_1 takes place in the CS_2 molecule, but the effect of this interaction on the thermodynamic properties of carbon disulfide is essentially smaller than in the case of carbon dioxide; the corresponding error of Φ^*_{6000} does not exceed 0.04 cal/mole•degree. Hence, corrections for the resonance interaction of the vibrational levels have not been taken into account when calculating the thermodynamic functions of CS_2. Owing to the lack of reliable data concerning the type of excited electron states of the CS_2 molecule and their excitation energies, these were also not taken into account. The errors caused by the neglection of these states do not exceed 0.05-0.1 cal/mole•degree in the value of Φ^*_{6000}. The total errors in the calculated values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} are of the order of 0.03; 0.1 and 0.5 cal/ /mole•degree.

Earlier, the thermodynamic functions of CS_2 were calculated by Cross [1227] ($T \leqslant 1800°$ K), Kelly [2364] ($T \leqslant 1800°$ K), Papousek [3183] ($T \leqslant 1000°$ K). Obviously, all these calculations were carried out in the rigid-rotator harmonic oscillator model approximation. Owing to the fact, however, that they were carried out only at relatively low temperatures, the differences between these results and those of the present Handbook do not exceed 0.05 cal/mole·degree for the values of Φ^*_T and S°_T. The data by Cross are cited by Ribaud [3426], Zeise [4384] and other reference books.

Data for CS_2 are absent in the first edition of the Handbook.

TABLE 194

Values of the Constants for the Calculation of the Thermodynamic Functions of CS_2 and OCS

1/ Вещество	θ_1	θ_2	θ_3	C_Φ	C_S
	2/ град			3 кал/моль·град	
CS_2^a	963,62	569,72(2)	2219,7	7,9338	14,8893
COS	1236	754(2)	2970	7,3721	14,3276

$^a x_1 = 0.001574$, $x_2 = 0$, $x_3 = 0.003328$.

1) Substance; 2) degree; 3) cal/mole·degree.

COS. The thermodynamic functions of carbon sulfoxide, quoted in Table 206 (II), were calculated by Eqs. (II.241) and (II.242) in the rigid rotator-harmonic oscillator model approximation for temperatures from 293.15-6000°K. The values of the constants C_Φ and C_S in Eqs. (II.241) and (II.242) and also the values of θ_n used for the calculation of the vibrational constants, are quoted in Table 194.

The errors in the calculated values of thermodynamic functions of COS are caused mainly by the fact that the anharmonicities of the molecular vibrations of this gas were not taken into account in the calculation. The total errors in the values of Φ^*_T are 0.1; 1 and 2 cal//mole·degree at 298.15; 3000 and 6000°K, respectively. A number of authors (see [4384]) calculated earlier the thermodynamic functions of COS. Among these calculations, the paper by Cross [1227] deserves special attention for in it the thermodynamic functions of COS are calculated for T ≤ 1800°K. The results of the calculation by Cross are cited in a number of reference books, including that of Zeise [4384], Ribaud [3426] and the book [2775]. They conform within 0.01-0.03 cal/mole·degree to the values quoted in Table 206 (II).

The thermodynamic functions of COS, calculated in Papousek's paper [3183] up to 1000°K, conform to the values for the same range, quoted in the present Handbook.

Kemp and Giauque [2366a] found $S^\circ_{298.15} = 55.27 \pm 0.1$ cal/mole·degree based on the measurement of the specific heat of solid and liquid carbon sulfoxide at temperatures higher than 15°K and also of the melting and evaporation heats. This value is recommended by Kelley [2364]. It conforms to the value quoted in Table 206 (II) (55.324 cal/mole·degree) within the limits of accuracy in the measurement.

$\underline{C_2N_2}$. The thermodynamic functions of dicyan, quoted in Table 231 (II), are calculated by Eqs. (II.241) and (II.242) in the rigid rotator-harmonic oscillator model approximation for temperatures from 293.15-6000°K, using the constants given in Table 192. The values of the constants C_Φ and C_S in Eqs. (II.240) and (II.242) and also the values of θ_n for the calculation of the vibrational components are given in Table 195.

The main errors in the calculated values of the thermodynamic functions of dicyan, especially at temperatures higher than 1000°K, are caused by the fact that it is impossible to take into account the anharmonicity of the vibrations and other deviations of the C_2N_2 from the rigid rotator-harmonic oscillator model (up to 1.5-2.0 cal/mole·degree in Φ^*_T). The errors due to the insufficient accuracy of the adopted values of the fundamental frequencies of the C_2N_2 molecule, especially of the ν_5 frequency (see page 1330), are essentially smaller (of the order of 0.02 and 0.06 cal/mole·degree in $\Phi^*_{298.15}$ and Φ^*_{3000}).

The total errors in the calculated values of $\Phi^{\circ}_{298.15}$, Φ°_{3000} and Φ^{*}_{6000} amount to 0.2; 2 and 3 cal/mole·degree.

TABLE 195

Values of the Constants for the Calculation of the Thermodynamic Functions of C_2N_2, HCN and FCN

1 Вещество	θ_1	θ_2	θ_3	θ_4	θ_5	C_Φ	C_S
	2 град					3 кал/моль·град	
C_2N_2	3350,2	1223,8	3103	729,75(2)	345,31(2)	6,0694	13,0249
HCN	3028,2	1022,6(2)	4839,7	—	—	1,0457	8,0007
FCN	1540	575,5(2)	3252	—	—	5,4289	12,3844

1) Substance; 2) degree; 3) cal/mole·degree.

The thermodynamic functions of dicyan have been obviously calculated in a number of papers. Tables of the thermodynamic functions of dicyan for various temperature intervals have been calculated by Stevenson [3852] ($T \leqslant 1000^\circ$ K), Thompson [3971] ($T \leqslant 1000^\circ$ K), Miyazawa [2928] ($T \leqslant 1500^\circ$ K), and McLain and Scheller [2721] ($T \leqslant 4500^\circ$ K); Thompson's data is cited in the books by Ribaud [3426] and Zeise [4384]. The results of the calculation carried out by Miyazawa [2928] conform best to the values quoted in Table 235 (II). The systematic differences from Miyazawa's data, amounting to 0.05-0.08 cal/mole·degree, are entirely explainable by the difference in the values of ν_5, adopted in the calculations.

The differences between the data in the Handbook and the results of McLain's and Scheller's calculations [2721] amount to 0.15-0.18 cal/ /mole·degree in the whole temperature range and are 3-4 times higher than differences which could be caused by any discrepancies in the values of molecular constants of C_2N_2 used in the calculation.

Ruehrwein and Giauque [3548a] found $S^{\circ}_{298} = 57.64 \pm 0.1$ cal/mole·degree, based on their investigation of the specific heat of solid and liquid C_2N_2 in the temperature range from 15-251.95°K and also of the melting and evaporation heats of dicyan. This value is also recommended by Kelley [2364]; it is almost independent of the values of the vibrational constants of C_2N_2 and conforms well to the value quoted in Table 231 (II) (57.712 cal/mole•degree).

HCN. The thermodynamic functions of hydrocyanic acid, quoted in Table 208 (II), are calculated based on the constants found in the paper by Douglas and Sharma [1383] and cited in Table 189. The calculation of the vibrational-rotational components was carried out by Kassel's method [see Eqs. (II.210) and (II.211)]; the corrections of the Φ_T^* values with regard to the anharmonic vibrations of the HCN molecule, the interaction between the rotations and vibrations, and the centrifugal stretch by rotation were calculated by these equations for the temperatures 298.15; 500, 700, 1000, 1500, 2000, 2500, 3000, 4000, 5000 and 6000°K. At $T < 4000°K$, the terms with $\Sigma \Pi_{ijk} Y_{ijk}$ in the sums $i+j+k \leqslant 2$; the terms with $i+j+k \leqslant 4$. were calculated for 4000, 5000 and 6000°K. The values of $R \ln \alpha$ in Eqs. (II.210) and (II.211) for the other temperatures were obtained by interpolation. The corresponding correction in the values of S_T° was calculated by numerical differentiation of the $R \ln \alpha$ values.

The values of the constants C_Φ and C_S in Eqs. (II.241) and (II.242) and also of the quantities θ_n for the calculation of the harmonic oscillator components in the values of Φ_T^* and S_T° are quoted in Table 195.

The excited electron states of the HCN molecule possess an energy higher than 50,000 cm^{-1}; they were not taken into account when calculating the thermodynamic functions. The fundamental errors in the obtained values of the thermodynamic functions of hydrocyanic acid are caused by the use of insufficiently accurate data for the vibrational constants of the HCN molecule and by the fact that the calculation was carried out by Kassel's method in which, besides a number of other simplifications, the upper limits in the partition functions of $\underline{v}_{\circ}$ and J are assumed as being infinite. It should be noted that the differences in the Φ^*_T values calculated by the vibrational constants found in papers [1383, 516] (see page 1319) do not exceed 0.01 cal/mole•degree. The total errors in the $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} values amount to about 0.03, 0.1 and 0.4 cal/mole•degree.

The thermodynamic functions of hydrocyanic acid have been previously calculated by Gordon [1807] (Φ^*_T for $T \leqslant 2000°$ K, calculated by Gordon's method, Eqs. (II.195)), Stamm, Halverson and Whalen [3834] ($T \leqslant 1000°$ K), and Bradly, Haar and Friedman [889] ($T \leqslant 5000°$ K). In the latter paper, the calculation was carried out by the complicated Mayer and Goeppert-Mayer method. The thermodynamic functions of HCN, calculated in papers [1807, 3834] conform to those in the present Handbook within the limits caused by the difference of the values of the HCN molecular constants and the physcial constants adopted in the calculations. At the same time, the differences between the data quoted in the present Handbook and in paper [889] essentially exceed the values which would be expected due to a difference of the vibrational constants of HCN used in the calculation.* Due to the fact that the methods used in both calculations are similar, it is impossible to explain the observed differences in the values of Φ^*_T and S°_T amounting to the order of 0.3-0.5 cal/mole•degree. Let us note that similar differences exist also between the results of other calculations carried out by Friedman and Haar and the data of the present Handbook (for example, for OH and H_2O, see pages 414 and 427). The calculations carried out in the Handbook by immediate summation over the energy levels, prove that there are obviously some systematical errors in these papers.

The thermodynamic functions of HCN calculated in Gordon's paper

[1807] are cited in the books by Zeise [4384] and Ribaud [3426], and the data by Bradly, Haar and Friedman - in the book [2775].

The tables of the thermodynamic properties of hydrocyanic acid, given in the first and present editions of the Handbook, are identical.

Giauque and Ruehrwein [1718a] found $S^{\circ}_{298.16} = 47.92 \pm 0.2$ cal/mole·degree based on the results of the measurement of the specific heat and of the heats of phase transitions of hydrocyanic acid within the temperature range of 15 to 298.80°K. The same value is quoted in Kelley's Handbook [2364]. The difference between this value and that calculated in the Handbook (48.211 cal/mole·degree) exceeds somewhat the uncertainty pointed out in Giauque's and Ruehrwein's paper [1718a].

FCN. The thermodynamic functions of cyan fluoride, quoted in Table 209 (II), were calculated by Eqs. (II.241) and (II.242) based on the values of the molecular constants of FCN adopted in Table 190. The calculation was carried out by the rigid rotator-harmonic oscillator model approximation.

The values of the constants C_{Φ} and C_S in Eqs. (II.241) and (II.242) and also the values of θ_n for the interpolation in the harmonic oscillator tables are quoted in Table 195.

The errors in the values of the thermodynamic functions of FCN, quoted in Table 209 (II), are caused mainly by the fact that the anharmonicity of the vibrations and the vibrational-rotational interaction were not taken into account in the calculation, and also because estimated values of molecular constant were used. The errors in the values of molecular constant were used. The errors in the values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000}, occasioned by the mentioned causes, are estimated as equal to 0.1; 1.5 and 3 cal/mole·degree.*

The thermodynamic functions of FCN have been calculated earlier by Luft [2673] for temperatures up to 1000°K, using molecular constants based on estimations by Thomas and Luft (see §86). When calculating the thermodynamic functions of FCN for the first edition of the Handbook, the same molecular constants were used, on which Luft's calculations [2673] were based, with the exception of r_{C-F}, which was assumed as being equal to 1.27 A, whereas the value of 1.30 A was used in paper [2673]. The differences between the values of Φ^*_T and S°_T in the first and present editions of the Handbook do not exceed 0.1 cal/mole••degree, and are explainable by some difference in the adopted molecular constants, mainly in the value of the frequency ν_2 of the deformation vibration.

§86. THERMOCHEMICAL QUANTITIES

CS (gas). Owing to an unreliable extrapolation of the vibrational levels of the ground state of the CS molecule, Lagerqvist, Westerlund, Wright and Barrow [2537] found $C_0(CS)$ = 181 kcal/mole ($\Delta H^\circ f_0$= 53,3 kcal/mole).

Lewis and Lacey [2603] investigated the equilibrium between carbon monoxide and elementary sulfur (see the parts for COS and CS_2) and, based on the results of the analysis of the reaction products and on some assumptions with regard to the character of the reactions taking place, they found the value of the constants of the following equilibrium:

$$CS_2(\text{gas}) = CS(\text{gas}) + S(\text{liq.}). \qquad (XXI.1)$$

On the basis of this data, the authors of the Handbook found $\Delta H^\circ f_0$ (CS) = 31 kcal/mole.*

The dissociation of CS_2 on a tungsten film was studied by Blanchart and Le-Goff [839] in a continuous flow system. The dissociation products were determined by a mass spectrometer. It was found that at 1850°K the potential of the formation of CS^+ and CS_2 is equal to 17.7 ± 0.1 ev, and that the ionization potential of CS is equal to

11.8 ± 0.2 ev. Hence it follows $D_{1850}(CS) = 90 \pm 10$ kcal/mole, and $\Delta H^\circ f_0\,(CS) = 51{,}5 \pm 10$ kcal/mole. The potential of the occurence of CS^+ ions by dissociating ionization of CS_2 and the ionization potential of CS were also measured by Smyth and Blewett [3807]. The values obtained in this work are lower by about 1 ev than those obtained in the work by Blanchard and Le-Goff. However, the difference and, therefore, the energy of the S — CS bond, proved to be sufficiently similar.

Schafer and Wiedemeier [3602] investigated the equilibrium of the reaction of carbon bisulfide with an incandescent carbon filament. Varying the carbon bisulfide pressure and the temperature, the authors achieved such reaction conditions that the thickness of the filament neither increased nor decreased, a fact which corresponds to the reaction

$$2CS_2\,(\text{gas}) = S_2\,(\text{gas}) + 2CS\,(\text{gas}. \qquad (XXI.2)$$

The partial pressure of S_2 may be calculated in such a system by the equilibrium

$$CS_2\,(\text{gas}) = C\,(\text{тв.}) + S_2\,(\text{gas}). \qquad (XXI.3)$$

The calculation of the heat of formation of CS by the experimental data by Schafer and Wiedemeier and the values of the thermodynamic properties of the components of this reaction, adopted in the Handbook, results in $\Delta H^\circ f_0$ (CS, gas) = 57.7 kcal/mole. A similar value was calculated by Schafer and Wiedemeier [3602].

Besides the equilibrium between carbon bisulfide and carbon filament, Schafer and Wiedemeier [3602] also investigated the equilibriums of the reactions of manganese, magnesium and copper sulfides with carbon

$$MS\,(\text{тв.}) + C\,(\text{тв.}) = M\,(\text{gas}) + CS\,(\text{gas}) \qquad (XXI.4)$$

and found $\Delta H^\circ f_{298.15}$ (CS, gas) = 60 ± 6 kcal/mole ($\Delta H^\circ f_0 = 59{,}2$ kcal//mole), which conforms well to the value cited above.

In the Handbook, a value of the heat of formation of CS is adopted, equal to the mean between the value calculated by the results of the investigation of the reaction of carbon bisulfide with carbon filament and of the reactions of metal sulfides with carbon [3602]

$$\Delta H^{\circ}f_0(\text{CS, газ}) = 58{,}5 \pm 5 \text{ Kcal/mole.}$$

The equation

$$D_0(\text{CS}) = 175{,}772 \pm 5 \text{ kcal/mole,}$$

corresponds to the adopted value and conforms well to the value obtained by linear extrapolation.

CS_2 (gas). Thomsen [3982, 3981] measured the combustion heat of gaseous carbon bisulfide and found the value -265.1 kcal/mole (the heat of formation of carbon bisulfide is 28.8 kcal/mole [813]). In Berthelot's paper [785], the combustion heat of liquid carbon bisulfide was determined, resulting in a heat of formation of CS_2 (gas) equal to 17.2 kcal/mole [813]. Later on, Berthelot [789] carried out a new determination of the combustion heat of carbon bisulfide. Calculations based on this work resulted in the considerably higher value: 24.6 kcal/mole [813].

Guerin, M. Bastick, J. Bastick and Adam-Gironne [1876] determined anew the combustion heat of gaseous carbon bisulfide. It was found by chemical analysis that SO_2 and SO_3 are formed during the combustion in proportions which vary in each experiment. Introducing amendments to the formation of SO_3, the authors of paper [1876] found from three experiments the value $\Delta H_{298{,}16} = -265.8$ kcal/mole for the reaction

$$CS_2(\text{gas}) + 3O_2(\text{gas}) = CO_2(\text{газ}) + 2SO_2(\text{gas}) \qquad \text{(XXI.5)}$$

and estimated its error as equal to ±2 kcal/mole. The value $\Delta H^{\circ}f_{298{,}16}$ (CS_2, gas) = 29.9 ± 2 kcal/mole, or 29.7 kcal/mole at 0°K, corresponds to this value.

The heat of formation of carbon bisulfide may be calculated on the basis of an equilibrium investigation. Evaluating together the results obtained by Terres and Wesemann [2958] and Stock, Siecke and Pohland [3868] (see below, the part dealing with COS), the authors of the Handbook obtained $\Delta H^\circ f_0 = 27{,}6$ kcal/mole.

Wieland [4258] investigated the dissociation of carbon bisulfide at temperatures from 688-1015°K according to the Eq. (XXI.3). The concentration of S_2 molecules in equilibrium with CS_2 and solid carbon was determined by comparison of the absorption spectra of S_2 in equilibrium mixture to the absorption spectra of the vapor of elemental sulfur. The calculation of ten experiments gave for the reaction heat the mean value of -6.1 ± 0.4 kcal/mole. The recalculation of two experiments, the initial data of which is cited in paper [4258], and the use of the thermodynamic functions adopted in the Handbook resulted in a coincident value. The dissociation heat, found in paper [4258], corresponds to the heat of formation of CS_2 (gas) equal to $\Delta H^\circ f_0 = 24{,}8 \pm 0{,}45$ kcal/mole.

Lewis and Lacey [2603] investigated the equilibrium between carbon monoxide and elemental sulfur. Aside from the fundamental reaction (XXI.11), these authors, by using the results of the analysis of the reaction products as a basis, also found the value of the equilibrium constant of the reaction

$$2COS\,(gas) \rightleftarrows CO_2\,(gas) + CS_2\,(gas). \qquad (XXI.6)$$

The calculation adopted in the Handbook, using the data of paper [2603] and the values of thermodynamic functions of the components of this reaction, gives $\Delta H^\circ f_0$ (CS_2, gas) = 28.3 kcal/mole. Thus, the results of the measurements of the formation heat of carbon bisulfide show a poor mutual accordance. A thorough analysis of this data is hindered by the fact that the fundamental papers [1876, 4258] are very briefly stated.

The following mean value is adopted in the Handbook:

$$\Delta H^\circ f_0(CS_2, \text{gas}) = 27 \pm 3 \text{ kcal/mole},$$

which corresponds to

$$D_0(CS_2) = 271{,}959 \pm 3{,}1 \text{ kcal/mole}.$$

COS (gas). Lochte-Holtgreven and Bown [2634] found in the absorption spectrum of COS the limit λ 2550 Å, of the region of continuous absorption and explained it on the grounds of thermochemical calculations by the dissociation

$$COS \rightarrow CO + S(^1D). \qquad (XXI.7)$$

The modern, more accurate thermochemical and spectroscopical data, however, does not permit this limit to be referred with sufficient accuracy for the dissociation process of COS.

The combustion heat of gaseous COS was measured by Thomsen [3981]. The heat of formation of carbon sulfoxide equal to -34.3 kcal//mole [813] corresponds to the value found by him. The accuracy of this value is reduced by the necessity of introducing a correction for the formation of sulfur trioxide in the combustion products.

The results of equilibrium investigations with partition of COS may serve as a more reliable source of information on the heat of formation of the latter. The most thorough investigation of equilibria of such type was carried out by Terres and Wesemann [3958]. These authors found the equilibrium constants of the reaction

$$H_2S(\text{gas}) + CO_2(\text{gas}) = COS(\text{gas}) + H_2O(\text{gas}). \qquad (XXI.8)$$

investigating both the direct and the inverse reaction. The calculation of the heat of the reaction, investigated by Terres and Wesemann [3958], and the use of the values of thermodynamic functions adopted in the Handbook gave $\Delta H_0 = 7{,}0 \pm 0{,}1$ kcal/mole (direct reaction, 623--873°) and $\Delta H_0 = 6{,}9 \pm 0{,}1$ kcal/mole (inverse reaction, 723-873°K). These values correspond to the heat of formation of COS being equal to

$\Delta H^\circ f_0 = -34$ kcal/mole.

In paper [3958], also the equilibrium

$$COS(\text{gas}) + H_2S(\text{gas}) = H_2O(\text{gas}) + CS_2(\text{gas}). \qquad (XXI.9)$$

was investigated. The reaction heat $\Delta H_0 = 8.5$ kcal/mole was calculated by this data. However, owing to a number of experimental hindrances noted by the authors of paper [3958], the quoted equilibrium constants are insufficiently accurate (see page). The same remark also concerns the work by Stock, Siecke and Pohland [3868], in which the equilibrium

$$2COS(\text{gas}) = CS_2(\text{gas}) + CO_2(\text{gas}). \qquad (XXI.10)$$

was investigated.

Using the data obtained in [3868], $\Delta H_0 = 1.15 \pm 0.3$ kcal/mole was calculated. The evaluation of the results of investigations of the equilibria (XXI.9) [3958] and (XXI.10) [3868], mentioned above, makes it possible to exclude the heat of formation of carbon disulfide from the corresponding thermochemical equations and to find $\Delta H^\circ f_0$ (COS, gas) = -34 kcal/mole.

Lewis and Lacey [2603] investigated the reaction

$$CO(\text{gas}) + S(\text{liq.}) = COS(\text{gas}) \qquad (XXI.11)$$

and found the values of its equilibrium constant at 575 and 533°K. Based on these values and on the thermodynamic functions quoted in the Handbook, the heat effect of the reaction (XXI.11) was calculated as equal to $\Delta H_0 = -5.6$ kcal/mole. $\Delta H^\circ f_0(COS)$ = -32.8 kcal/mole corresponds to this value. It should be noted that the latter is less accurate than that calculated on the basis of the data of Terres and Wesemann [3958].

In the Handbook, the value of the heat of formation of carbon oxysulfide is adopted as

$$\Delta H^\circ f_0(COS, \text{газ}) = -34 \pm 1 \text{ kcal/mole},$$

which is based on the measurement results by Terres and Wesemann [3958].

$$D_0(\mathrm{COS}) = 327{,}259 \pm 1{,}2 \text{ kcal/mole.}$$

corresponds to the adopted value.

CN (gas). In spite of the fact that developed system of bands reaching from the near infrared to the vacuum ultraviolet region of the spectrum have been observed in the spectrum of the CN molecule, the results of the numerous investigations of the CN spectrum make it impossible to recommend a sufficiently reliable value of D_0(CN).

The extrapolation of the vibrational levels of $X^2\Sigma$ states by the equation found by Douglas and Routly [1382] [for $v'' < 18$ (see page)] leads to a dissociation limit lying by 77,720 cm^{-1} (9.64 ev) higher than the level of v = 0. The extrapolation of the $A^2\Pi$ vibrational states gives a dissociation limit the energy of which is equal to 70,470 cm^{-1} (8.74 ev) with respect to the level v = 0 of the $X^2\Sigma$ state. A lower accurate linear extrapolation for the $X^2\Sigma$ and $A^2\Pi$ states gives values of D_0(CN) which are equal to 80,542 cm^{-1} (9.99 ev) and 73,460 cm^{-1} (9.11 ev).*

Investigating the cyan spectrum in the vacuum ultraviolet region, Carroll [1063] found that the levels of the $J^2\Delta$ state converge very quickly and that, therefore, the extrapolation of the vibrational levels to the dissociation limit may be more reliably carried out for this state than for the $X^2\Sigma$ and $A^2\Pi$ states. The linear extrapolation of the vibrational levels of the $J^2\Delta$ state leads to a dissociation limit lying by 87,500 cm^{-1} higher than the v = 0 level of the $X^2\Sigma$ state. If we assume that the CN molecule in the $J^2\Delta$ state dissociates into $C(^3P) + N(^2D)$,**this dissociation limit corresponds to the value D_0(CN) = 195.3 kcal/mole (8.48 ev) which is recommended by Carroll [1063].

The investigations of the dissociation energy of dicyan [2099, 2414, 4242, 3455] lead to inaccurate and contradictory values of $D(NC-CN)$; this data is discussed in Gaydon's [1668] and Long's [2642] papers.

Glockler [1760] estimated the energies of NaCN and KCN lattices and, assuming the electron affinity of CN as being equal to that of the Br atom, he calculated $D(NC-CN)=120+8$ kcal/mole: a heat of formation $\Delta H^\circ f_0(CN)=97$ kcal/mole corresponds to this value.

Based on the longwave limits of the continuous absorption in the spectra of CH_3CN and ICN and on the extrapolation of the vibrational levels of the HCN molecule, Long [2642] calculated the value of the heat of formation: $\Delta H^\circ f_0(CN)=92{,}5$ kcal/mole. A recalculation of Long's data, taking into account more accurate values of some thermodynamic magnitudes gives $\Delta H^\circ f_0(CN)$ = 93.0 kcal/mole. Cottrell [255] points out that the value of the heat of formation obtained in this way may be considered only as the upper limit of the possible values.

The equilibrium of the formation of cyan from elements

$$C(\text{graphite})+\frac{1}{2}N_2(\text{gas})=CN(\text{gas}) \qquad (XXI.12)$$

was investigated by Brewer, Templeton and Jenkins using the intensity of the emission spectrum of CN. By the slope of the straight line expressing lg K_p as a function of 1/T, Brewer et al calculated the reaction heat at 2750°K as equal to 83.5 kcal/mole (a correction taking into account the electron excitation and the vibrational and rotational energy of the CN molecule was introduced into the value measured immediately). Using the thermodynamic functions calculated in the present Handbook, a heat of formation $\Delta H^\circ f_0(CN)=85$ kcal/mole* conforms to this value.

The heat of formation of CN may also be calculated by determining the potentials of occurrence of ions from cyan compound molecules under the action of electronic impacts. Based on the potential of occurrence of CN^+ from HCN and C_2N_2, Stevenson [3853] calculated the value $\Delta H^\circ f_0$ (CN, gas) = 89.2 kcal/mole. He assumed that CN in the excited $A^2\Pi$ state is formed by dissociation McDowell and Warren [2703] determined the potential of occurrence of CN^+ from CH_3CN and calculated on this basis $D_{298.15}(NC—CH_3) = 104,2$ kcal/mole, which conforms to $\Delta H^\circ f_0$ (CN, gas) = 90.2 kcal/mole. It was proved in the same paper that the fragments of CN and CN^+ formed by dissociation of C_2N_2 under the effect of electronic impacts possess an excess kinetic energy, a fact which was not taken into account in paper [3853].

Herron and Dibeler [2011a] measured the potential of occurrence of Cl^+, Br^+ and I^+ from ClCN, BrCN and ICN. Assuming that CN is formed in the $A^2\Pi_i$, state, they calculated $\Delta H^\circ f_{298.15}$ (CN, gas) $\leq$ 89 kcal/ /mole. The kinetic energy of the fission fragments was not measured in this paper and, therefore, the final result is given as a limit of possible values. The recalculation of the measurements of [2011a] using the values of ionization potentials of halogen atoms, cited in paper [2941] and taking into account the potential of occurrence of Cl^+ from ClCN, determined by Stevenson [3853] gave the value $\Delta H^\circ f_0$ (CN, gas) $\leq$ 88.3 kcal/mole.*

Thus, the results of measurement of the formation heat of CN in papers [933, 3853, 2011a] conform well together. In the Handbook, the mean value

$$\Delta H^\circ f_0 (CN, gas) = 88 \pm 5 \text{ kcal/mole},$$

is adopted, to which corresponds

$$D_0 (CN) = 194,121 \pm 5 \text{ kcal/mole}.$$

This value of the dissociation energy conforms well to the value $D_0(CN) = 195,3$ kcal/mole, cited above and calculated by extrapolation of the vibrational levels of the $J^2\Delta$ state of the CN molecule.**

<u>C_2N_2(gas)</u>. Bichowsky and Rossini [813] discussed the results of a

number of previous works dealing with the determination of the combustion heat of dicyan and assumed for this quantity the value of -260 kcal/mole. Wartenberg and Schutze [4172], and Knowlton and Prosen [2448] measured the heat of combustion of dicyan in oxygen. The combustion was carried out in a burner under constant pressure. Similar values of the combustion heat, -261.3 kcal/mole [4172], and -261.94 ± ±0.43 kcal/mole [2448] were obtained.

In the Handbook the heat of formation of dicyan

$$\Delta H^\circ f_{298.15}(C_2N_2,\ gas) = 73,83 \pm 0,5 \text{ kcal/mole},$$

is adopted, calculation by means of the data by Knowlton and Prosen [2448]. The value

$$D_0(C_2N_2) = 490,890 \pm 1 \text{ kcal/mole}.$$

corresponds to this adopted value.

HCN (gas). The combustion heat of HCN (gas) was measured by Berthelot [787] and Thomsen [3981]. They obtained the values -159.3 and -158.5 kcal/mole, respectively. Based on the amendment for the formation of nitric oxide found by Wartenberg and Schutze [4172] and obtained on the occasion of measurement of the combustion heat of dicyan, Gordon [1807] improved the measurement results of Thomsen and obtained the value -159.4 kcal/mole for the combustion heat of HCN, which almost conforms to the value found by Berthelot. The heat of formation $\Delta H^\circ f_{298.15}$ (HCN, gas) = 31.2 kcal/mole corresponds to this value.

Long [2642] reduced the value of the combustion heat of HCN, obtained by Thomsen [3981], by 0.4%, as it was recommended by Kharasch [2392]. The heat of formation $\Delta H^\circ f_{298.15} = 29,8$ kcal/mole corresponds to the value of the combustion heat (-158.0 kcal/mole) assumed by Long.

The amendments of Thomsen's measurement results [3981] by Gordon [1807] and Long [2642] are very approximate. In the Handbook, a value of the formation heat of HCN is adopted equal to the mean between the values calculated by Gordon [1807] and Long [2642]:

$$\Delta H^{\circ}f_{298.15}(\text{HCN, gas}) = 30{,}5 \pm 1{,}0 \text{ kcal/mole.}$$

The expression

$$D_0(\text{HCN}) = 303{,}183 \pm 1{,}1 \text{ kcal/mole.}$$

conforms to this value.

FCN (gas). An estimation of the heat of formation of cyan fluoride by the half-sum method [470], using the values of the formation heats of ClCN and BrCN [2648], gives the value -16 kcal/mole. The value -18 kcal/mole was found when using the method by Kharsch [2392, 468].

The change of the dissociation energy of the carbon-halogen bonds in cyan halides depending on the ionization potentials of the halogen atoms leads to $D_{298}(\text{F}-\text{CN})$ = 125 kcal/mole, and, accordingly, to $\Delta H^{\circ}f_{298.15}$ (FCN, gas) = -17 kcal/mole.*

The value

$$\Delta H^{\circ}f_{298.15}(\text{FCN, gas}) = -17 \pm 20 \text{ kcal/mole,}$$

is adopted for the formation heat of FCN, and, accordingly,

$$D_0(\text{FCN}) = 317{,}776 \pm 20 \text{ kcal/mole.}$$

CP (gas). The dissociation energy of CP was determined by Barwald, G Herzberg and L. Herzberg [673] by linear extrapolation of the vibrational levels of the $X^2\Sigma$ electron ground state. The dissociation energy was found to be equal to 6.9 ev (in the order of 160 kcal/mole). Similar values gives the linear extrapolation of the levels of the excited $A^2\Pi$ and $B^2\Sigma$ states. Gaydon [1668] considers this value as being somewhat overevaluated and recommends the value 6 ± 1 ev. Experimental data on the formation heat or dissociation energy of CP are missing in literature. Owing to the fact that the linear extrapolation of the ground electron state levels results in overevaluated values in the case of the CN molecule, the value recommended by Gaydon

$$D_0(\mathrm{CP}) = 138 \pm 23 \text{ kcal/mole.}$$

is adopted in the Handbook. The expression

$$\Delta H^\circ f_0(\mathrm{CP,\ gas}) = 106{,}956 \pm 23 \text{ kcal/mole .}$$

corresponds to this value.

TABLE 196

Adopted Values (in cal/mole) of the Thermochemical Quantities of Carbon Compounds with Sulfur, Nitrogen and Phosphorus in Gaseous State

Вещество 1)	D_0	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293,15}$	$\Delta H^\circ f_{298,15}$	$H^\circ_{293,15} - H^\circ_0$	$H^\circ_{298,15} - H^\circ_0$
CS	175 772	58 500	59 295	59 294	2045	2081
CS_2	271 959	27 000	27 220	27 209	2495	2549
COS	327 259	−34 000	−33 946	−33 952	2324	2373
CN	194 121	88 000	88 795	88 803	2038	2073
C_2N_2	490 890	73 352	73 815	73 830	2950	3018
HCN	303 183	30 570	30 501	30 500	2167	2210
FCN	317 776	−17 155	−17 006	−17 000	2429	2480
CP	138 000	106 956	107 542	107 541	2047	2083

1) Substance

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[Footnotes]

1303 The values of ω_e''/ω_e' are equal to 1.46 ± 0.04 for the whole group of molecules, and for CS ω_e''/ω_e' = 1.20.

1306 Barrcw, Dixon, Lagerqvist and Wright [650b] analyzed in 1961 the rotational structure of a number of bands in the absorption spectrum of CS obtained by pulse photolysis of CS_2. Besides the 0-0, 1-0 and 2-0 bands of the $A^1\Pi - X^1\Sigma$, system, three other bands of the $a^\bullet(\Pi) \leftarrow X^1\Sigma$ system and bands of the two forbidden $a'^3\Sigma^+ \leftarrow X^1\Sigma$ and $e^3\Sigma^- \leftarrow X^1\Sigma$. system were observed in the CS spectrum. The analysis carried out in paper [650b] results in molecular constants of CS in the $a'^3\Sigma^+$ and $e^3\Sigma^-$, states which are almost similar to those quoted in Table 186. In paper [650b], also the CS constants in the $a^\bullet(\Pi)$ state were determined $(T_0 < 38613{,}9,\ \omega_e > 780,\ \omega_e x_e \sim 10,\ B_e > 0{,}629$ and $\alpha \sim 11 \cdot 10^{-3}$

cm^{-1}).

1312 It should be noted that the value of the anharmonicity of x_{22} obtained by Stoicheff [3877] possesses a positive sign. This is obviously caused by the fact that only three overtones of the ν_2 vibration could be observed in the CS_2 spectrum.

1315 Wentink [4206] calculated the zero frequencies and anharmonicity constants of the COS molecule by the data of Callomon and Thompson [1046] which takes into account the resonance perturbation of the levels: $\omega_1 = 876$, $\omega_2 = 530$, $\omega_3 = 2091$, $x_{11} = -4{,}0$, $x_{22} = -0{,}4$, $x_{33} = -7$, $x_{12} = -6{,}80$, $x_{13} = -4{,}5$, $x_{23} = 11{,}5$ and $g_{\ell\ell} = 3.2$ cm^{-1}. Wentink emphasizes, however, that in contrast to the constants of CO_2 and CS_2, the values of the vibrational constants of COS, calculated by him, should be regarded as only approximate, because the presence of Fermi resonance must result in perturbation of a number of Raman bands used for the calculation of the anharmonicity constants of the COS molecule.

1316 This conclusion by Allen et al [513] was corroborated by the results of the papers by Saksena [3574a] and Saksena, Wiggins and Rank [3575], who carried out very accurate measurements and found the values of ν_0, B' – B" and D' – D" for five bands ($2\nu_3$, $4\nu_2+\nu_3$, $3\nu_1+\nu_3$, $2\nu_1+2\nu_2+\nu_3$ and $3\nu_3$) in the infrared absorption spectrum of CS_2.

1318 Stoicheff's work was not published.

1320 According to the opinion of Douglas and Sharma, these differences are caused by the fact that in their work the resonance perturbation of the levels and the cubic terms in the expression for the energy of the vibrational levels were not taken into account.

1321 This value of B_{000} together with the results of the microwave measurements carried out by Nethercot, Klein and Townes [3148] and Simons, Anderson and Gordy [3728, 3729] leads to the value of the velocity of light c = 299,793.2 ± 1.8 km/sec, similar to the most accurate value of this magnitude (see Appendix 2).

1324 In C_2N_2 $r_{C\equiv N} = 1{,}157$ Å (see page 1328).

1324 The same value of f_{C-F} for FCN was obtained by three different methods: by graphic representation of the f_{C-X} values of cyan halides as a function of the ionization potential of the halogen atom: by the behavior of the corresponding values of the f_{C-X} constants of the XCN and C_2X_4 (X = Br, Cl, F) molecules; and by the logarithm of the constant f_{C-X} of cyan halides as a function of the logarithm of the length of the carbon-halogen bond.

1326 After this chapter had been written, papers were published dealing with the study of the infrared [592, 1359b, 1537a] and the microwave [3705] spectra of cyan fluoride. Aynsley, Dodd and Little [592, 1359b] observed two bands, at 1077 and 2290 cm^{-1}, in the infrared FCN spectrum. The study of the find structure of the 1077 cm^{-1} band and also of the shape of the 2290 cm^{-1} band led to the conclusion the both bands are parallel bands of the linear threeatomic FCN molecule with a moment of inertia equal to $7.89 \cdot 10^{-39}$ $g \cdot cm^2$, and with the corresponding interatomic distances $r_{C-P} = 1{,}26$ and $r_{C-N} = 1{,}16$ A. The values of the interatomic distances and the observed frequencies excellently correspond, within the error limits, to those adopted in the present Handbook. In the paper by Fawcett and Lipscomb [1537a], bands at 2290 and 1078 cm^{-1} were found in the infrared FCN spectrum, which are identical with the previously observed [592, 1359b], and a triplet band at 451 cm^{-1} which corresponds to the deformation vibration of FCN.
Sheridan et al. [3705] observed the transitions $1 \leftarrow 0, 2 \leftarrow 1, 3 \leftarrow 2.$ in the microwave FCN spectrum. Measurements gave the values of the rotational constant $B_{000} = 10{,}554.20 \pm 0.9$ Mcps = $= 0.35205$ cm^{-1} and of the constant of centrifugal stretch $D_{000} = 0.0053 \pm 0.0003$ Mcps = $0.18 \cdot 10^{-6}$ cm^{-1}. Based on the analysis of the obtained spectrum, the authors of [3705] drew the conclusion that the value of r_{C-N} must be somewhat greater than the value of r_{C-N} in ClCN which is equal to 1.163 A [164]. Assuming $r_{C-N} = 1.165$ A, the value of 1.26 A was found for r_{C-F} which conforms well to the structural parameters of FCN adopted in the present Handbook.

1329 The paper [2928] was published after the calculations of the thermodynamic functions of C_2N_2 quoted in Table 231 (II) had been finished.

1340 In paper [889], the calculations of the thermodynamic functions are carried out using the constants found by Allen, Tidwell and Plyler [516].

1341 The thermodynamic functions of FCN, calculated by means of the molecular constants found experimentally (see page 1323) conform to the values quoted in Table 209 (II) within 0.06 cal/mole•degree.

1342 Using the experimental data obtained in this paper, Brewer [1093] found the very similar value $\Delta H^{\circ}f_{298.16}$ (CS, gas) = 31.5 kcal/mole.

1348 The ground state $X^2\Sigma$ and the excited $A^2\Pi$ state of the CN molecule correlate with the normal $C(^3P) + N(^4S)$ states.

1348 According to the correlation rules, the $J^2\Delta$ state may correlate with the following states: $C(^3P) + N(^2D)$; $C(^3P) +$ $+ N(^2P)$; $C(^1D) + N(^2D)$.

1349 In the paper by Brewer et al, the value of 94.3 ± 6 kcal/ /mole was obtained when reducing to 0°K. The difference from the value cited above may be explained by the fact that Brewer et al assumed $(H^\circ_{2750} - H^\circ_0) = 13{,}750$ cal/mole (calculated on the assumption that the enthalpy of CN depends only on the translational constant), while, according to Table 207 (II), we have $H^\circ_{2750} - H^\circ_0 = 22{,}840$ cal/mole. It is noted in the paper by Knight and Rink [2447c] that Brewer et al could obtain an underestimated value of the heat of formation of CN owing to self-absorption in the cooler zones of the King furnace.

1350 The results of paper [2011a] were corroborated later on by Dibeler et al [1329a] on the basis of measurement of the potentials of occurrence of a number of ions in ionization of dicyan and of three cyan acetylenes.

1350 After this chapter had been written, in the paper by Knight and Rink [2447b] the density of gas was measured in a shock wave propagating in a mixture of dicyan or hydrocyanide with krpton. Based on the density as a function of the velocity of the shock wave, the authors of paper [2447b] calculated the dissociation energy of dicyan as equal to 145 ± 6 kcal/ /mole (or ΔH°_{f0} (CN, gas) = 109.6 kcal/mole) which is considerably higher than the values adopted in the present Handbook.

1352 Glockler [1767] determined the value of $D_0(F - CN) = 133$ kcal/mole using the graph of the dissociation energy of the carbon-halogen bond in cyan halides as a function of the interatomic distance. It must be noted that the estimation of $D_0(F - CN)$ given in paper [1767] possesses a low reliability because the function $D_0(X - CN)$ vs. r_{C-X} is not linear.

[Transliterated Symbols]

1325 П = P = prilozheniye = supplement.

Chapter 22

SILICON AND ITS COMPOUNDS

(Si, Si_2, SiO, SiO_2, SiH, SiF, SiF_2, SiF_3, SiF_4, $SiCl$, $SiCl_2$, $SiCl_3$, $SiCl_4$, SiN, SiC, SiC_2, Si_2C)

The present chapter deals with silicon and its simplest compounds with oxygen, hydrogen, fluorine, chlorine, nitrogen and carbon.

Silicon vapor contains Si atoms and the molecules Si_2, Si_3, Si_4 , Si_5, Si_6, Si_7[2118]. The present Handbook deals only with the two simplest substances Si and Si_2 which, according to the available data, are the fundamental components of the vapor. Results of measurements of silicon vapor pressure show, however, that the possibility of the presence of heavier molecules as basic vapor components cannot be excluded under equilibrium conditions within a certain temperature range.

The basic osygen compounds of silicon, SiO_2 (solid, liquid and gas) and SiO (gas), are treated in the Handbook. The thermodynamic properties of all equilibrium modifications in condensed state are given for SiO_2. The data on inequilibrium modifications (glass-like SiO_2 and quartz above 1140°K, for example) are not treated in the Handbook. At one time it was supposed that silicon monoxide was also stable in condensed state. Thus, the thermodynamic properties of SiO in solid state were treated in the first edition of this Handbook. Later on, however, was proved that SiO is thermodynamically unstable in solid state and decomposes into Si and SiO_2 (see [891, 922]).

Literature data point to the existence of Si_2O_2 (gas) molecules in the silicon-oxygen system in gaseous phase and under reducing conditions. This substance, however, is instable (the ratio $p_{Si_2O_2}: p_{SiO}$ is equal to $4 \cdot 10^{-4}$ at 1463°K [3304]) and is not treated in the Handbook.*

A great number of silicon-hydrogen compounds is known. All these compounds, however, have a low stability. So, SiH_4, the most stable silane, decomposes into the elements at only 400°C. These components often decompose explosively in the presence of water or oxidants. Only the simplest hydrogen compound of silicon, SiH, is treated in the Handbook.

The silicon-fluprine and silicon-chlorine compounds SiF_4 and $SiCl_3$ and the products of their stepwise dissociation: SiF_3, SiF_2, SiF, $SiCl_3$, $SiCl_2$ and SiCl are treated in the Handbook. Thus, the quoted data give a sufficiently comprehensive concept of the properties of the silicon-fluorine and silicon-chlorine systems. The large group of mixed compounds of the type SiF_3Cl, $SiHCl_2F$, etc., however, is not treated in the Handbook.

SiN (gas) is the sold compound of the silicon-nitrogen system, which is treated in the Handbook. Silicon nitrides in condensed state, possessing a considerable stability, are not dealt with in the Handbook.

The mass-spectrometrical investigation of the evaporation of silicon carbide, carried out recently [1406], has shown that the molecular composition of the gaseous phase of the Si — C system is very complex. Formerly, it was assumed that SiC was the main component of this system. New data proved, however, that elemental silicon is the main product of evaporation of silicon carbide, and that the partial pressure of SiC_2 and Si_2O exceed the pressure of SiC by more than three orders. Moreover, the compounds Si_2C_2, Si_2C_3 and Si_3C have been found in quantities comparable with that of SiC. Nevertheless, the data on SiC (solid, gas), Si_2C, SiC_2, Si and Si_2 and also on C (solid), given in the Handbook, permit the calculation of the composition and the thermodynamical properties of this system with sufficient accuracy since the other gaseous compounds are formed in significantly lower quantities.

§87. MOLECULAR CONSTANTS

Si. In the ground state ^3P, the silicon atom possesses the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^2$, to which two other states, ^1D and ^1S correspond. The excitation of one 3p electron of the Si atom entails a group of states with the electron configuration $3s^2 3p(^2P)n\underline{l}$. The first of these states $3s^2 3p 4s ^3P^0$) possesses an energy of about 40,000 cm^{-1}. and the ionization limit of this group has an energy of 65,743 cm^{-1}. In Table 197, the energy levels of Si up to 54,000 cm^{-1}, corresponding to the transition of the 3p electron into the 4s-, 4p- and 3d- states, and also the states ^5S and ^3D, which correspond to the electron configuration $1s^2 2s^2 2p^6 3s 3p^3$, are quoted. The other states of Si, connected with excitation of 3p- and 3s- electrons or simultaneous excitation of two and more electrons, are not dealt with in the Handbook. The excitation energies of the silicon atom levels, quoted in Table 197, are adopted according to the quantities recommended by Moore [2941], with the exception of the $3s3p^3\,{}^5S$ level, for which the data are cited according to the paper by Yel'yashevich and Nikitina [187].

In Table 197, levels of the silicon atom with similar excitation energies are joined together with a total statistical weight and a mean energy.

Si_2. The spectrum of the Si_2 molecule has been only very incompletely investigated. Downie and Barrow [1399] observed in the spectrum of a hydrogen-air flame with addition of $SiCl_4$ a band system in the 4200-5700 A region, which they suppositionally ascribed to the Si_2 molecule. The spectrum was recorded on a device with low dispersion, a fact which did not permit the carrying out of an analysis of the rotational structure. An approximate analysis of the vibrational structure led to the following values of constants: $\nu_e = 19\,000,\ \omega'_e = 1050,\ \omega''_e = 750$ см$^{-1}$. These data are quoted in Herzberg's monograph [2020] and in the Handbook [649]; the assignment of the bands observed by Dawnie and Barrow, however, to the Si_2 molecule, cannot be considered as unequivocal. More reliable data on the spectrum of the Si_2 molecule were obtained by Douglas [1371] who investigated the glowing that occurs in xenon atmosphere in a pipe with aluminum electrodes covered by a thin silicon layer, when weak electric discharge takes place. Two weak band systems reaching from 3480 A to the visible region, have been observed. The analysis of the spectrograms, obtained by a device with high dispersion, showed that the bands lying in the 3480-3980A region are caused by the $^3\Pi_g \rightarrow {}^3\Pi_u$ transition, and the weaker bands, lying in the visible and in the near ultraviolet region, are connected with the $^3\Sigma_u \rightarrow {}^3\Sigma_g$ transition. Douglas analyzed the rotational structure of the 0-1, 0-2 and 0-3 bands of the $^3\Pi - {}^3\Pi$ system and determined the rotational constants and the constants of the spin-orbital interaction in both $^3\Pi$ states and the vibrational constants in the lower $^3\Pi_u$ state. Douglas also carried out an analysis of the structure of the bands of the $^3\Sigma - {}^3\Sigma$, system; owing to the fact, however, that the isotopic structure of the edges was not observed, it was impossible to numerate unequivocally the bands of this system.

Owing to the fact that the absorption spectrum of the Si_2 molecule was not observed, and the experimental data on the emission spectrum are not numerous, the problem of the type of electron ground state and the relative position of the excited electron states of the Si_2 molecule is obscure up to date. Obviously, a comparison with the energy states of the C_2 molecule may serve as the sole source of information in this case. Based on the analogy of the configuration of the electron shells of C_2 and Si_2, Douglas [1371] assumed that the $^3\Sigma_g$ state (the lower state of the $^3\Sigma - ^3\Sigma$) system observed in the Si_2 spectrum) is the electron ground state of Si_2. Douglas proceeded in this case from an erroneous conception of the type of ground state of C_2, existing at this time, and he assumed that the type of the ground state changes from $^3\Pi$ into $^3\Sigma$ when changing the principal quantum number of the C_2 valence electrons into that of Si_2.

TABLE 197

Energy Levels of the Silicon Atom

A Номер уровня	B Состояние		E Статистический вес	F Энергия, $см^{-1}$
	C электронная конфигурация	D терм		
0	$1s^2 2s^2 2p^6 3s^2 3p^2$	$^3P_0$	1	0
1	$1s^2 2s^2 2p^6 3s^2 3p^2$	$^3P_1$	3	77,15
2	$1s^2 2s^2 2p^6 3s^2 3p^2$	$^3P_2$	5	223,31
3	$1s^2 2s^2 2p^6 3s^2 3p^2$	^1D	5	6298,81
4	$1s^2 2s^2 2p^6 3s^2 3p^2$	^1S	1	15394,24
5	$1s^2 2s^2 2p^6 3s 3p^3$	^5S	5	33326
6	$\ldots 3s^2 3p\ (^2P)\ 4s$	^3P	9	39860
7	$\ldots 3s^2 3p\ (^2P)\ 4s$	^1P	3	40992
8	$\ldots 3s^2 3p\ (^2P)\ 3d$	^3D	15	45303
9	$\ldots 3s^2 3p\ (^2P)\ 4p$ $\ldots 3s^2 3p\ (^2P)\ 3d$	^1P ^1D	8	47326
10	$\ldots 3s^2 3p\ (^2P)\ 4p$ $\ldots 3s 3p^3$	^3D ^3D	30	48420
11	$\ldots 3s^2 3p\ (^2P)\ 4p$ $\ldots 3s^2 3p\ (^2P)\ 3d$	^3P, ^3S ^3F	33	49690
12	$\ldots 3s^2 3p\ (^2P)\ 4p$ $\ldots 3s^2 3p\ (^1P)\ 3d$	^1D, ^1S ^3P, ^1F, ^1P	25	51650

A) Number of the level; B) state; C) electron configuration; D) term; E) statistical weight; F) energy, cm^{-1}.

Later on, Douglas and Rao [1379] suggested the assumption, based on an analysis of the possible configuration of the electron shells of P_2 and N_2 in their ground states, that the singlet state of the $^1\Sigma_g$ type can be the ground state of the Si_2 molecule. Owing to the fact that recent investigations of the C_2 spectrum, carried out in 1960 proved that the $^1\Sigma_g$ state is the ground electron state of C_2 (see page 866), this assumption seems to be very probable, and it is adopted in the present Handbook. Based on the analogy with C_2, it is assumed in the Handbook that the $a^3\Pi_u$ and $b^3\Sigma_g$ states (the lower states of the band systems $^3\Pi - {}^3\Pi$ and $^3\Sigma - {}^3\Sigma$), respectively, observed in the Si_2 spectrum) are the first excited states of Si_2. The energies of these states are estimated as equal to 800 ± 200 and 8000 ± 2000 cm^{-1}.

The molecular constants (ω_e, B_e and r_e) of Si_2 in the ground state $X^1\Sigma_g$, quoted in Table 198 and adopted in the Handbook, are estimated on the basis of a comparison of the corresponding constants of C_2 in the $X^1\Sigma, a^3\Pi_u$ and $b^3\Sigma_g$ states with the Si_2 constants in the $a^3\Pi_u$ and $b^3\Sigma_g$ states. The molecular constants estimated in this way may contain significant errors (equal to ± 60, ± 0.05 cm^{-1} and ± 1 A, respectively).

The experimentally observed molecular constants of Si_2 in the $^3\Pi$ and $^3\Sigma$ states, quoted in Table 198, are adopted in the Handbook on the basis of data by Douglas [1371].

It should be noted that in analogy to C_2 the existence of states of the $A^1\Pi_u$ and $c^3\Sigma_u^+$ type with excitation energies not exceeding 20,000-25,000 cm^{-1} may be expected in the scheme of the energy states of Si_2.

TABLE 198

Adopted Values of the Molecular constants of Si_2, SiO, SiH, SiF, SiCl, SiN and SiC.

1 Моле-кула	2 Состояние	T_e	ω_e	$\omega_e x_e$	B_e	α_1	$D_0 \cdot 10^6$	r_e
		в $см^{-1}$						А
Si_2	$X^1\Sigma_g^{а}$	0	$630^{б}$	—	$0,29^{б}$	—	—	$2,04^{б}$
	$a^3\Pi_u^{а}$	$800^{б}$ b	547,94	2,47	0,2596	0,00155	—	2,155
	$b^3\Sigma_g^-$	$8000^{б}$	506,72	1,97	0,2376	0,00135	—	2,252
	$^3\Pi_g^{г}$	28859,1	—	—	0,2370	—	—	2,255
	$^3\Sigma_u^-$	32075,7	$271,32^{д}$ e	$1,99^{д}$	$0,1699^{е}$ f	0,00135	—	$2,663^{е}$
SiO	$X^1\Sigma$	0	1241,44	5,92	0,7273	0,00508	1,02	1,509
	$A^1\Pi^{ж}$	42834,9	852,71	6,44	0,6313	0,00695	1,43	1,620
SiH	$X^2\Pi_r$	$0^{з}$ h	2042,47	35,67	7,498	0,214	395	1,521
	$A^2\Delta_r$	$24393,15^{и}$ i	1858,13	98,73	7,470	$0,347^{к}$ k	523	1,523
SiF	$X^2\Pi_r$	$0^{л}$ l	857,6	4,67	m $0,5817^{м}$	m $0,00566^{м}$	1,08	1,600
	$A^2\Sigma$	22858,4	718,58	$10,167^{н}$ n	0,57839	$0,00941^{о}$ o	1,57	1,6049
	$B^2\Sigma$	34561,5	1011,23	4,825	0,62707	0,00462	—	1,5414
	$C^2\Sigma$	39438,4	891,5	5,8	0,6043	0,0067	—	1,57
	$C'^2\Pi$	41964,9	1031,8	4,45	0,6376	0,0039	—	—
	$D'^2\Pi$	46606,7	1032,9	5,28	0,6329	0,0044	—	—
	$D^2\Sigma$	47418,6	1003,2	5,64	0,625	0,0055	—	1,54
SiCl	$X^2\Pi_r$	$0^{п}$ p	535,4	2,20	$0,2558^{р}$ r	0,0016 s	$0,234^{с}$	2,07 s
	$B^2\Sigma^{т}$	34102,7	701,5	$1,40^{у}$ u	0,2790	0,00150	0,175	—
	$C^2\Delta$	41165,4	674,3	2,20	—	—	—	—
	$D^2\Sigma$	44941,5	663	—	—	—	—	—
SiN	$X^2\Sigma$	0	1151,68	6,56	0,7310	0,00567	1,183	1,571
	$A^2\Pi$	8000	1032,3	6,4	—	—	—	—
	$B^2\Sigma$	24299,4	1031,01	$16,743^{ф}$ v	0,743	0,01037	1,439	1,579
	$C^2\Pi$	34493	697,3	3,3	—	—	—	—
SiC	$X^1\Sigma^{а}$	0	$1000^{б}$	—	$0,65^{б}$	—	—	$1,75^{б}$
	$a^3\Pi^{б}$	$700^{б}$	—	—	—	—	—	—
	$b^3\Sigma^{б}$	$7000^{б}$	—	—	—	—	—	—

a) Adopted in analogy to C_2

b) Estimate

c) $A = -71.6$ cm^{-1}

d) The existence of $A^1\Pi$ and $c^3\Sigma$ states with an excitation energy lower than 20,000 cm^{-1} is possible

e) the value of the constants are obtained, supposing that the lowest vibrational level which was observed corresponds to

$v' = 0$.

f) the values of B_0 and r_0 are quoted.

g) in analogy to CO it can be expected that the SiO molecule posses a $a^3\Pi$ state with an energy of 36,000 cm^{-1} (estimate on basis of (1.31)) and two more triplet states with an excitation energy lower than T_e ($A^1\Pi$). Another three excited singlet states and one triplet state with an excitation energy lower than 45,000 cm^{-1} (see page 1365) are known on the basis of the analysis of perturbations.

h) $A = 143.35$ cm^{-1}

i) $A = 3.83$ cm^{-1}

k) $\alpha_2 = -0.041$ cm^{-1}

l) $A = 161.92$ cm^{-1}

m) The value of α_1 in the $X^2\Pi$ state was found by the difference of the wave numbers of the edge and the head of the band; the value of B_e was calculated by the α_1, found by this way, and the value of B_0

n) $\omega_e y_e = 0{,}157$ см^{-1}.

o) $\alpha_2 = 1{,}3 \cdot 10^{-4}$ см^{-1}.

p) $A = 207{,}9$ см^{-1}.

r) The value of B_e for the $X^2\Pi_{1/2}$ state is given. $B_e = 0{,}2564$ см^{-1}. is valid for $X^2\Pi_{3/2}$.

s) The value of D_e for the $X^2\Pi_{1/2}$ state is given. $D_e = 0{,}2355 \cdot 10^{-6}$ см^{-1} is valid for $X^2\Pi_{3/2}$.

t) The excited $A^2\Sigma$ state was not observed in the spectrum. In analogy to SiF, the excitation energy of this state must be lower than the excitation energy of the $B^2\Sigma$ state. Estimation on the basis of (1.31) gives $T_e(A^2\Sigma) \sim 18\,000 \pm 2000$ см^{-1} .

u) This value of $\omega_e x_e$ may be inaccurate because the assignment of the 2-0 and 3-0 bands in the $B^2\Sigma - X^2\Pi$ system is doubtful.

v) $\omega_e y_e = 0{,}11722$ см^{-1}.

1) Molecule;
2) state;
3) cm^{-1}.

SiO. The $^1\Sigma^+$ state is the ground electron state of the Sio molecule. The experimentally observed first excited electron state $A^1\Pi$ has an excitation energy $T_e = 42{,}834.9$ cm^{-1}. Until recently, only these two electron states of the SiO molecule were known (see [2020, 649]).

Based on an analysis of the perturbations of the vibrational levels of the $A^1\Pi$ state, Lagerqvist and Uhler [2535] concluded that another four excited electron states of SiO exist with excitation energies of the order of 43,000-44,000 cm^{-1}. The approximate estimations of the excitation energies and constants of SiO, given by the authors of paper [2535] are not reliable and must be checked and specified. Owing to this fact and also to the high excitation energies, these SiO states are not treated in the present Handbook. Another four excited electron states of the SiO molecule with excitation energies exceeding 52,500 cm^{-1} were determined by Barrow and Rowlinson [3539, 660, 662] when investigating the absorption spectrum of silicon oxide in the vacuum-ultraviolet region. These states are also not treated in the Handbook.

The band system $A^1\Pi - X^1\Sigma$ observed in both the emission spectrum [2247, 3581, 3693, 642, 2525, 2535] and the absorption spectrum of SiO [3539, 660, 662] is most thoroughly investigated. In Herzberg's monograph [2020] and in the Handbook [649], those values of molecular constants of SiO in $X^1\Sigma$ and $A^1\Pi$ states are recommended which were determined by Saper [3581] when analyzing the rotational structure of the 0-1, 0-2, 0-3, 0-4 and 1-4 bands of the $A^1\Pi - X^1\Sigma$ system. In subsequent investigations [2529, 2535, 3539, 660, 662], the values of the molecular constants of SiO in the $X^1\Sigma$ and $A^1\Pi$ states have been determined more accurately.

The values of the molecular constants of SiO in the $X^1\Sigma$ and $A^1\Pi$ states, adopted in the Handbook and quoted in Table 198, were determined by Lagerqvist and Uhler [2535] when analyzing the rotational structure of nine bands of the $A^1\Pi - X^1\Sigma$ system, obtained by a device with an dispersion of 0.6 A/mm.

Owing to the structural similarity of the valence electron shells of the CO, CS and SiO molecules, a definite analogy in types and excitation energies of the lower electron states of these molecules can be expected. In analogy to CO and CS, especially, it can be expected that the SiO molecule possesses triplet electron states, the lower of which (the $a^3\Pi$ state) must have an excitation energy of about 36,000 ± 3000 cm^{-1} [estimated by Eq. (1.31)].

SiH. The $^2\Pi_r$ state is the ground electron state of the SiH molecule. Only one band system near to 4100 A was observed in the SiH spectrum. The emission spectrum of the SiH molecule was investigated in papers [2196, 2979, 3462, 1372]. The absorption spectrum was obtained rather recently by Nelson and Ramsay [3038b] and Thrush [3988a] when studying the pulse photolysis of silane and also of $SiCl_4$ in the presence of hydrogen.

SiH bands, appearing in the arc spectrum when various silicon compounds are introduced, were first observed by Jackson [2196]. The analysis of the rotational structure of 0-0 and 1-1 bands, obtained by a highly resolving device, proved that they are connected with the $A^2\Delta - X^2\Pi$ transition. The experimental data by Jackson were subsequently analyzed by Mulliken and Christy [3003] and Mulliken [2979], who proved that the spin-orbital coupling in the $X^2\Pi_r$ state belongs to the case intermediate between the Hund cases a and b.

An analysis of the rotational structure of the 1-1 band of SiH and the 0-0 bands of SiH and SiD was also carried out by Rochester [3462]. The bands were obtained in an arc spectrum and photographed in the second order of a concave 21-feet grating. The results of the analysis carried out by Rochester [3462] differ somewhat from the data obtained by Mulliken [2979] and Jackson [2196] because in the latter paper a number of lines with low J values was erroneously assigned to insufficient resolution. The values of the SiH constants found by Rochester [3462] are recommended in Herzberg's monograph [2020] and in the Handbook [649]. Owing to the fact that only the 0-0 and 1-1 bands were observed in papers [2196] and [3462], the values of the vibrational frequencies of SiH in the $^2\Pi$ and $^2\Delta$ states, quoted in the Handbooks [2020] and [649], were estimated by Kratzer's formula and are not completely accurate.

The most thorough investigation of the $A^2\Delta-X^2\Pi$ band system was carried out by Douglas [1372] who obtained the 0-0, 1-1, 2-2, 1-0 and 2-1 bands of the SiH molecule, parallel with Si_2 bands, in the spectrum of a discharge in SiH. Owing to a device with a very high dispersion (0.35 A/mm) and an analysis of the 2-2, 1-0 and 2-1 bands, Douglas succeeded in defining the values of rotational constants, already known earlier, and in determining the values of rotational constants of the SiH molecule. The values of the SiH molecular constants in the $X^2\Pi$ and $A^2\Delta$ states, found by Douglas [1372] are adopted in the present Handbook and quoted in Table 198.

The SiH molecule is an analogon to the methine (CH) molecule. Both molecules possess the $^2\Pi_r$ electron ground state and the first excited state of the $^2\Delta$ type, and the energies of the $A^2\Delta$ states are similar in both molecules (see Tables 176 and 198). Another two states, $B^2\Sigma$ and $C^2\Sigma$, with excitation energies of about 26,000 and 32,000 cm^{-1}, respectively, are known in the CH molecule. It can be assumed that the SiH molecule possesses analogous states with similar excitation energies.

<u>SiF</u>. The $X^2\Pi_r$ state is the ground electron state of the SiF molecule. Experimentally, the existence of six excited doublet states with excitation energies which do not exceed 50,000 cm^{-1} was determined (see Table 198), and also that of four excited states with higher excitation energies [2257], which are not treated in the present Handbook.

In the emission spectrum of SiF [3299, 2265, 1394, 2257, 647, 601, 582, 1518], the band systems $A^2\Sigma \rightarrow X^2\Pi_r$, $B^2\Sigma \rightarrow X^2\Pi_r$ and $C^2\Sigma \rightarrow X^2\Pi$ (termed also α, β and γ systems), $D^2\Sigma \rightarrow X^2\Pi_r$, $C'^2\Pi \rightarrow X^2\Pi$, $D'^2\Pi \rightarrow X^2\Pi$, $B^2\Sigma \rightarrow A^2\Sigma^+$, $C'^2\Pi \rightarrow A^2\Sigma$, $D'^2\Pi \rightarrow A^2\Sigma$, $D'^2\Pi \rightarrow B^2\Sigma$, and four slightly investigated systems ($E \rightarrow X$, $G \rightarrow X$, $H \rightarrow X$ и $F \rightarrow X$), lying in vacuum ultraviolet, have been observed. The absorption spectrum of the SiF molecule has not been investigated.

The molecular constants of SiF in the ground electron state $X^2\Pi_r$ have been determined by a number of authors on the basis of investigations of the vibrational and rotational structure of the band systems $A^2\Sigma - X^2\Pi$, $B^2\Sigma - X^2\Pi$ and $C^2\Sigma - X^2\Pi$. Assundi and Samuel [582] were the first to prove that on the basis of the analysis of the vibrational structure of these systems, they have a common lower $^2\Pi$ state which is the ground electron state of the SiF molecule. The basic results of the investigations by Asundi and Samuel were confirmed by Eyster [1518] who obtained the α, β and γ bands of SiF on a device with a 0.78 and 0.58 A/mm dispersion. In addition to the analysis of the vibrational structure of the α-, β- and γ- bands (by the edges), Eyster also investigated the rotational structure of the 0-0 bands of the α- and β-systems, and proved that the spin-orbital coupling in the $X^2\Pi$ state of the SiF molecule is intermediate between the Hund cases a and b. This was subsequently confirmed by Jones and Barrow [2257] who carried out a thorough analysis of the rotational structure of the 0-0 band of the α- system recorded in the fourth order of a concave 21-feet grating. The values of the molecular constants of SiF in the $X^2\Pi$ state, recommended in paper [2257], are adopted in the present Handbook and quoted in Table 198. Very similar values, obtained by Eyster [1518], are recommended in Herzberg's book [2020] and in the Handbook [649].

In obsolete investigations [2265, 601, 582, 1518], the upper state of the α- system of SiF was regarded as a $A^2\Pi$ state (see also [2020, 649]). However, on the basis of an analysis of the rotational structure of B → A band system and the 0-0 bands of the α- system, Jones and Barrow [2257] proved that the $^2\Sigma$ state is the first excited electron state of SiF. The molecular constants of SiF in the $A^2\Sigma$ state, found in paper [2257], are adopted in the present Handbook and quoted in Table 198.

The molecular constants of SiF in the higher electron states $A^2\Sigma$ ($B^2\Sigma$, $C^2\Sigma$, $D^2\Sigma$, $C'^2\Pi$ and $D'^2\Pi$) adopted in the Handbook and quoted in Table 198, were found by Jones and Barrow and their co-workers [2257, 647] by analysis of the structure of the $B^2\Sigma - X^2\Pi$, $B^2\Sigma - A^2\Sigma$, $C^2\Sigma - X^2\Pi$, $D^2\Sigma - X^2\Pi$ and $D'^2\Pi - A^2\Sigma$, systems.

<u>SiCl</u>. The $X^2\Pi_r$ state is the ground electron state of the SiCl molecule. The existence of three excited electron states of SiCl was experimentally proved: $B^2\Sigma$, $C^2\Delta$ and $D^2\Sigma$. On the basis of a comparison with the wellknown electron states of SiF (see Table 198), it can be assumed that a series of stable states with excitation energies lower than 50,000 cm^{-1} must additionally exist in the SiCl molecule. Among them, the excited electron state of the $A^2\Sigma$ type, not observed experimentally, is the most important with regard to the calculation of the thermodynamic functions of SiCl. Calculation by Eq. (1.31) gives an estimate of the excitation energy of the $A^2\Sigma$- state as equal to approximately 18,000 ± 2000 cm^{-1}.

Three band systems: $B^2\Sigma \rightarrow X^2\Pi_r$, $C^2\Delta \rightarrow X^2\Pi_r$ and $D^2\Sigma \rightarrow X^2\Pi_r$ [1264, 2245, 2247, 2253, 325] have been observed in the emission spectrum of SiCl excited by discharge in $SiCl_4$ vapor. Only bands of the $B^2\Sigma \rightarrow X^2\Pi$ system were observed in the absorption spectrum [645, 3988a, 4258a].

The analysis of the vibrational structure of the $B^2\Sigma - X^2\Pi_r$ band system, the most intense system in the SiCl spectrum, was carried out for the first time by Datta [1264]. Later on, the results obtained by Datta were confirmed by Jevons [2253] who measured the edge positions of 12 bands $X^2\Pi, C^2\Delta - X^2\Pi$ systems, and those of six bands of the $D^2\Sigma - X^2\Pi$ system. The values of the vibrational constants of SiCl in the $X^2\Pi, B^2\Sigma, C^2\Delta$ and $D^2\Sigma$ states, found in paper [2253], are adopted in the present Handbook and quoted in Table 198. The same values are recommended in Herzberg's monograph [2020] and in the Handbook [649].

The rotational constants of the SiCl molecule remained unknown until very recently because SiCl bands with a resolved rotational structure had not been obtained. Only in 1960, a paper by Ovcharenko, Tunitskiy and Yakutin [325] was published in which the authors carried out a fine structure analysis of the 1-0, 0-0 and 0-1 bands of the $B^2\Sigma \rightarrow X^2\Pi$ system. The bands have been photographed in the third order of a spectrum by a DFS-3 spectrograph with a dispersion of 0.57 A/mm. The rotational constants of SiCl in the $X^2\Pi$ and $B^2\Sigma$ states, found in paper [325], are adopted in the present Handbook and quoted in Table 198.

It must be observed that the value of the rotational constant of SiCl in the ground state, estimated in the first edition of the Handbook, conforms satisfactorily to the value found in paper [325].

SiN. Just as in the case of the CN molecule, the $^2\Sigma^+$ state is the ground electron state of the SiN molecule. The existence of three excited electron states of SiN: $A^2\Pi, B^2\Sigma^+$ and $C^2\Pi$, has been experimentally proved.

Two band systems, $B^2\Sigma^+ - X^2\Sigma^+$, and $C^2\Pi - A^2\Pi$, lying in the regions λλ 3800-5200 and 3200-5600 A, respectively, have been observed in the SiN spectrum. The band system $B^2\Sigma^+ - X^2\Sigma^+$ was repeatedly investigated in emission [2245, 2234, 2713, 2714, 2715, 2973], and it was obtained in absorption by Thrush [3988a] when studying the pulse photolysis of a $SiCl_4$ and N_2 mixture. The less intense band system $C^2\Pi - A^2\Pi$ was investigated in emission by Mulliken [2973].

The most thorough investigation of the band system $B^2\Sigma^+ - X^2\Sigma^+$ was carried out by Jenkins and Laszlo [2234]. These authors photographed the bands of the sequences $\Delta v = 0\,(v', v'' \leqslant 5)$ and $\Delta v = 1\,(v' = 3, 4, 5, 6$ and $v'' = 2, 3, 4, 5)$ in the second order of a spectrograph with concave grating (0.96 A/mm dispersion). As a result of the analysis of the vibrational and rotational structure of the $B^2\Sigma - X^2\Sigma$ band system, Jenkins and Laszlo determined the values of the molecular constants of SiN in the $X^2\Sigma^+$ and $B^2\Sigma^+$ states, which are quoted in Table 198.

The analysis of the vibrational structure of the $C^2\Pi - A^2\Pi$ system was carried out by mulliken [2973] on the basis of the band edges. The values obtained by him of the vibrational constants of the SiN molecule in the A-Π and $C^2\Pi$ states, are quoted in Table 198. The excitation energy of the $A^2\Pi$ state is unknown because the $A^2\Pi - X^2\Sigma$ transition was not observed in the SiN spectrum. By reason of the similar excitation energies of the $B^2\Sigma$ states of CN and SiN molecules (see Tables 18 and 198), it can be assumed that the excitation energies of the $A^2\Pi$ states of these molecules must possess similar values. As a result of this fact, the excitation energy of the $A^2\Pi$ state may be estimated as equal to 8000 ± 2000 cm^{-1}. An estimation by means of Eq. (1.31) gives the same value. Based on this value and on the value $\nu_{00} = 26\,493\ cm^{-1}$ for the $C^2\Pi - A^2\Pi$ system, the excitation energy of the $C^2\Pi$ state can be assumed as equal to 34,493 ± 2000 cm^{-1}.

SiC. The existence of the SiC molecule was proved by mass-spectrometrical investigations by Drowart et al [1406]; the spectrum of this molecule, however, was not observed experimentally. Thus the molecular constants of SiC, necessary for the calculation of the thermodynamic functions, can be estimated only approximately on the basis of the wellknown constants of C_2 and Si_2 molecules which are the nearest analoga to the SiC molecule, and also by comparison of the force constants of the C,C and Si-C bonds in the C_2, SiC and SiC_2 molecules.

In analogy to the Si_2 and C_2 molecules, it is assumed in the present Handbook that a state of the $X^1\Sigma$ type is the ground electron state of the SiC molecule. It may be expected that the SiC molecule must possess stable electron states of the $a^3\Pi$ and $b^3\Sigma$ types with low excitation energies, approximately equal to 700 and 7000 cm^{-1}, respectively.

As was noted above, the comparison of the vibrational frequencies of C_2 and Si_2 is one of the possible ways of estimating the vibrational frequencies of the SiC molecule in the electron ground state. Several authors [1121, 1122, 2135, 2746, 2925, 4071] suggested various relations which connect the vibrational frequency of the XY molecule with those of X_2 and Y_2 molecules. Based on the comparison of the calculated values of frequencies of many molecules with the experimentally found frequencies of these molecules, it was proved by Varshni [4071] and Majumdar and Varshni [2746] that the estimation on the basis of formulas suggested by Majumdar and Varshni [2746] $\left(\omega_e^{0,65}(XY) = \frac{1}{2}\left[\omega_e^{0,65}(XX) + \omega_e^{0,65}(YY)\right]\right)$ and Varshni [4071] $\left(\omega_e(XY) = 0,3\sqrt{\omega_e(XX)\,\omega_e(YY)} + 0,7\left[\frac{\omega_e(XX) + \omega_e(YY)}{2}\right]\right)^{1}$ * conforms to the experiment.

The calculation by means of this formula, carried out with the aid of the frequencies of C_2 and Si_2, adopted in the Handbook, gives almost conformal values of ω_e (SiC) equal to 1185 and 1195 cm^{-1}. It must be noted that the values of ω_e (SiC) estimated in this way may contain a significant error owing to the fact that the value of ω_e (Si_2) in the $X^1\Sigma$ ground state is itself an approximate value (see page1360).

Under these conditions, the following method of estimating ω_e (SiC) is also quite reasonable. A comparison of the force constant of the C=C bond in the SiC_2 molecule ($f_{CC} = 9.71 \cdot 10^5$ dyne·cm^{-1}) with the force constants k_e of the C_2 molecule in various electron states shows that the constant k_e (C_2) = $9.53 \cdot 10^5$ dyne·cm^{-1} in the $a^3\Pi_u$. state is most similar to f_{CC} (SiC_2). Assuming that a similar relation remains valid also for the Si = C bond in SiC_2 molecules ($f_{Si=C} = 2.88 \cdot 10^5$ dyne·cm^{-1}) and passing from the $a^3\Pi_u$ states to the $X^1\Sigma_+$ states, we obtain for the force constant of SiC the value k_e (SiC) = $3.7 \cdot 10^5$ dyne·cm^{-1}, corresponding to $\omega_e\,(\mathrm{SiC}) = 870\ \text{см}^{-1}$. Owing to the approximate nature of both estimation methods, the mean value $\omega_e = 1000 \pm 150\ \text{см}^{-1}$ is adopted for the SiC frequency in the present Handbook. The interatomic distance r_{Si-C} was assumed as equal to 1.75 ± 0.1 A (the half sum of the interatomic distances r_{C-C} and r_{Si-Si} in the C_2 and Si_2 molecules). The value of the rotational constant which corresponds to this interatomic distance is quoted in Table 198.

Earlier, the molecular constant of SiC was estimated by Drowart, De-Maria and Inghram [1406], who assumed $k_e = 3.1 \cdot 10^5$ dyne·cm^{-1}, $\omega_e = 796\ \text{см}^{-1}$ and r_e = 1.9 A (obtained for the Si-C bond as the results of an analysis of infrared and Raman spectra of various organo-silicon compounds). Such an estimation cannot be regarded as competent because the Si-C bond in organo-silicon compounds is a single bond whereas that in C_2 is a jultiple one. In analogy to Si_2, the multiplicity of the electron ground state of SiC was assumed in [1406] as equal to three.

$\underline{SiO_2}$. References to experimental investigations of the spectrum and the structure of the silicon dioxide molecule are totally lacking in literature. The molecular constants of this compound, adopted in the Handbook and quoted in Table 199, have been estimated by Korobov when preparing the first edition of the Handbook. It was assumed in the estimate that, in analogy to the carbon dioxide molecule, the SiO_2

molecule possesses a linear-symmetrical structure and belongs to the symmetry point group $D_{\infty h}$. The calculation of the fundamental frequencies of SiO_2 was carried out by means of Eqs. (P4.31) and the following values of the force, constants and the interatomic distance: $f_d = 7{,}5 \cdot 10^5$, $f_{dd} = 0{,}7 \cdot 10^5$, $f_\alpha/d^2 = 0{,}39 \cdot 10^5$ dyne•cm^{-1}, and r_{Si-O} = 1.554 A, obtained by comparison of the corresponding constants of SiO, CO and CO_2 molecules. The probable error of the fundamental frequencies of SiO_2, calculated by this way, amounts to about 10%. The principal moment of inertia of the SiO_2 molecule was calculated under the assumption that r_{Si-O} = 1.554 ± 0.03 A.

TABLE 199

Adopted Values of the Molecular Constants of SiO_2, SiF_2, $SiCl_2$, SiF_3, $SiCl_3$, SiF_4, $SiCl_4$, SiC_2, Si_2C

Молекула	ν_1	ν_2	ν_3	ν_4	$I_A I_B I_C$	σ
	см$^{-1}$				10^{-117} (г·см^2)^3	
SiO_2	940	420 (2)	1240	—	12,8^a	2
SiF_2	937	427	1000	—	286	2
$SiCl_2$	540	248	610	—	5800	2
SiF_3	830	430	980 (2)	390 (2)	2640	3
$SiCl_3$	480	240	600 (2)	200 (2)	80500	3
SiF_4	800	268 (2)	1031 (3)	391 (3)	7940	12
$SiCl_4$	424	150 (2)	621 (3)	221 (3)	255100	12
SiC_2	591	430 (2)	1742	—	14^a	1
Si_2C	430	340 (2)	980	—	28,6^a	2

[a] The value $1 \cdot 10^{39}$ g•cm^2 is given.

1) Molecules; 2) cm^{-1}; 3) (g•cm^2)^3.

The structure and fundamental frequencies of the SiO_2 molecule have also been estimated by Schick [3622a]. On the basis of an analogy with CO_2, Schick assumed that the SiO_2 molecule possessed linear symmetry and belonged to the point group $D_{\infty h}$. The interatomic distance r_{Si-O} was assumed as equal to 1.54 A (on the basis of a comparison of the interatomic distances in CO, SiO and Co_2). Estimating the fundamental frequencies of the SiO_2 molecule, Schick compared the frequencies of CO_2 and CS_2, CO and CS, and found that the ratio ν_{CS_2}/ν_{CO_2} changes from 0.49 to 0.65, and $\nu_{CS}/\nu_{CO} = 0{,}59$ is valid. Assuming that the ratio $\nu_{SiO_2}/\nu_{CO_2} = \nu_{SiO}/\nu_{CO} = 0{,}572$, has an error limit of 15%, Schick calculated $\nu_1 = 767, \nu_2 = 382$, and $\nu_3 = 1340\ cm^{-1}$; Schick estimated that the error of these values may be as high as 15-20%. The values, found by Schick, conform to the frequency values adopted in the present Handbook within the mentioned error limits.

SiF_2. The structure of the SiF_2 molecule was not studied experimentally. It is assumed in the present Handbook that, similar to the CX_2 molecules (where X = F and Cl), the SiF_2 molecule possesses nonlinear symmetry and belongs to the symmetry point group C_{2v}. The interatomic distance r_{Si-F} is assumed as equal to 1.57 ± 0.05 A (the mean between the values of r_{Si-F} in SiF and SiF_4 molecules) and $\angle FSiF = 110 \pm 5°$ (in analogy with CF_2).

A molecule with C_{2v} symmetry must possess three fundamental frequencies: a symmetrical (ν_1) and an antisymmetrical (ν_3) valence vibration of the bonds, and the deformation vibration (ν_2).

The SiF_2 spectrum was first obtained and investigated in 1958 by Johns, Chantry and Barrow [2259]. The authors of paper [2259] proved that the δ- system observed earlier by Johnson and Jenkins [2265] in a spectrum of a discharge in SiF_4 vapor does, in fact, not belong to the SiF molecule (as Johnson and Jenkins assumed) but to the SiF_2 molecule. The analysis of the vibrational structure of these bands, lying in the 2200-2500 A region,* enabled Johns, Chantry and Barrow to find two frequencies, 937 and 427 cm^{-1}, which, in analogy to CF_2, have been assigned to the ν_1 and ν_2 vibrations, respectively, of the symmetrical nonlinear SiF_2 molecue. This interpretation of the SiF_2 spectrum was confirmed in paper [2259] by the conformity between the observed frequencies and those calculated by Eqs. (P4.28), using SiF_2 force constants (in 10^5 dyne·cm^{-1}) equal to $f_d=6{,}173, f_{dd}=0{,}330, f_{d\alpha}=0{,}0897$, and two values of the constant f_α/d^2, equal to 0.535 and 0.669 ($\nu_1=927, \nu_2=390$ and $\nu_1=931, \nu_2=425$ $\text{см}^{-1})^2$.* The value $\nu_3=1000\ \text{см}^{-1}$ corresponds to the values of the SiF_2 force constants assumed in paper [2259]. The calculation of the frequency ν_3 of the antisymmetrical vibration by means of Eqs. (P4.30) and of force constants, calculated on the basis of experimentally found values of ν_1 and ν_2, results in $\nu_3=1050\ \text{см}^{-1}$.

Earlier, an approximate calculation of the frequencies of normal vibrations of SiF_2 was carried out by Tatevskiy and Tyulin [56]. The force constants of SiF_2 required for the calculation SiF_2 ($f_d=9{,}1\cdot10^6$, $f_\alpha=2{,}75\cdot10^6$, $f_{dd}=0{,}50\cdot10^6$ and $f_{d\alpha}=0{,}80\cdot10^6\ \text{см}^{-2}$) have been estimated by the authors of [56] on the basis of a comparison of the force constants of $SiCl_2$, CF_2 and CCl_2, assuming the validity of the ratios

$$\frac{f_d(CF_2)}{f_d(CCl_2)}=\frac{f_d(SiF_2)}{f_d(SiCl_2)};\quad \frac{f_\alpha(CF_2)}{f_\alpha(CCl_2)}=\frac{f_\alpha(SiF_2)}{f_\alpha(SiCl_2)}\quad \text{etc.}$$

The calculation resulted in the following values: $\nu_1=870, \nu_2=500$, $\nu_3=970\ \text{см}^{-1}$; the values of ν_1 and ν_2 correspond within a limit of 10-15% to those found experimentally.

In the present Handbook the values found in paper [2259] by investigation of the electron spectrum of SiF_2 are adopted for the frequencies of the symmetrical valence and deformation vibrations of SiF_2. The value $\nu_3=1000\pm100\ \text{см}^{-1}$ is adopted for the frequency of the antisymmetrical vibration. The adopted frequency values are quoted in Table 199. In the same table, the value of the product of the moments of inertia is quoted, which corresponds to the structural parameters of SiF_2 quoted above and adopted in the Handbook. In analogy to the CF_2 molecule, it is assumed in the present Handbook that the electron ground state of SiF_2 is a singlet state.

$SiCl_2$. The structure of the $SiCl_2$ molecule was not investigated experimentally. It is assumed in the present Handbook that, similar to the CF_2 and CCl_2 molecules, $SiCl_2$ is a nonlinear symmetrical molecule and belongs to the symmetry point group C_{2v}. This assumption has been confirmed by the results of the investigation of the $SiCl_2$ spectrum [581]. The structural parameters of $SiCl_2$ have been estimated by Tatevskiy and Tyulin [56] who assumed $r_{Si-Cl} = 2,05 \pm 0,05$ Å (the rounded mean of the r_{Si-Cl} values in SiCl and $SiCl_4$) and $\angle ClSiCl = 110 \pm 5°$. These values are adopted in the present Handbook. The product of the principal moments of inertia of $SiCl_2$, corresponding to them, is quoted in Table 199.

The $SiCl_2$ spectrum was investigated by Asundi, Karim and Samuel [581] who, when studying the spectrum of the discharge in $SiCl_4$ vapor, observed broad diffuse bands with a nonresolved rotational structure. The authors of paper [581] assigned these bands to the triatomic $SiCl_2$* molecule and, on the basis of an analysis of the vibrational structure of the spectrum, they obtained the values of the symmetrical valence vibration $\nu_1 = 540$ см$^{-1}$ and the deformation vibration $\nu_2 = 248$ см$^{-1}$ of the electron ground state of $SiCl_2$. The calculation of the antisymmetrical vibration frequency ν_3 by means of Eqs. (P4.29) and of force constants, calculated on the basis of the experimentally determined frequencies ν_1 and ν_2, results in the value $\nu_3 = 612$ см$^{-1}$. Tatevskiy and Tyulin [56] calculated also the values of ν_3 by Eqs. (P4.28). Assuming for $SiCl_2$ the force constants $f_d = 4,84 \pm 0,25 \cdot 10^6$ and $f_{dd} = 0,36 \cdot 10^6$ см$^{-2}$, estimated by comparison of the force constant of the diatomic SiCl molecule with the force constants of $SiCl_4$, Tatevskiy and Tyulin obtained $\nu_3 = 610 \pm 30$ см$^{-1}$. The values of the frequencies ν_1 and ν_2, found in paper [581], are adopted in the present Handbook. The value $\nu_3 = 610 \pm$

$\pm$ 60 см$^{-1}$ is adopted for the frequency of the antisymmetrical valence vibration. The adopted values are quoted in Table 199.*

Corresponding to the assumed structure and the results of the analysis of the spectrum of the $SiCl_2$ molecule, it is assumed in the present Handbook that the ground electron state of $SiCl_2$ is a singlet state.

SiF_3. Experimental data on the structure and the spectra of the SiF_3 molecule are lacking in literature. In analogy to CF_3, it is assumed in the present Handbook that the SiF_3 molecule possesses a pyramidal structure with the silicon atom on the vertex and belongs to the point symmetry group C_{3v}. According to the recommendation of Tatevskiy and Tyulin [56], it is assumed that the interatomic distance is $r_{Si-F} = 1{,}57 \pm 0{,}05$ Å and $\angle FSiF = 110 \pm 10°$.

A molecule of such a symmetry type must possess four normal vibrations, two of which (with the frequencies ν_1 and ν_2) are totally symmetric and belong to the symmetry type A_1, and the two others (with the frequencies ν_3 and ν_4) are doubly degenerated and belong to the symmetry type E.

Tatevskiy and Tyulin [56] estimated the fundamental frequencies of the SiF_3 molecule, using certain simple regularities. Based on the fundamental frequencies of $ClCBr_3$, $DCBr_3$, $HCBr_3$ and $DSiBr_3$, $HSiBr_3$, the authors of paper [56] obtained by extrapolation the fundamental frequencies of CBr_3 and $SiBr_3$ molecules. Assuming the CBr_3 and $SiBr_3$ frequencies, found in this way, and also the frequencies of CF_3, CCl_3, $SiCl_3$ obtained by estimation (see pages 1263 and 1378), and by drawing graphs of the frequencies as a function of the halogen atom, the authors of [56] found the following values of the SiF_3 frequencies (in cm^{-1}): $\nu_1 = 780 \pm 80$, $\nu_2 = 470 \pm 50$, $\nu_3 = 1000 \pm 100$, $\nu_4 = 370 \pm 50$. It is obvious that such an estimation can give correct frequency values only when the estimations of the CF_3, CCl_3, $SiCl_3$ frequencies are correct.

The frequencies of the SiF_3 vibrations may also be calculated on the premise that the force constants of SiF_3 are equal to the corresponding force constants of SiF_4. The calculation by Eqs. (P4.37), using the force constants of SiF_4 found by Voelz et al [4116], results in values of the SiF_3 frequencies equal to $\nu_1=880$, $\nu_2=460$, $\nu_3=950$ and $\nu_4=400$ см⁻¹, and, when using the force constants recommended by Pistorius [3250], the values $\nu_1=890$, $\nu_2=390$, $\nu_3=1010$ and $\nu_4=220$ см$^{-1}$ are obtained.

The means of the values found by three different estimations are adopted in the Handbook for the frequencies ν_1, ν_2 and ν_3. The error of these values amounts to 10-15%. The value $\nu_4=220$ см$^{-1}$ (calculated by the SiF_4 constants obtained by Pistorius [3250]) differs strongly from the value recommended in paper [56] and also from the value calculated by means of the SiF_4 constants found by Voelz et al [4116]. Thus, the value $\nu_4=390$ см$^{-1}$, near to the mean of the values obtained in papers [56, 4116], is adopted in the Handbook. The error in the ν_4 value is of the order of ±100 cm^{-1}.

The values of the fundamental frequencies of SiF_3, adopted in the Handbook, and also the product of the principal moments of inertia of this molecule, calculated on the basis of the structural parameters of SiF_3, cited above, are quoted in Table 199. Owing to the fact that the SiF_3 molecule possesses one free electron, it is assumed in the Handbook that the ground state of SiF_3 is a doublet state.

$SiCl_3$. Literature pertaining to experimental data on the spectrum and the structure of $SiCl_3$ is lacking. According to the recommendation of Tatevskiy and Tyulin, and in analogy to the CX_3 molecules (where X = F and Cl), it is assumed in the present Handbook that $SiCl_3$ has a pyramidal structure with the silicon atom on the vertex, and belongs to the point symmetry group C_{3v}. The fundamental frequencies of the $SiCl_3$ molecule: $\nu_1 = 455 \pm 50$, $\nu_2 = 225 \pm 30$, $\nu_3 = 670 \pm 60$, $\nu_4 = 165 \pm 20\ \text{см}^{-1}$— , have been estimated by Tatevskiy and Tyulin [56] on the basis of an extrapolation in the molecules series $BrSiCl_3 \rightarrow ClSiCl_3 \rightarrow FSiCl_3 \rightarrow DSiCl_3 \rightarrow HSiCl_3 \rightarrow SiCl_3$ (the frequencies of these molecules, with exception of that of $FSiCl_3$, are wellknown [236]). The authors of paper [56] emphasize that such an extrapolation hields only approximate values of the $SiCl_3$ frequencies because while it takes into account only the diminution of the mass of one of the atoms to zero in the molecules mentioned above, it disregards, however, the change in the distribution of the electrons when one atom chlorine is detached from $SiCl_4$ (or one atom hydrogen from $HSiCl_3$). In both cases, not only the change in the configuration of the electron shells, but also a change in the angle between the bonds is possible [see [4139]).

In the paper by Venkatesvarlu and Sundaram [4087], dealing with the calculation of the force constants of pyramidal XY_3 molecules, it is assumed that the frequencies of $SiCl_3$ are equal to those of the corresponding frequencies of the $HSiCl_3$ molecule $HSiCl_3$ ($\nu_1 = 489$, $\nu_2 = 249$, $\nu_3 = 587$ and $\nu_4 = 179\ \text{см}^{-1}$) . The extrapolation of frequencies in a molecule series, carried out in paper [56], is more regular than the mechanical transfer of the frequencies of the $HSiCl_3$ molecule to the $SiCl_3$ molecule. It must be mentioned, however, that the frequency values of $SiCl_3$, recommended in papers [4087, 56], conform to one another within the error limits of the estimations (10-15%).

The calculation of the fundamental frequencies of $SiCl_3$ by Eqs. (P4.37), assuming the force constants of $SiCl_3$ as equal to those of $SiCl_4$ found in paper [3250] ($f_d = 2{,}757 \cdot 10^5$, $f_{dd} = 0{,}399 \cdot 10^5$, $f_{d\alpha} = 0{,}23 \cdot 10^5$, $f_\alpha / d^2 = 0{,}296 \cdot 10^5$, $f_{\alpha\alpha} = 0{,}07 \cdot 10^5$ dyne•cm^{-1}), results in the values $\nu_1 = 510$, $\nu_2 = 244$, $\nu_3 = 540$ and $\nu_4 = 236\ \text{см}^{-1}$. These values conform satisfactorily to the frequencies recommended in papers [56, 4087] within the accuracy limits (about 10-15%) of the calculation. Frequency values, being rounded means of the values found in papers [56, 4087] and of the values calculated above, are adopted in the Handbook, and it is assumed that the probable error in the recommended values does not exceed 15%. These frequency values are quoted in Table 199.

The product of the principal moments of inertia of $SiCl_3$, quoted in Table 199, is calculated for $r_{Si-Cl} = 2{,}05 \pm 0{,}05\,Å$ (the rounded mean of the r_{Si-Cl} values in SiCl and $SiCl_4$) and $\angle ClSiCl = 110 \pm 10°$.

Owing to the fact that the $SiCl_3$ molecule possesses one free electron, the ground state of $SiCl_3$ must be a doublet state.

SiF_4. The results of electron diffraction studies [965, 3203, 910, 954] show that the SiF_4 molecule has a tetrahedral structure and belongs, as well as the methane molecule, to the point symmetry group T_d. Such molecules must possess four fundamental frequencies. One of them (ν_1) belongs to the totally symmetrical vibration, one (ν_2) to a doubly degenerated, and two (ν_3 and ν_4) to threefold degenerated vibrations. All the vibrations are present in the Raman spectrum, and only the threefold degenerated vibrations are present in the infrared spectrum.

The values of the fundamental frequencies of the SiF_4 molecule, recommended in Herzberg's monograph [152] ($\nu_1 = 800$, $\nu_2 = 260$, $\nu_3 = 1022$, $\nu_4 = 520$ *см*$^{-1}$), are based on the results of the investigation of the infrared spectrum of gaseous SiF_4, carried out by Bailey, Hale and Thompson [621], and on the investigations of the Raman spectrum of liquid SiF_4, carried out by Yost, Lassetre and Grosse [4363]. 11 bands in the region 2-19 microns (5000-555 cm^{-1}) were found and identified in paper [621]. Only one line with a frequency of 800 cm^{-1} was observed in the Raman spectrum [4264]. In 1938, Yost [4358] published his findings that two other frequencies (268 and 463 cm^{-1}) are also present in the Raman spectrum obtained by Best and Tramp.*

Later on, Jones, Kirby-Smith, Woltz and Nielsen [4313, 2293] repeated a thorough investigation of the Raman and infrared spectrum of especially purified SiF_4 samples. Four lines, 268, 390, 800 and 1010 cm^{-1}, corresponding to the frequencies ν_2, ν_4, ν_1 and ν_3, were found in the Raman spectrum obtained by a prism device. The value of the ν_1 frequency coincides with that found in paper [4364], and the value of ν_3 with that cited by Yost [4358]. The lines 290 and 1010 cm^{-1} have not been observed earlier. The line with the frequency of 463 cm^{-1}, reported by Yost [4358] as present in the spectrum obtained by Jones et al [2293], was absent and is, obviously, caused by the presence of impurities.

The infrared spectrum of SiF_4 was investigated in the region from 2 to 38 microns (5000-260 cm^{-1}). The application of a diffraction grating device enabled the resolving of the structure of eight bands composed by P-, Q- and R- branches, and a more accurately defining of the position of the Q- branches. The value of the ν_4 frequency is almost the same in fluid and gas, whereas the value of ν_3, found in the infrared gas spectrum, is by 21 cm^{-1} higher than in the fluid.

By analysis of the obtained data and also by a critical examination of preceding papers, Jones and co-workers [2293] succeeded in more accurately determining the values of the fundamental frequencies of silicon tetrafluoride. The values, suggested by them later on, have been corroborated in the vapor by Schatz and Hornig [3609]. The values of the SiF_4 frequencies, found by Jones et al [2293], are quoted in Table 199. There is also given the value of the product of the inertia moments of SiF_4, calculated for $r_{Si-F} = 1.54 \pm 0.02$ Å, according to the results of electron diffraction studies [965, 3203, 910, 954].

$SiCl_4$. The $SiCl_4$ molecule, as well as SiF_4, has a tetrahedral structure and belongs to the point symmetry group T_d.

Based on the analysis of the results in investigations of $SiCl_4$ Raman spectra, collected in Kohlrausch's book [2456], Herzberg [152] recommends the following values of the fundamental frequencies (in cm^{-1}) for the molecule of silicon tetrachloride: $\nu_1 = 424$, $\nu_2 = 150$, $\nu_3 = 608$ and $\nu_4 = 221$.

The results of subsequent investigations of the Raman spectrum of liquid $SiCl_4$, carried out by Delwaulle and co-workers [1304, 1301, 1300, 1308], Goubeau and Warneke [1833], and Stock and Schneider [3880] confirmed the values of the fundamental frequencies of $SiCl_4$ recommended by Herzberg (the values of ν_1, ν_2 and ν_4 coincided fully, and 610 cm^{-1} [1833] and 609 cm^{-1} [3880] were found ν_3 instead of 608 cm^{-1}.

In 1953 Smith [3771] obtained for the first time the infrared spectrum of gaseous silicon tetrachloride in the region from 2 to 25 microns (5000–400 cm^{-1}). The spectrum was investigated by prism spectrometers; the errors in the found wave numbers did not exceed ± 2 cm^{-1}. The authors of paper [3771] observed only one strong line in the spectrum, referring to the fundamental vibration ν_3, and a series of combination bands and overtones, the frequencies of which could be satisfactorily interpreted on the basis of the fundamental frequencies recommended by Herzberg [152]. The value of the frequency $\nu_3 = 621$ cm^{-1} found in paper [3771], somewhat exceeds the ν_3 value obtained in the investigation of the Raman spectrum of liquid $SiCl_4$ [1300, 1301, 1304, 1308]. Obviously, this difference can be explained by a change of the vibration frequency by transfer from the liquid to the gaseous state. An analogous effect takes place in the spectrum of SiF_4 (see above).

In Table 199, the values of the frequencies ν_1, ν_2 and ν_4 are quoted, which are adopted in the Handbook and recommended by Herzberg

[152] on the basis of the investigation of the Raman spectrum of liquid $SiCl_4$, and the value of the ν_3 frequency, found by investigation of gaseous $SiCl_4$ [3771]. It can be expected that the true values of the fundamental frequencies of liquid $SiCl_4$ will somewhat differ from the values quoted in Table 199, because the latter were found by investigation of the spectrum of liquid $SiCl_4$.

The results of the electron diffraction studies [954, 2628, 4352] conform well to one another and give the value $r_{Si-Cl} = 2{,}01 \pm 0{,}02$ A. The product of the principal moments of inertia of the $SiCl_4$ molecule, calculated on the basis of this r_{Si-Cl} value, is quoted in Table 199.

$\underline{SiC_2}$. Kleman [2433], investigating the spectrum excited in a King furnace filled with silicon, discovered in the 4600-6700 A region a combined band spectrum which was subsequently identified with the greenish-blue bands observed earlier in star spectra [2853, 3578a] and also in the spectra of various comets [3909b]. The bands have been photographed by Kleman in the second order of a grating with an 1.25 A/mm dispersion. The analysis of the conditions of the appearance of these bands and also the investigation of the structure of the observed spectrum led Kleman to the conclusion that the emitter of the bands is the linear asymmetrical SiC_2 molecule. This assumption was confirmed by analogy with the spectrum of the C_3 molecule which appears by excitation in the King furnace under very similar conditions, and also in the emission spectra of astrophysical sources.

The linear asymmetrical $Si = C = C$ molecule belongs to the point symmetry group $C_{\infty v}$ and must have three fundamental frequencies: two frequencies (ν_1 and ν_3) refer to the valence vibrations of the $Si = C$ and $C = C$ bonds, and one doubly degenerated frequency ν_2 is caused by deformation vibrations.

Assuming that, similar to C_3, the SiC_2 molecule is linear in the ground and in the excited state, Kleman [2433], on the basis of an analysis of the observed electron spectrum, recommended the following values of the fundamental frequencies of SiC_2 (in cm^{-1}): $\nu_1''=591$, $\nu_1'=456$, $\nu_3''=1742$, $\nu_3'=1461$. The frequencies ν_1 and ν_3 of the ground electron state, found by Kleman, are adopted in the present Handbook and quoted in Table 199. For the estimation of the frequency of the doubly degenerated deformation vibration it is assumed that, in analogy to the force constants of other linear triatomic molecules,* the force constant has the value $f_\alpha=0{,}5\pm0{,}2\cdot10^{-11}$ dyne•cm•rad^{-1}. A frequency $\nu_2 = 430\pm80$ cm^{-1}. corresponds to this force constant.

The interatomic distances $r_{C=C}$ and $r_{Si=C}$ are assumed as equal to the corresponding distances in C_3 and SiC molecules: $1{,}28\pm0{,}05$ and $1{,}75\pm0{,}08$ Å. The value of the moment of inertia, quoted in Table 199, corresponds to the adopted values of the structural parameters of the SiC_2 molecule. In analogy to C_3, the multiplicity of the electron ground state of SiC_2 is assumed as equal to unit.

The fundamental frequency ν_2 and the structural parameters of the SiC_2 molecule have been estimated earlier by Drowart, De-Maria and Inghram [1406] who assumed $r_{C=C}=1{,}3$, and $r_{Si=C}=1{,}9$ Å (the mean value of the interatomic distances Si – C in various organo-silicon compounds).** Based on these values and on $f_\alpha=0{,}65\cdot10^{-11}$, dyne•cm•rad^{-1}, adopted in analogy to the force constants of deformation vibrations of the N_2O and SCO molecules, the authors of [1406] calculated by Eq. (P4. 27) the frequency value $\nu_2 = 465$ cm^{-1}.

Si_2C. The spectrum and the structure of the Si_2C molecule have not been studied experimentally, although the existence of such a molecule is proved by mass-spectrometrical investigations [1406]. In gaseous state, Si_2C may possess both the shape of symmetrical SiCSi molecules and that of Si_2C molecules with an asymmetrical structure. Owing to the fact that the Si-C bond is stronger than the bond between two silicon atoms (see page 143), it is assumed in the present Handbook that the Si_2C molecule is linear symmetrical and belongs to the point group $D_{\infty h}$. The interatomic distance r_{Si-C} is assumed as equal to the corresponding distance in the SiC molecule (1.75 ± 0.08 A). The value of the moment of inertia of Si_2C, corresponding to the adopted structural parameters, is quoted in Table 199.

A linear symmetrical Si_2C molecule must possess three fundamental frequencies, caused by the symmetrical (ν_1) and antisymmetrical (ν_2) vibrations of the Si – C bonds, and the doubly degenerated deformation vibration ν_2. The calculation of the fundamental frequencies of Si_2C by Eqs. (P4.32), assuming that the force constant of the Si – C bond (f_d) and the deformation constant (f_α) are equal to $2.9 \cdot 10^5$ dyne•cm^{-1} and $0.5 \cdot 10^{-11}$ dyne•cm•rad^{-1}, respectively (assumed in analogy to SiC_2), results in the values $\nu_1 = 420, \nu_2 = 335$ and $\nu_3 = 1000\ cm^{-1}$. The appropriate calculation by Eqs. (P4.31), taking into account the constant of the bond interaction, which is assumed as equal to $0.25 \cdot 10^5$ dyne•cm^{-1}, gives almost the same frequency values: $\nu_1 = 440$, $\nu_2 = 335$ and $\nu_3 = 950\ cm^{-1}$. The rounded off values $\nu_1 = 430 \pm 50,\ \nu_2 = 340 \pm 50$ and $\nu_3 = 980 \pm 100\ cm^{-1}$ are adopted in the present Handbook. In analogy to the C_3 molecule, the multiplicity of the ground electron state of Si_2C is assumed as equal to unit.*

Earlier, the structural parameters and fundamental frequencies of the Si_2C molecule were estimated by Drowart, De-Maria and Inghram [1406]. In analogy to SiC_2, the authors of paper [1406] assumed that the Si_2C molecule possesses a linear asymmetrical structure with the interatomic distances $r_{Si-C} = 1.9$ Å (like the organo-silicon compounds) and $r_{Si-Si} = 2.25$ Å (as in Si_2 in the $^3\Sigma_g^-$ state). Assuming that the force constant of the f_{Si-Si} bond is equal to the constant k_e in the

the Si_2 molecule ($2.1 \cdot 10^5$ dyne•cm^{-1}), the bond constant f_{Si-C} and the deformation constant f_α are equal to $3.1 \cdot 10^5$ dyne•cm^{-1} and $0.65 \cdot 10^{-11}$ dyne•cm•rad^{-1}, as in SiC_2, the following frequencies have been found in paper [1406] (in cm^{-1}): $\nu_1 = 446, \nu_2 = 265$ and $\nu_3 = 799$. It must be mentioned that (see above) Drowart et al [1406], when estimating the interatomic distance and the force constant of the Si – C bond, proceeded from the assumption of an analogy with organo-silicon compounds which, as well as in the case of the SiC_2 molecule, is incorrect in the present case.

§88. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of silicon and its compounds in the ideal gas state, calculated according to the molecular constants adopted in the previous section for temperatures from 293.15 to 6000°K, are quoted in Tables 233-235, 237-247 and 249-251 of the 2nd volume of the Handbook. The calculations are carried out without taking into account the differences in the constants of individual isotopic modifications of the gases in question.

In Table 386 (II), the values of the virial coefficients and of their derivatives are given for silicon tetraflupride; analogous data for the other gases discussed in this chapter are unknown.

Si. The thermodynamic functions of gaseous monatomic silicon, quoted in Table 233 (II), are calculated by Eqs. (II.22) and (II.23). The partition function of the electron states and its derivative with respect to the temperature are calculated by direct summation [Eqs. (II.20) and (II.21)] over the energy levels quoted in Table 197, and the translational components are calculated by Eqs. (II.8) and (II.9) assuming $A_\Phi = 2,6595$ and $A_S = 7,6274$ cal/g-atom•degree.

At temperatures up to 5000°K, the accuracy of the calculated values of thermodynamic functions depends solely on the accuracy of the adopted values of physical constants, and the corresponding errors in the values of Φ_T^* and S_T° do not exceed 0.003-0.004 cal/g-atom•degree. At higher temperatures, errors become noticeable which are caused by the fact that electron states with an excitation energy higher than 52,000 cm^{-1}, corresponding to values from 4 to 11 of the principal quantum number of the valence electron of Si, are not taken into account in the calculation; however, the contribution of these states is small in the temperature range in question and does not exceed 0.01 cal/g-atom•degree in the values of S_{6000}°.

Earlier, the tables of thermodynamic functions of monatomic silicon have been calculated for a wide temperature range by Kolsky et al [2462] (up to 8000°K) and in the US Bureau of Standard [3680] (up to 5000°K). The results of both calculations correspond to the data of Table 233 (II) within 0.005-0.007 cal/g-atom•degree. In the book by Stull and Sinke [3894], thermodynamic functions of monatomic silicon are given which are identical with the data of [3680].

The thermodynamic functions of monatomic silicon, quoted in the first and the present edition of the Handbook, differ by not more than 0.003 cal/g-atom•degree.

Si_2 and SiC. The thermodynamic functions of gaseous diatomic silicon and silicon carbide, quoted in Tables 234 (II) and 249 (II), respectively, are calculated by Eqs. (II.161) and (II.162). The calculations are carried out in the rigid rotator-harmonic oscillator model approximation on the basis of the constants of the Si_2 and Si_C molecules quoted in Table 198. In Table 200, the values of the constants C_Φ and C_S of Eqs. (II.161) and (II.162) are given, and also the value of θ, calculated on the basis of the adopted constants of both substances. As mentioned in §87, the Si_2 and SiC molecules must obviously possess a series of excited electron states with low energies. The components of the $a^3\Pi$ and $b^3\Sigma$ electron states of the Si_2 molecule (see Table 198) are calculated by Eqs. (II.120) and (II.121), i.e., without taking into account the difference of the Si_2 constants in these states and in the $X^1\Sigma$ ground state.

TABLE 200

Values of the Constants for the Calculation of the Thermodynamic Functions of Gaseous Si_2, SiO, SiH, SiF, SiCl, SiN and SiC

Вещество 1	θ	$x \cdot 10^3$	$\beta_1 \cdot 10^2$	$\beta_2 \cdot 10^4$	$\frac{q_0}{T}$	$\frac{d_0 \cdot 10^6}{T}$	$\frac{f_0 \cdot 10^{10}}{T}$	C_Φ	C_S
	2 град				град$^{-1}$		град$^{-2}$	3 кал/моль·град	
Si_2	906,43	—	—	—	—	—	—	5,0846	12,0401
SiO	1785,8	4,7527	0,7009	0,50	0,959168	2,65	—	3,9208	10,8758
SiH	2938,7	17,464	2,8954	8,38	0,094037	10,05	1,05	—0,5565	6,3990
SiF	1233,9	5,4454	0,9778	0,96	1,20066	8,96	—	5,9399	12,8954
SiCl	768,03	4,1027	0,6307	0,40	2,73957	5,01	—	8,4725	15,4280
SiN	1656,7	5,696	0,7786	0,62	0,954681	3,10	—	5,1489	12,1039
SiC	1438,8	—	—	—	—	—	—	3,8532	10,8087

1) Substance; 2) degree; 3) cal/mole·degree.

The SiC molecule must also possess excited electron states with low energies. The $a^3\Pi$ and $b^3\Sigma$ states of SiC have been taken into account when calculating the thermodynamic functions of this molecule. The calculation of the corresponding components was carried out by means of Eqs. (II.120) and (II.121) on the basis of the excitation energies of these states, estimated in §87.

The main errors in the calculated values of thermodynamic functions of Si_2 and SiC are caused by the lack of experimental data for the constants of these molecules in the basic electron states (up to 0.5 cal/mole·degree in the values of Φ_T^*), by the calculation in the rigid rotator-harmonic oscillator model approximation (up to 0.2-0.3 cal/mole·degree in the values of Φ_T^*) and by the lack of experimental data for the excitation energies of the $a^3\Pi$ and $b^3\Sigma$ states (in the order of 0.3 cal/mole·degree in the Φ_T^* values of both gases).

The total errors of the Φ_T^* values quoted in Tables 234 (II) and 249 (II), disregarding the errors caused by the uncertainty of the ground state type, are at T = 298.15; 3000 and 6000°K of the order of 0.4; 0.8 and 1.3 cal/mole•degree for both gases.

Earlier, the thermodynamic functions of Si_2 have been calculated in the first edition of the present Handbook and also in the work by Inghram and co-workers [1406] (Φ_T^* values for four temperatures in the 2000°K range). Both calculations were carried out in the rigid rotator-harmonic oscillator model approximation. It was assumed in the first edition that the $^3\Pi$ state was the ground state of Si_2, and the calculation was carried out by means of the constants found by Downie and Barrow (see page 1359). In paper [1406] it was assumed that $^1\Sigma_g^+$ was the ground state, and the constants were adopted from Douglas' paper [1371]. The differences between the data quoted in Table 234 (II) and in the first edition of the Handbook amount to 0.3 and 0.9 cal/mole•degree in the Φ_T^* and S_T° values, respectively; the analogous differences with regard to the calculation results of Inghram and co-workers amount to 0.01-0.12 cal/mole•degree in the values of Φ_{2000}^*.

The table of the thermodynamic functions of SiC is published first. Φ_T^* values for 2000-2200°K have been calculated in paper [1406]; the calculation was carried out by means of estimated values of the molecular constants, assuming the $^1\Sigma_g^+$ state as the ground state. The difference between the Φ_{2000}^* value obtained in this work and that quoted in Table 249 (II) amounts to 0.5 cal/mole•degree.

SiO and SiN. The thermodynamic functions of gaseous silicon monoxide and nitride, quoted in Tables 235 (II) and 247 (II), are calculated by Eqs. (II.161) and (II.162) on the basis of the molecular constants adopted in §87 (see Table 198). The values of $\ln\Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations have been calculated by the Gordon-Barnes method

[Eqs. (II.137) and (II.138)] without corrections limiting the number of rotational levels of both gas molecules. In Table 200, the values of θ and x, of the constants C_Φ and C_S in Eqs. (II.161) and (II.162), and of the coefficients of Eqs. (II.137) and (II.138) are quoted, calculated on the basis of the molecular constants of SiO and SiN. Owing to the fact that the SiN molecule has the $^2\Sigma$ ground state, the addends R ln 2 are included in the C_Φ and C_S values of this gas. The components of the excited states of the gas molecules in question ($A^1\Pi$ for SiO, $A^2\Pi$ and $B^2\Sigma$ for SiN) are calculated by Eqs. (II.120) and (II.121), i.e., without taking into account the difference in the constants of these molecules in the excited and ground state. In the case of SiN it is impossible to use a more accurate method for the calculations of the components of the $A^2\Pi_i$ state possessing a low excitation energy because data on the magnitude of the excitation energy are lacking (see page 1371). The triplet states of SiO were not taken into account in the calculations because their excitation energies are high, and the contributions to the Φ_T^* and S_T° values are sufficiently small.

The main errors in the calculated values of thermodynamic functions of silicon monoxide and nitride are caused by the lack of experimental data on the lower excited electron states of their molecules ($A^2\Pi_i$ in SiN, triplet states in SiO). For SiN they are of the order of 0.05 and 0.1 cal/mole•degree in the values of Φ_{3000}^* and Φ_{6000}^*, respectively; for SiO they do not exceed 0.02 cal/mole•degree in the Φ_T^* values. The errors caused by the lack of experimental data on the energy of the high vibrational and rotational levels of the ground electron states of SiO and SiN must be smaller than these values; the errors caused by neglection of the corrections which take into account the necessary limitation of the number of rotational states are unessential in the investigated temperature range owing to the high dissociation energies of both molecules.

The total errors in the values of Φ_T^* at 298.15; 3000 and 6000°K are of the order of 0.01; 0.02 and 0.05 cal/mole•degree for silicon monozide, and 0.02, 0.03 and 0.2 cal/mole•degree for silicon mononitride.

The thermodynamic functions of SiO have been calculated in papers by Brewer and Edwards [920] ($T \leq 2000°K$) in the rigid rotator-harmonic oscillator model approximation, and by Schick [3622a] (four temperatures in the range from 298.15 to 3000°K), who introduced corrections by the Mayer and Goeppert-Mayer method. The results of the calculations carried out in these papers correspond to the data of Table 235 (II) within 0.08 cal/mole•degree for the Φ_T^* values and 0.08 cal/mole•degree for the S_T° values. The existing differences are caused mainly by the different methods of calculation.

The thermodynamic functions of SiO quoted in the first and in the present edition of the Handbook are identical; the thermodynamic functions of SiN differ in the Φ_T^* values by up to 0.5 cal/mole•degree, and in the S_T° values by up to 1.4 cal/mole•degree due to the fact that the components of the $A^2\Pi$ state of SiN have not been taken into account in the first edition.

Other calculations of the thermodynamic functions of SiN are unknown in literature.

SiH. The thermodynamic functions of silicon monohydride, quoted in Table 238 (II), are calculated on the basis of constants adopted above (see page 1367) and using Eqs. (II.161) and (II.162). The values of $\ln\Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations are calculated by the Gordon and Barnes method [Eqs. (II.137) and (II.138)] without corrections for the limiting of the number of rotational levels of the energy of the ground electron state of SiH. The $^2\Pi_r$ state with a bond type near to the Hund case a ($A/B \sim 20$) is the ground electron state of SiH. Thus, the values of $\ln\Delta$ and $T\frac{\partial}{\partial T}\ln\Delta$ in Eqs. (II.151) and (II.152).* The components of the excited $A^2\Delta$ state of the SiH molecule are calculated by Eqs. (II.126) and (II.127), i.e., taking into account the difference in the constants of SiH in this and in the ground electron state. In Table 200, the values of θ and x, the constants C_Φ and C_S in Eqs. (II.161) and (II.162), and also the coefficients in Eqs. (II.137) and (II.138) are quoted, calculated on the basis of the adopted molecular constants of SiH.

The main errors in the calculated thermodynamic functions of SiH are caused by the insufficient accuracy of the known vibrational constants, the lack of data on a number of excited states of SiH, and also by the neglection of corrections which take into account the necessary limitation of the number of rotational levels of the ground electron state of this molecule. The total error of the $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} values, quoted in Table 238 (II), can be estimated as equal to 0.02, 0.05 and 0.2 cal/mole•degree. The thermodynamic functions of silicon monohydride, quoted in Table 238 (II), differ essentially from the data in the first edition of the present Handbook. These differences (up to 0.5 cal/mole•degree in Φ^*_T and up to 0.8 cal//mole•degree in S°_T) are caused by the use of more accurate values of the molecular constants of SiH and a more accurate calculation method.

Other calculations of thermodynamic functions of SiH are unknown in literature.

<u>SiF and SiCl.</u> The thermodynamic functions of silicon monofluoride and monochloride, quoted in Tables 239 (II) and 242 (II), are calculated on the basis of the molecular constants adopted in §87 (see Table 198) by means of Eqs. (II.161) and (II.162). The values of $\ln\Sigma$ and

$T\frac{\partial}{\partial T}\ln\Sigma$ in these equations are calculated by the Gordon and Barnes method [Eqs. (II.137) and (II.138)] without corrections which limit the number of rotational energy levels of the ground electron states of both gases. The ground electron states of the SiF and SiCl molecules are states of the $^2\Pi_r$ type with a bond type corresponding to the Hund case a (A/B >> 1), thus the values of $\ln\Delta$ and $T\frac{\partial}{\partial T}\ln\Delta$ in Eqs. (II.161) and (II.162) have been calculated by Eqs. (II.151) and (II.152). In Table 200, the values of θ and x, of the constants C_Φ and C_S in Eqs. (II.161) and (II.162), and of the coefficients in Eqs. (II.137) and (II.138) are quoted, calculated on the basis of the adopted molecular constants of SiF and SiCl.

The SiF and SiCl molecules possess a number of excited states (see the preceding section). The components of the $A\,^2\Sigma$ state of the SiF molecule are calculated by Eqs. (II.126) and (II.127), the components of the $B\,^2\Sigma$ and $C\,^2\Sigma$ states of the SiF molecule and of the $B\,^2\Sigma, C\,^2\Delta, D\,^2\Sigma$ states of the SiCl molecule are calculated by Eqs. (II.120) and (II.121), i.e., without taking into account the difference in the molecular constants of the excited and the ground electron states.

The main errors of the thermodynamic functions of the gases in question are caused by the lack of data on the energy of high vibrational and rotational levels of the ground electron states of their molecules and by the neglection of corrections which permit a limitation of the number of rotational levels of the ground electron states. However, owing to the relatively high dissociation energies of SiF and SiCl, these errors are small. They may be assumed as equal to 0.02; 0.05 and 0.2 cal/mole•degree in the Φ_T^* values at 298.15; 3000 and 6000°K. The differences between the values of the thermodynamic functions of the gases in question quoted in the first and the present edition of the Handbook are caused by more accurate values of the molecular constants of both gases and also by the altered method of calculation of the thermodynamic functions of SiCl. They do not exceed 0.02 and 0.04 cal/mole•degree in the values of Φ_T^* and S_T° for SiF and amount to 0.2 and 0.5 cal/mole•degree in the values of these functions for SiCl.

Other calculations of the thermodynamic functions of SiCl are unknown in literature. The values of Φ_T^* of silicon monofluoride for a series of temperatures from 298.15 to 5000°K are cited by Margrave in the book [2775] without indicating the paper in which the calculation was carried out. These data (with exclusion of T = 500°K) conform to these quoted in Table 239 (II) of the present Handbook within a limit of 0.07 cal/mole•degree.

TABLE 201

The Values of θ_n, C'_Φ and C'_S for the Calculation of the Thermodynamic Functions of Gaseous SiO_2, SiF_2, SiF_3, SiF_4, $SiCl_2$, $SiCl_3$, $SiCl_4$, SiC_2, Si_2C

1 Вещество	θ_1	θ_2	θ_3	θ_4	C'_Φ	C'_S
	2 град				3 кал/моль·град	
SiO_2	1352,5	604,29	1784,1	—	5,8464[a]	12,8015[a]
SiF_2	1348,2	614,36	1438,8	—	6,4369	14,3860
SiF_3	1194,2	618,68	1410,0	561,13	9,9703	17,9194
SiF_4	1151,0	385,60	1483,4	562,57	7,5333	15,4820
$SiCl_2$	776,95	356,82	877,7	—	10,6330	18,5817
$SiCl_3$	690,62	345,31	863,3	287,76	14,7300	22,6791
$SiCl_4$	610,05	215,82	893,5	317,97	12,4411	20,3902
SiC_2	850,33	618,68	2506,4	—	6,9773[a]	13,9328[a]
Si_2C	618,68	489,19	1410,0	—	7,8210[a]	14,7765[a]

a) The values of C_Φ and C_S are given.
1) Substance; 2) degree; 3) cal/mole•degree.

$\underline{SiO_2}$. The thermodynamic functions of gaseous sislicon dioxide, quoted in Table 237 (II), are calculated by Eqs. (II.241) and (II.242) using the rigid rotator-harmonic oscillator model approximation and on the basis of the molecular constants adopted in §87 (see page 1374). In Table 201, the values of the constants C_{Φ} and C_S in Eqs. (II.241) and (II.242), and also the values of θ_n are quoted, calculated on the basis of the adopted molecular constants of SiO_2.

The main errors of the thermodynamic functions of silicon dioxide quoted in Table 237 (II), are caused by the fact that they are calculated on the basis of estimated molecular constants of SiO_2 (up to 0.8 cal/mole•degree in the Φ_T^* values) and that the calculation was carried out by the rigid rotator-harmonic oscillator model approximation (up to 1-1.5 cal/mole•degree in the Φ_T^* values). The total errors amount to 0.2; 1.5 and 2.5 cal/mole•degree in the Φ_T^* values at 298.15; 3000 and 6000°K, respectively.

The tables of the thermodynamic functions of silicon dioxide, quoted in the first and the present edition of the Handbook are identical. In 1960, a paper by Schick [3622a] was published in which the thermodynamic functions of gaseous silicon dioxide were calculated for $T \leqslant 3000°K$ on the basis of estimated values of the molecular constants of SiO_2. The differences between the data of Schick's calculations and the data of Table 237 (II) amount to 0.6 cal/mole•degree in the Φ_T^* and S_T° values.

SiF_2 and $SiCl_2$. The thermodynamic functions of SiF_2 and $SiCl_2$, quoted in Tables 240 (II) and 244 (II), were calculated by Eqs. (II.243) and (II.244) in the rigid rotator-harmonic oscillator model approximation. The calculation was carried out using the constants adopted above (see Table 199). In Table 201, the values of the constants C'_{Φ} and C'_S in Eqs. (II.243) and (II.244) and the values of θ_n are quoted, calculated by means of the adopted molecular constants of SiF_2 and $SiCl_2$.

The fundamental errors in the values of the thermodynamic functtions of SiF_2 And $SiCl_2$, quoted in Tables 240 (II) and 244 (II), are caused by the inaccuracy of the adopted values of the molecular constants of these molecules (about 0.5 cal/mole•degree in the Φ_T^* values) and also by the fact that the calculations have been carried out in the rigid rotator-harmonic oscillator model approximation (up to 0.1 cal/mole•degree in the values of these quantities). The total error in the Φ_T^* values of both gases at 298.15; 3000 and 6000°K is estimated as equal to 0.3; 1.5 and 2.5 cal/mole•degree.

The thermodynamic functions of $SiCl_2$, quoted in the first and the present edition of the Handbook, are identical. The thermodynamic functions of SiF_2 differ by quantities of the range of 0.2 cal/mole••degree. These differences are caused by the fact that in the first edition the calculation was carried out on the basis of estimated fundamental frequencies of SiF_2 (see page 1375). Other calculations of the thermodynamic functions of the gases in question are unknown in literature.

$\underline{SiF_3 \text{ and } SiCl_3}$. The thermodynamic functions of SiF_3 and $SiCl_3$, quoted in Tables 241 (II) and 245 (II), were calculated by Eqs. (II.243) and (II.244) in the rigid rotator-harmonic oscillator model approximation. The calculation was carried out using the molecular constants adopted in §87 (see Table 199). In Table 201, the values of the constants C'_Φ and C'_S of the equations (II.243) and (II.244) and also of θ_n are quoted which have been found on the basis of the adopted molecular constants of SiF_3 and $SiCl_3$. Owing to the fact that the molecules of SiF_3 and $SiCl_3$ possess doublet electron ground states, the addends R ln 2 are included into the values of C'_Φ and C'_S.

The fundamental errors in the thermodynamic functions of SiF_3 and $SiCl_3$, quoted in Tables 241 (II) and 245 (II), are caused by the lack of experimental data on the vibration frequencies and structural parameters (or moments of inertia) of both molecules and also on the values of other constants necessary for the accurate calculation (constants of anharmonicity, interaction, etc.). These errors are of the order of 1 and 3 cal/mole•degree in the values of $\Phi^*_{298.15}$ and Φ^*_{3000} of both gases, and they can obviously exceed 5 cal/mole•degree in the values of Φ^*_{6000}.

The differences between the thermodynamic functions of SiF_3 and $SiCl_3$, quoted in the first and present edition of the Handbook, are caused by some alterations of the constants of these molecules adopted in the corresponding calculations; they do not exceed 0.1 cal/mole•degree for SiF_3 and 0.5-0.6 cal/mole•degree for $SiCl_3$. Other calculations of the thermodynamic functions of both gases are unknown in literature.

SiF_4 and $SiCl_4$. The thermodynamic functions of gaseous silicon tetrafluoride and tetrachloride, quoted in Tables 242 (II) and 246 (II) were calculated by Eqs. (II.243) and (II.244) in the rigid rotator-harmonic oscillator model approximation. The calculations were carried out on the basis of the molecular constants adopted in the preceding section (see Table 199). In Table 201, the values of the constants C'_Φ and C'_S in the Eqs. (II.243) and (II.244) and also those of θ_n, found by means of the adopted molecular constants of SiF_4 and $SiCl_4$, are quoted.

The errors in the calculated values of the thermodynamic functions amount to about 0.4; 3 and 5 cal/mole•degree in the values of $\Phi^*_{298.15}$; Φ^*_{3000} and Φ^*_{6000} for SiF_4, and about 0.7; 4 and 6 cal/mole•degree for $SiCl_4$. The errors caused by inaccuracy of the adopted values of fundamental frequencies and structural parameters, however, do not exceed 0.1-0.2 cal/mole•degree, and the fundamental errors are casued by lack of data on the anharmonicity of the vibrations, constants of centrifugal stretching and vibrational-rotational interaction.

The thermodynamic functions of silicon tetrafluoride and tetrachloride have been calculated in a number of papers for moderate temperatures. Thus, the thermodynamic functions of SiF_4 have been calculated by Voelz, Meister and Cleveland [4116, 4117] $(T \leqslant 1000°K)$; Ryss [354] $(T \leqslant 600°K)$ and Mikawa [2911a] $(T \leqslant 1500°K)$, and those of $SiCl_4$ by Cerny and Erdos [1078] $(T \leqslant 1000°K)$, Schneider and Pliva [3645] $(T \leqslant 1500°K)$ and Mikawa [2911a] $(T \leqslant 1500°K)$. The results of all these calculations conform to the data quoted in Tables 242 (II) and 246 (II) within the limits 0.05-0.15 cal/mole•degree; the existing differences are caused by somewhat different values of the fundamental frequencies of SiF_4 and $SiCl_4$ assumed in the calculations. A table of the thermodynamic functions of SiF_4, calculated in paper [4116] is cited in Zeise's book [4384].

Strelkov and co-workers [48] measured the specific heat of SiF_4 at temperatures from 13 to 194.4°K and also the melting and evaporation heats of this substance. On the basis of the data obtained, the authors of this paper found $S^{\circ}_{193,66} = 60,682 \pm 0,04$ cal/mole•degree and $S_{298,16} = 67,52 \pm 0,1$ cal/mole•degree,* which conforms satisfactorily to the value $S^{\circ}_{298,15} = 67,435$ cal/mole•degree quoted in Table 242 (II).

The thermodynamic functions of SiF_4, quoted in the first and present edition of the Handbook, are identical; the thermodynamic functions of $SiCl_4$ differ by 0.1-0.15 cal/mole•degree due to a more accurate determination of the fundamental frequency ν_3.

<u>SiC_2 and Si_2C.</u> The thermodynamic functions of gaseous SiC_2 and Si_2C, quoted in Tables 250 (II) and 251 (II), were calculated by Eqs. (II.241) and (II.242) in the rigid rotator-harmonic oscillator model approximation. The calculation was carried out on the basis of the molecular constants estimated in the foregoing section (see Table 199). In Table 201, the values of the constants C_{Φ} and C_S of Eqs. (II.241) and

(II.242) and also of θ_n are given, calculated on the basis of the adopted molecular constants of the gases in question.

The errors in the thermodynamic functions of SiC_2 and Si_2C, quoted in Tables 250 (II) and 251 (II), were caused by the lack of experimental data on fundamental frequencies and structural parameters of these molecules (see page 674) and also by the fact that the deviation of the molecules of both gases from the rigid rotator-harmonic oscillator model was not taken into account in the calculations. These errors are of the order of 0.5; 1.5 and 3 cal/mole•degree. Tables of thermodynamic functions of SiC_2 and Si_2C have not been previously published in literature; the values of Φ^*_T of both gases for $T = 2000-2300°K$ have been calculated in the work by Inghram and co-workers [1406]. The values for SiC_2, quoted in this paper, conform to the data of Table 250 (II) within limits of 0.02 cal/mole•degree in spite of the essential difference in the values of ν_2 and r_{Si-C} adopted in the calculations (see page 1385). The Φ^*_T values of silicon semicarbide differ by cal//mole•degree. These differences were caused mainly by the fact that a different symmetry of the SiC_2 molecule was assumed in paper [1406] than that in the present Handbook (see pages 1385 and 1386).

§89. THERMODYNAMIC PROPERTIES OF Si, SiO_2 AND SiC IN SOLID AND LIQUID STATES

The thermodynamic functions of Si, SiO_2 and SiC in solid and liquid states [Tables 242 (II) 236 (II) and 248 (II)] were calculated by Eqs. (III.9)-(III.11) on the basis of the values of thermodynamic quantities quoted in Table 202. The errors of the calculated Φ^*_T values at temperatures 298, 1000, 1500, 2000 and 3000°K, estimated on the basis of an analysis of the possible errors in the initial data, are quoted in Table 203.

Si. Silicon has a diamond type crystal structure with the coordination number 4. Data on a polymorphism of silicon are lacking.

The specific heat of silicon at low temperatures has been measured by Nernst and Schwers [3046] (20—90°K) ; Anderson [549] (61—296°K) Pearlman and Keyes [3207] (1—100°K) ; Keyes and Seidel [2344] (1,2—4,2°K) , and Flubacher, Leadbetter and Morrison [1570] (8—300°K). The data obtained by these investigators conform satisfactorily to one another. The measurements carried out by Flubacher et al are the most reliable (with an accuracy of ±0.2% in the 20—300°K range, and with an accuracy of ±0.5% at temperatures lower than 20°K). The values $S^{\circ}_{298,15}=4,50\pm0,02$ cal/g-atom•degree and $H^{\circ}_{298,15}-H^{\circ}_{0}=770\pm3$ cal/g-atom were adopted in the Handbook on the basis of the data of [1570], also taking into account the measurement results of the other investigators.

The enthalpy of solid silicon at high temperatures was measured by Magnus [2733] (298—1174°K) ; Serebrennikov and Gel'd [372] (298—1556°K) ; Olette [3127] (1473—1685°K) and Kantor, Kisel' and Fomichev [207] (1245—1690°K) . The obviously most reliable data of enthalpy of solid silicon were obtained by Serebrennikov and Gel'd [372] who carried out the greatest number of measurements (48) of the enthalpy of three different specimens of silicon and obtained values which conformed well to one another and also to the measuring results of Magnus [2733] (below 1174°K), Kantor et al [207] (above 1245°K), Olette [3127] (above 1473°K). On the basis of the values $H^{\circ}_{1500}-H^{\circ}_{298,15}=7380$ and $H^{\circ}_{900}-H^{\circ}_{298,15}=3460$ cal/g-atom, obtained by the data of [372], and also the value $C_{p_{298,15}}=4,73$ cal/g-atom•degree [2364], the authors of the Handbook developed an equation for the specific heat of solid silicon, which is cited in Table 202.

The measurements of the melting point of silicon, carried out by diverse investigators, results in values from 1683 to 1696°K: Hoffmann and Schulze [2095] (1683 ± 2°K) ; Olette [3127] (1685°K) ; Gayler

[1674] (1688±2°K) , Kantor et al [207] (1690±4°K) , and Wartenberg [4160] (1696°K) . The causes of the essential differences in the data of these authors remain unknown. It is impossible to estimate the accuracy of the highest value of 1696°K , obtained by Wartenberg [4160], because the measuring methods are not described in his paper. In the Handbook the value 1690°K is adopted according to the data of Kantor and co-workers [207]; the accuracy of this value is estimated as ±6°K.

TABLE 202

Adopted Values of the Thermodynamic Functions of Silicon and Its Compounds in Solid and Liquid State

1 Вещество	2 Состояние	$H^\circ_{298,15} - H^\circ_0$	$S^\circ_{298,15}$	$C^\circ_{p\,298,15}$	3 Коэффициенты в уравнении для C_p^{a}			4 Интервал температуры	T_m или T_{tr} 5	ΔH_m или ΔH_{tr} 5
		кал/моль 6	7 кал/моль·град		a	$b\cdot10^3$	$c\cdot10^{-5}$	°K	°K	кал/моль
Si	8 Крист.	770	4,50	4,73	5,664	0,79	1,04	298,15—1690	1690	11900
Si	9 Жидк.	—	—	—	7,1	—	—	1690—5800	—	—
SiO_2	10 Кварц II	1657	10,00	10,63	11,22	8,20	2,70	298,15—848	848	290
SiO_2	Кварц I	—	—	—	14,41	1,94	—	848—1140	1140	120
SiO_2	11 Тридимит I	—	—	—	13,64	2,64	—	1140—1743	1743	50
SiO_2	12 Кристобалит I	—	—	—	14,40	2,04	—	1743—2001	2001	1840
SiO_2	Жидк.	—	—	—	24,0	—	—	2001—4900	—	—
SiC	13 Крист., гекс.	777	3,935	6,39	9,93	1,92	3,66	298,15—1800	—	—
SiC	Крист., гекс.	—	—	—	12,26	0,56	—	1800—3100	3100	—

a) $C_p^\circ = a + bT - cT^{-2}$ (cal/mole·degree)

1) Substance
2) state
3) coefficient of the equation for C_p
4) temperature range
5) or
6) cal/mole
7) cal/mole·degree
8) crystalline
9) liquid
10) quartz
11) tridymite
12) crystobalite
13) crystalline, hexagonal.

The enthalpy of liquid silicon was measured by Korber and Oelsen [2463] (1873°K) ; Olette [3127] (1685—1823°K , 15 measurements), and

Kantor et al [207] ($1698-1915^\circ K$, 14 measurements). The value $C^\circ_p=11{,}2$ cal/g-atom•degree of the specific heat of liquid silicon, calculated by Chipman and Grant on the basis of the data of [2463], is erroneous. The value $C^\circ_p=6{,}12$ cal/g-atom•degree obtained by Olette [3127] is based on enthalpy measurements with in a relatively small temperature range (about 140°K); owing to this fact this value is very inaccurate. Numerical values of enthalpy are not given in paper [3127], and it is therefore impossible to estimate the accuracy of the C°_p value. The most reliable data on the enthalpy of liquid silicon have been obtained by Kantor, Kisel' and Fomichev [207]. According to the equation $C^\circ_p= 6{,}02+0{,}597\cdot10^{-3}T$ derived by them, the specific heat of Si (liqui.) changes from $C^\circ_{p_{1690}}=7{,}03$ to $C^\circ_{p_{1915}}=7{,}16$ al/g-atom•degree. Based on the data of paper [207] the constant value $C^\circ_p=7{,}1\pm0{,}3$ cal/g-atom•degree is adopted in the Handbook as the specific heat of liquid silicon, and this values was also used in the calculations of the thermodynamic functions of silicon at temperatures above 1915°K.

The melting heat of silicon is, according to the data by Olette [3127], equal to 12.1 ± 0.1 kcal/g-atom, and, according to Kantor and co-workers [207],-11.95 ± 0.18 kcal/g-atom. The first value is less reliable owing to the inaccuracy of the data on the specific heat of liquid silicon in [3127] (see above). Using the data of [207] on the enthalpy of solid and liquid silicon, the value $\Delta Hm_{1690}=11{,}9\pm0{,}2$ kcal/ /g-atom is adopted in the Handbook; the insignificant alteration in comparison to the data recommended in [207] is due to the alteration in the form of the equation for the specific heat of liquid silicon.

The values of the thermodynamic functions of silicon in solid and liquid states, calculated for temperatures from 293,15 to 5800°K, are quoted in Table 232 (II). The values of the errors of the calculated Φ^*_T values are quoted in Table 203.

The values of the thermodynamic functions of solid silicon, quoted in Table 232 (II), do not differ from the values calculated in the first edition of the Handbook. The differences between the thermodynamic functions of liquid silicon, quoted in the first edition of the Handbook and the values by Stull and Sinke [3894] at temperatures up to 3000°K do not exceed 0.2 and 0.5 cal/g-atom•degree in the Φ_T^* and S_T° values, respectively, and are caused by a more accurate determination of the melting and specific heat of liquid silicon.

SiO$_2$. Three crystalline modifications of solid silicon dioxide are known: quartz, tridymite and cristobalite, each of which is in a thermodynamical equilibrium in a certain temperature range:*

$$\text{quartz II} \underset{848^\circ\text{K}}{\rightleftarrows} \text{quartz I} \underset{1140^\circ\text{K}}{\rightleftarrows} \text{tridymite I} \underset{1743^\circ\text{K}}{\rightleftarrows} \text{cristobalite I}$$

In the present Handbook, the thermodynamic functions of silicon dioxide are calculated for the equilibrium states indicated above.

The specific heat of quartz at low temperatures has been measured by Abderson [551] **(25—233°K)** and Nernst [3042] **(53—297°K)** . Based on these data, Mosesman and Pitzer [2959], and Kelley [2364] calculated the values $S^\circ_{298.15} = 10{,}00 \pm 0{,}1$ cal/mole•degree and $H^\circ_{298.15} - H_0^\circ = 1657 \pm 10$ cal//mole, which have been adopted in the Handbook.** The equations for the specific heat of the diverse SiO$_2$ modifications, recommended by Kelley [2364a] on the basis of an analysis of the results of numerous measurements of specific heat and enthalpy of silicon dioxide, carried out by Mosesman and Pitzer [2959], are adopted in the Handbook (see Table 202). The accuracy of the corresponding equations for the enthalpy of the diverse SiO$_2$ modifications amounts, according to an estimate by Kelley, to ±0.1% for quartz, ±0.7% for tridymite, and ±0.2% for cristobalite. The heat of the quartz conversion at 848°K, equal to 290 cal/mole,*** was also adopted according to the recommendation of Kelley [2364a]. The values recommended by Mosesman and Pitzer [2959] are adopted for the temperatures and heats of the equilibrium conversions of quartz into tridymite ($\Delta H_{1140}=120$ cal/mole) and tridymite into cristobalite ($\Delta H_{1743}=50$ cal/mole). The values of the conversion heats were obtained by these authors from the differences in the entropies of these modifications at the equilibrium conversion temperatures, which are equal to $1140\pm3°K$ and $1743\pm10°K$, according to the data by Kracek [2407b] and Fenner [1549a], respectively. Mosesman and Pitzer estimated the accuracy of the values of conversion heats obtained by them as equal to ±50 cal/mole; in fact, the errors of these values may obviously amount to some hundred calories.

The melting point of cristobalite was assumed as equal to 2001°K [3508]. Immediate determinations of the melting heat of cristobalite have not been carried out. The calculation of the melting heat of cristobalite on the basis of the heat of conversion of cristobalite into glass at room temperature (using the heat of dissolution) and the change of their enthalpy at room temperature and at the melting point gives values from 0.9 to 5.7 kcal/mole [2959]. From these, the value 1.7 kcal/mole, obtained by Roth and Troitzsch [3532], is the most reliable. The calculation of the melting heat of cristobalite on the basis of the state diagrams of cristobalite and alkali metal oxides, carried out by Kracek [2470a], gives the value $\Delta Hm_{2001}=1{,}84$ kcal/mole, which is adopted in the Handbook of the US Bureau of Standards [3508] and also in the present Handbook.

The specific heat of liquid silicon dioxide is estimated as equal to 24 cal/mole•degree (see page 261).

The values of the thermodynamic functions of silicon dioxide in solid and liquid state, calculated for temperatures from 293.15 to 4900°K, are quoted in Table 236 (II). The values of the errors of the calculated Φ_T^* values are given in Table 203.

The Tables of the thermodynamic functions of SiO_2, quoted in the first and present edition of the Handbook, are identical.

SiC. Silicon carbide forms a series of crystalline modifications from which the cubic low-temperature modification (β-SiC) and the high-temperature hexagonal modification (α-SiC) are thermodynamically in equilibrium. According to the various data, the conversion of β-SiC into α-SiC occurs at temperatures from 1800 to 2200°K. The conversion heat at room temperature, determined from the difference in the combustion heats of both modifications [2158], amounts to 1.1 kcal/mole.

The calculation of the thermodynamic functions of silicon carbide was carried out for the hexagonal high-temperature modification, because the temperature and heat of the polymorphous equilibrium conversion of β-SiC into α-SiC has not yet been determined. It was assumed that the values of thermodynamic functions of both modifications are similar, because, owing to the data of [2158], the difference between the entropies of the cubic and hexagonal modification amounts to only 0.03 cal/mole•degree at 298.15°K.*

The specific heat of silicon carbide at low temperatures was measured by Kelley [2361] (53—295°K), who calculated the value $S^{\circ}_{298.15}=3{,}95$ cal/mole•degree. The extrapolation of the specific heat above 53.1°K gives only 0.043 cal/mole•degree. The values $S^{\circ}_{298.15}=3{,}935$ cal/mole•degree and $H^{\circ}_{298.15}-H^{\circ}_{0}=777$ cal/mole are recommended on the basis of the same data in the Handbook of the US Bureau of Standards, and are also adopted in the present Handbook. The possible errors of these values amount to ±0.05 cal/mole•degree and ±10 cal/mole, respectively.

The enthalpy of solid silicon carbide at high temperatures was measured by Magnus [2733] (290—1173°K), Weigel [4192] (273—1224°K) Miehr, Immke and Kratzert [2901, 2902] (290—1629°K), Humphrey, Todd, Coughlin and King [2158] (298—1789°K), Maksimenko and Polubelova [287] (288—1273°K), and Fomichev, Krasovitskaya and Kantor [15] (1220—2469°K). The most reliable data among the first four papers are obviously those of Humphrey et al [2158]. The values of the enthalpy of the hexagonal and cubic modifications of SiC, obtained by them, differ only by 0.5%. Based on these data, Kelley [2364a] derived an equation for the specific heat of the hexagonal SiC modification which is adopted in the present Handbook up to 1800°K (see Table 202). Kelley [2364a] estimated the accuracy of the corresponding equation for the enthalpy as equal to ±0.6%. The measuring results, carried out by the authors of [287, 15] for "black" and "green" specimens of silicon carbide* fer considerably from each other. The experimental values of the enthalpy, obtained by the authors of [15] for the "black" silicon carbide specimen (98.85% SiC), are at 1200°K by 0.7% lower than the data of [2364a]. The difference increases systematically with rising temperature up to 1.5% at 1800°K. The data of [15] for the "green" SiC specimen (99.05% SiC) are, on an average, by 10% higher than the data of [2364a]. Owing to such essential differences, which are explained in paper [15] by different structure and states of the investigated specimens, the authors of the present Handbook developed an equation for the specific heat of silicon carbide in the range from 1800 to 3100°K (see Table 202) on the basis of the value $C^{\circ}_{p_{1800}} = 13{,}27$ cal/mole•degree [2364a] and the estimated value of the specific heat at the temperature of decomposition of SiC $C^{\circ}_{p_{3100}} = 14.0$ cal/mole•degree (see page 257).

The values of the enthalpy of SiC, calculated by means of this equation for the temperature range from 1800 to 2500°K, are by 1.5-3% higher than the values obtained in paper [15] for the "black" SiC specimen. This difference obviously characterizes the accuracy of the values of SiC enthalpy adopted in the Handbook for 2500°K.

According to the data by Scace and Slack [3598a], an incongruent fusion of silicon carbide and decomposition into graphit and a liquid solution of carbon in silicon (with the composition 19% C and 81% Si) occurs at3100 ± 40°K. When the temperature rises, the separated graphite dissolves, and a more concentrate solution of carbon in silicon results; a single-phase solution with the composition SiC is formed at temperatures of the order of 3600°K [3598a]. In Table 248 (II), the thermodynamic functions of silicon carbide are given, but only up to 3100°K.

The values of the thermodynamic functions of silicon carbide in solid state, calculated for temperatures from 293.15-3100°K, are quoted in Table 248 (II). The magnitudes of the errors in the calculated Φ_T^* values are given in Table 203.

TABLE 203

Errors (in cal/mole•degree) of the Φ_T^* Values of Silicon and Its Compounds in Solid and Liquid States

T, °K	298	1000	1500	2000	3000
Si	±0,02	±0,05	±0,08	±0,15	±0,5
SiO_2	±0,1	±0,2	±0,3	±0,4	±1,2
SiC	±0,05	±0,2	±0,3	±0,4	±0,8

§90. THERMOCHEMICAL QUANTITIES

Si (cryst.)is the standard state of silicon.

Si (gas). The sublimation heat of silicon can be calculated on the basis of measurements, carried out by different authors, of the vapor pressure of silicon and silicon carbide, and also on the basis of the quantity $D_0(SiO)$. The results of the corresponding calculations, carried out by the authors of the Handbook, are quoted in Table 204.

The calculations have been carried out under the presumption, that the silicon vapor is monatomic.

TABLE 204

Results of the calculation of the Sublimation Heat of Silicon

1 Авторы	2 Год	3 Метод	4 Интервал температур, °K	ΔHs_0, ккал/г-атом 5
Руфф, Коншак [3556] 6	1926	14 Кипения 15 (разложение SiC)	2673—2990	100
Баур, Бруннер [691] 7	1934	Кипения 14	1980—2373	89
Руфф и др. [3550, 3556] 8	1935	»	2163—2607	89
Барроу, Роулинсон [662] 9	1954	D_0 (SiO)		104±8
Хониг [2118] 10	1954	Масс-спектрометрический 16	1450—1600	105±12
Дроварт и др. [1406] 11	1958	Масс-спектрометрический (разложение SiC)	2149—2316	111±5
12 Несмеянов и др. [22, 13, 452a]	1958	Кнудсена 17	1493—1585	91±1,5
Батдорф, Смитс [676] 13	1959	Испарение с поверхности 18	1473—1623	105

1) Authors
2) year
3) method
4) temperature range
5) kcal/g-atom
6) Ruff, Konshak
7) Ruff, Brunner
8) Ruff et al.
9) Barrow, Rowlinson
10) Honig
11) Drowart et al.
12) Nesmeyanov et al.
13) Batdorf, Smits
14) boiling
15) decomposition of SiC
16) mass-spectrometrical
17) Knudsen
18) evaporation from the surface.

Ruff and Konshak [3556] investigated the evaporation of silicon carbide and determined the equilibrium constants of the reaction

$$\mathrm{SiC}\,(\text{cryst.}) = \mathrm{C}\,(\text{graphite}) + \mathrm{Si}\,(\text{gas}) \qquad (\text{XXII.1})$$

and its thermal effect $\Delta H_0 = 106{,}6$ kcal/mole. The calculation by means of the thermodynamic functions of the components of reaction (XXII.1), adopted in the present Handbook, results in a higher value $\Delta H_0 = 111$ kcal/mole, to which ΔHs_0 (Si, cryst.) = 100 kcal/g-atom corresponds.

The concurrent values $\Delta Hs_0 = 89$ kcal/g-atom have been obtained in papers [691, 3550, 3556] by determination of the boiling point. The similar value $\Delta Hs_0 = 91$ kcal/g-atom was found by An. Nesmeyanov et al

[22, 13, 452a] by the Knudsen method, using effusion chambers with an orifice ratio of 1:22,600. As noted in paper [13], the calculated values of the pressure of silicon vapor decrease and the values of the sublimation temperature increase when the orifice ratio of the effusion chamber exceeds 1:800.

In the paper by Batdorf and Smits [676], the evaporation rate of silicon on an open surface was measured, and the sublimation heat was found as equal to $\Delta Hs_0 = 105$ kcal/g-atom.

The mass-spectrometrical investigation of the evaporation of silicon, carried out by Honig [2118], gave the temperature dependence of the Si^+ ion current, corresponding to $\Delta Hs_{1480} = 105 \pm 12$ kcal/g-atom (the reduction to 0°K hardly changes this value).

The investigation of the composition and the partial pressures of the evaporation products of silicon carbide, carried out by the mass-spectrometrical method by Drowart, De-Maria and Inghram [1406], showed that monatomic silicon is the main product of evaporation. The values of the partial pressures of the silicon vapor, generated as a result of the reaction (XXII.1), have been found in this work. These values correspond to a thermal effect of the reaction (XXII.1) equal to $\Delta H_0 = 122,9 \pm 3$ kcal/mole,* and ΔHs_0 (Si, cryst.) = 111 ± 5 kcal/g-atom.

Thus, the investigation of surfacial evaporation [676] and the mass-spectrometrical investigations [2118, 1406] result in a value of ΔHs_0 (Si, cryst.), which is considerably higher than that which was obtained by the Knudsen method [22, 452a] and the determination of the boiling point [3556, 691, 3550]. It was mentioned above that the calculated values of the sublimation heat increase when the ratio of the effusion orifices increases. Since the orifice ratio in mass-spectrometrical investigations is usually greater than 1:800 (1:500, for example, in paper [1406]), it remains uncertain whether or not these results are really contradictory, because it is possible that the mass-spectrometrical and effusion method will give similar results under equal conditions.

The determination of the sublimation heat of silicon gives results very similar to those obtained for carbon (see page 948) and boron (see page 1514). Just as in the case of carbon and boron, the experimental data for silicon may be explained if one assumes the formation of associated Si_n molecules with very low evaporation coefficients in the saturated silicon vapor. In this case, the effusion measurements give the pressure of saturated silicon vapor, the main component of which are the hypothetical Si_n molecules, and the mass-spectrometrical measurements give the partial pressure of monatomic silicon. The other possible explanation, a very low value of the evaporation coefficient of monatomic silicon, is hardly probable because the evaporation of the atoms proceeds, as a rule, at an evaporation coefficient hear to the unity.

The value of $D_0(SiO)$, obtained by Barrow and Rowlinson [662], also argues in favor of a higher value of the sublimation heat of silicon. On the basis of the vibrational constants of the SiO molecule in the excited E state, and a comparison of the convergence of the vibrational levels of the E state and the ground electron states of the molecules of oxides, sulfides and selenides of germanium, silicon and stannum, Barrow and Rowlinson obtained $D_0(SiO) = 185 \pm 7$ kcal/mole. ΔHs_0 (Si, cryst.) = 185 ± 7 kcal/g-atom corresponds to this value.

In accordance with the considerations quoted above, the value

$$\Delta Hs_0(\mathrm{Si,\ cryst.}) = \Delta H^{\circ}f_0(\mathrm{Si,\ gas}) = 111 \pm 5 \text{ kcal/g-atom},$$

obtained by Drowart et al [1406] is adopted in the Handbook.

The adopted interpretation of the experimental data on the determination of the sublimation heat of silicon is not indisputable. The definitive solution of this problem requires additional experimental investigations.*

Si_2 (gas). The linear extrapolation of the vibrational levels of the Si_2 molecule, carried out on the basis of the data by Douglas [1371], results in a dissociation energy equal to approximately 92 kcal/mole. If, in accordance with Gaydon's recommendation [141, 1668], we decrease this value by 20%, the dissociation energy of Si_2 will be equal to 74 kcal/mole with a possible error of approximately ± 18 kcal/mole. The estimation of the dissociation energy of Si_2 on the basis of Lippincott's and Schroeder's relation [2625] gives $D_0(Si_2)=72$ kcal/mole.**

The value of the dissociation energy of Si_2 can be calculated on the basis of the investigations of the evaporation of silicon and silicon carbide. Honig [2118] determined by this method the composition of the silicon vapor and calculated by the temperature dependence of the Si^+ and Si_2^+ ionic currents the sublimation temperature of silicon atoms as equal to $\Delta Hs_{1880}=105\pm12$ kcal/g-atom and the heat of the reaction

$$2Si\,(\text{cryst.})=Si_2\,(\text{gas}), \qquad (XXII.2)$$

as equal to $\Delta H_{1880}=135\pm12$ kcal/mole. $D_{1880}(Si_2)=75\pm18$ kcal/mole or $D_0(Si_2)=71\pm18$ kcal/mole correspond to these values.

Drowart, De-Maria and Inghram [1406] investigated by the mass-spectrometrical method the composition of the evaporation products of silicon carbide. The values of the partial pressures of Si and Si_2, found in this work, correspond to the dissociation energy $D_0(Si_2)=77\pm5$ kcal/mole (the similar value of 75 kcal/mole was calculated by the authors of [1406]). The data quoted in paper [1406] also permit the determination of the thermal effect of the reaction

$$2SiC(\text{cryst.}) = 2C(\text{graphite.}) + Si_2(\text{gas})$$

equal to $\Delta H_0=170{,}7$ kcal/mole, to which corresponds $D_0(Si_2)=74{,}5$ kcal/mole.

The results of the calculations of $D_0(Si_2)$ by the data by Honig [2118] and Drowart et al [1406] show a sufficient conformity. The mean value

$$D_0(Si_2) = 74 \pm 5 \text{ kcal/mole.}$$

is adopted in the Handbook.

To this adopted value corresponds

$$\Delta H^\circ f_0(Si_2, \text{ gas}) = 148 \pm 9 \text{ kcal/mole.}$$

SiO (gas). The value of the heat of formation of gaseous silicon monoxide can be calculated by the results of the investigations of the heterogeneous equilibria

$$Si(\text{cryst.}) + SiO_2(\text{cryst.}) = 2SiO(\text{gas}).$$

$$SiO_2(\text{cryst.}) + H_2(\text{gas}) = SiO(\text{gas}) + H_2O(\text{gas}).$$

The equilibrium (XXII.3) was investigated by Schafer and Hornle [3600], Gel'd and Kochnev [144, 145], and Brewer and Mastik [925], and the equilibrium (XXII.4) was investigated by Grube and Speidel [1866]. Tombs and Welch [3998] investigated both equilibria. The results of these words have been discussed by Brewer and Edwards [920], Baughan [686] and Gel'd and Yesin [143]. Baughan recalculated the results, obtained in the papers mentioned above, and obtained for the thermal effect of the reaction (XXII.3) the values 164.7 [3600], 167.2 [3998] and 171.2 kcal/mole [3998] (in the paper by Tombs and Welch [3998], two series of measurements of the equilibrium (XXII.3) have been carried out), and for the reaction (XXII.4) the values 134.7 [1866] and 130.3 kcal/mole [3998]. Owing to the fact that the thermodynamic functions, adopted by Baughan [686] for these calculations, differ only insignificantly from those adopted in the present Handbook, the values of the thermal effects of the reactions (XXII.3) and (XXII.4), calculated by Baughan, are used in the subsequent calculations. The data by Schafer and Hornle [3600] and Tombs and Welch [3998], to which correspond the heats of formation of silicon monoxide $\Delta H^{\circ}f_0 = -22{,}0 \pm 0{,}5$ kcal/mole [3600] and -21.4 ± 1.5 kcal/mole [3998], are the most reliable data.

Brewer and Mastik [925] and Nesmeyanov and Firsova [Belykh) [317, 21] studied by the effusion method the pressure of silicon dioxide vapor in the temperature ranges 1840-1951 and 1601-1754°K, respectively. At these temperature ranges the vapor of silicon dioxide consists almost of SiO and oxygen, and, therefore, the thermal effect of the reaction

$$SiO_2\,(\text{крист.}) = SiO\,(\text{gas}) + O\,(\text{gas}) \qquad \text{(XXII.5)}$$

and the heat of formation of SiO can be calculated on the basis of these experiments.

Brewer and Edwards [920] corrected the results of the calculation in [925] and found the heat of the reaction (XXII.5) as equal to $\Delta H_0 = 245{,}6 \pm 2{,}7$ kcal/mole, to which corresponds $\Delta H^{\circ}f_0$ (SiO, gas) = = -22.2 ± 2.9 kcal/mole. On the basis of the data obtained in [317, 21 the value of the thermal effect of the reaction (XXII.5) was found as equal to $\Delta H_0 = 247{,}1 \pm 1{,}2$ kcal/mole, and thus, $\Delta H^{\circ}f_0$ (SiO, gas) = = -21.7 ± 2 kcal/mole.

Thus, the results of the most accurate determinations of the equilibrium constants of (XXII.3), (XXII.4) and (XXII.5) conform well to one another. In the Handbook, the rounded off value

$$\Delta H^{\circ}f_0\,(SiO,\ \text{gas}) = -22{,}0 \pm 1\ \text{kcal/mole}.$$

is adopted.

The value of the dissociation energy of silicon monoxide, calculated by the spectroscopical data, is used for the choice of the sublimation energy of silicon, because the latter value is less accurate in comparison with the heat of formation of SiO (gas).

The value

$$D_0(\mathrm{SiO}) = 191{,}987 \pm 5{,}1 \text{ kcal/mole.}$$

corresponds to the adopted values $\Delta H^\circ f_0$ (SiO, gas) and ΔHs_0 (Si, cryst.).

SiO_2 (quartz). The results of measurements of the combustion heat of elemental silicon in oxygen, carried out up to 1936, are discussed in the Handbook by Bichowsky and Rossini [813]. The values obtained in these words are inaccurate and contradictory, a fact which may be explained mainly by an insufficient purity of the silicon samples.

Roth and co-workers [3513, 3519, 3529, 3532] carried out several determinations of the combustion heat of silicon and obtained values of the heat of formation of quartz within the limits from -204 to -208.3 kcal/mole.

Humphrey and King [2157] carried out the most accurate measurement of the combustion temperature of silicon. These authors ananlyzed roentgenographically the combustion products and introduced corrections for the formation of the various crystalline modifications of silicon dioxide. In paper [2157], the value of the heat of formation of the main product of combustion of silicon, cristobalite II, was found as equal to $\Delta H^\circ f_{298,16} = -209{,}33 \pm 0{,}25$ kcal/mole. Coughlin [1193] recalculated this value, taking into account the altered atomic weight of silicon, and obtained $\Delta H^\circ f_{298,16} = -209{,}55 \pm 0{,}25$ kcal/mole.

Many investigators (references are given in [2155a]) determined the heat of the conversion of cristobalite II into quartz by measuring the heat of solution of these modifications in hydrofluoric acid. Humphrey and King [2157] found the value $\Delta H_{298,16} = -0{,}93 \pm 0{,}09$ kcal/mole. Humel and Schwiete [2155a] carried out a very minute determination by this method. They showed in particular that, in contrast to the more obsolete measurements, the heat of dissolution obtained by them does not depend on the degree of pulverization of the initial sample. The value of the heat of conversion $\Delta H_{298.15} = -1,80 \pm 0,23$ kcal/mole was obtained in this paper.

Another way of determining the heat of conversion of cristobalite into quartz is also possible; it was first used by Mosesman and Pitzer [2959]. These authors used data on the heats of the equilibrium conversions quartz – tridymite and tridymite – cristobalite, calculated by them on the basis of the different entropies of these modifications in the conversion points (more in detail, see page), and found the heat of conversion of cristobalite into quartz as equal to $\Delta H_{298.15} = -0,35$ kcal/mole. This value was also adopted by Coughlin [1193]. The calculation based on the more accurate data on the enthalpies of quartz, cristobalite and tridymite, recommended by Kelley [2364a] and adopted in the present Handbook, leads to the value $\Delta H_{298.15} = -0,42$ kcal/mole.

Thus, the results of calculations of the heat of conversion of cristobalite into quartz, based on measurements of the heat of solution and on the thermodynamic functions of these modifications are not uniform. Owing to the necessity of coordinating all data in the Handbook, including the accordance between the heats of formation and the thermodynamic functions, a heat of conversion of cristobalite into quarts equal to $\Delta H_{298.15} = -0,42$ kcal/mole is adopted in the Handbook for the subsequent calculations, and

$$\Delta H^{\circ}f_{298.15}(\mathrm{SiO_2},\ \text{кварц}) = -210 \pm 1,5 \text{ kcal/mole.}$$

corresponds to this value.

There is no reason, however, to regard the results of measurements of the heats of dissolution as being erroneous. Thus, a considerable error must be ascribed to the heat of formation of quartz, adopted in the Handbook.

SiO_2 (gas). The values of the sublimation temperature of silicon dioxide, calculated by the authors of the Handbook on the basis of measurements of the pressure of silicon dioxide vapor, are quoted in Table 205. With the exception of papers [3304, 88], the calculations have been carried out under the assumption that the vapor contains only SiO_2 (gas) molecules. The thermodynamic calculations, however, based on the data for SiO (gas), show that the evaporation of silicon dioxide must be accompanied by a dissociation of SiO_2 (gas) into SiO (gas). The mass-spectrometrical investigation [3304] corroborates these calculations. Thus, the values of $\Delta H_{s0}(\mathrm{SiO_2})$, calculated by the data of [3564, 3556, 2181, 2182, 925, 317, 21], must be considered as only the lower limits of the possible values of this quantity. Moreover, it was found that the vapor pressures obtained in papers [3564, 3556] are over-evaluated owing to the fact that the investigations were carried out in ampoules, the material of which reduced the silicon dioxide to monoxide.

In the paper by Bergman and Medvedev [88], the heat of sublimation of silicon dioxide was determined according to the results of measurements of the explosion pressures of mixtures containing disilyl ethane, carbon monoxide and oxygen. The calculations showed that silicon dioxide has a low stability as a vapor and that its partial pressures are relatively small even under oxidizing conditions. Thus, only the lower limit of the possible values of the sublimation heat of silicon dioxide, equal to 130 kcal/mole, could be calculated on the basis of these experiments.

Porter, Chupka and Inghram [3304] investigated mass-spectrometrically the composition of the evaporation products of silicon dioxide, which emanated from an effusion cell. On the basis of the temperature dependence of the SiO_2^+ ionic current, the authors of [3304] the sublimation heat of silicon dioxide $\Delta Hs_{298} = 136 \pm 8$ kcal/mole, to which corresponds $\Delta Hs_0 = 135 \pm 8$ kcal/mole. Porter, Chupka and Inghram gaged the device by the wellknown vapor pressures of silver and gold and calculated the equilibrium partial pressures of SiO_2, SiO and O. The partial pressures of SiO_2 found in this way correspond to the value $\Delta Hs_0 = 140$ kcal/mole.

In the Handbook, the value of the sublimation heat of silicon dioxide

$$\Delta Hs_0(SiO_2, \text{quartz}) = 135 \pm 5 \text{ kcal/mole},$$

was adopted, which was calculated on the basis of the data by Porter, Chupka and Inghram [3304].

To the adopted value of the sublimation heat correspond

$$\Delta H^\circ f_0(SiO_2, \text{gas}) = -73{,}812 \pm 5{,}1 \text{ kcal/mole},$$

$$D_0(SiO_2) = 302{,}786 \pm 7{,}1 \text{ kcal/mole}.$$

SiH (gas). The linear extrapolation of the wellknown vibrational levels of the ground electron state of SiH gives the value $D_0(SiH) = 80{,}7$ kcal/mole.

The investigation of the spectrum of SiH, carried out by Douglas [1372], showed that the excited $^2\Delta$ state of this molecule possesses a small minimum on the potential curve; thus, a sufficiently reliable value of $D_0(SiH)$ can be obtained by a short extrapolation of the observed vibrational levels of this state. The corresponding value of the dissociation energy of SiH in the $^2\Delta$ state is equal to 7840 ± 2000 см$^{-1}$.

A correlation of the electron states of SiH with the states of Si and H atoms was carried out by Mulliken [2982] who proved that the SiH molecule in the $X^2\Pi$ ground state must dissociate into $Si(^3P) + H(^2S)$ atoms, and, in the excited $^2\Delta -$ state, into $Si(^1D) + H(^2S)$ atoms. A dissociation energy of SiH, equal to 25730 ± 2000 см$^{-1}$, or

$$D_0(SiH) = 74 \pm 6 \text{ kcal/mole.}$$

correspond to the SiH dissociation energy in the $^2\Delta$ state found in paper [1372] and to the correlation of the electron states of SiH, Si and H, suggested by Mulliken.

This value is adopted in the Handbook; to it corresponds

$$\Delta H^{\circ}f_0(SiH, \text{gas}) = 88{,}632 \pm 7{,}8 \text{ kcal/mole.}$$

Schafer and Klemm [3604a] investigated the equilibrium of the interaction of hydrogen with silicon. However, the authors failed to determine to which reaction the found hydrogen pressures correspond. Barrow and Deutsch [650a] proved that the reaction investigated in paper [3604a] cannot be the reaction of formation of SiH.

SiF (gas). The linear extrapolation of the vibrational level of the $X^2\Pi$ ground state of the SiF molecule gives the value $D_0(SiF) = 111$ kcal/mole. Gaydon [1668] obtained the too low value $D_0(SiF) = 88$ kcal/mole on the basis of erroneous data about the type of the first excited state of the SiF molecule and the inaccurate molecular constants of SiF in this state, found by Eyster [1518]. The inaccuracy of the $D_0(SiF)$ value adopted by Gaydon becomes evident when we compare it with the dissociation energies of CF and CH and the mean bond energies in SiF_4, CF_4 and CH_4. The mean energy of the Si – F bond in SiF_4 is equal to 139 kcal/mole, i.e., it is by 58% higher than the $D_0(SiF)$ value adopted by Gaydon, whereas the mean bond energies in CH_4 and CF_4 are considerably more similar to the dissociation energies of CH and CF.

The investigation of the SiF spectrum, carried out by Johns and Barrow [2257], proved that the $^2\Sigma$ state and not the $^2\Pi$, state, as it was assumed by Gaydon, is the first excited state of SiF. The comparison of the $D_0(SiF)$ values, found by linear extrapolation of the observed electron states of SiF, carried out by the authors of [2257], proved that the value 136 kcal/mole is the upper limit of the dissociation energy of SiF, and that 115 kcal/mole is its lower limit. Thus, Johns and Barrow [2257] recommend

$$D_0(\mathrm{SiF}) = 125 \pm 10 \text{ kcal/mole},$$

as the most probable value which is adopted in the present Handbook. To this value corresponds

$$\Delta H^{\circ}f_0(\mathrm{SiF}, \text{gas}) = 4{,}5 \pm 11{,}2 \text{ kcal/mole}.$$

TABLE 205

Results of the Calculation of the Sublimation Head of Silicon Dioxide

1 Авторы	2 Год	3 Метод	4 Интервал температур, K°	5 Количество опытов	6 ΔH_{s_0}, ккал/моль
7 Руфф, Шмидт [3564]	1921	Кипения 14	2073—2503	19	102±2
8 Руфф, Коншак [3556]	1926	»	2333	1	115
9 Инудзука, Агеа [2181, 2182]	1942	Испарения с поверхности 15	1273 и 1473	2	103±5
10 Бруэр, Мастик [925]	1951	Эффузионный 16	1840—1951	3	122±3
11 Портер, Чупка, Инграм [3304]	1955	Масс-спектрометрический 17	1200—1950	—	135±8
12 Несмеянов, Фирсова [317, 21]	1956	Эффузионный	1601—1754	24	125,4±1,0
13 Бергман, Медведев [88]	1959	Взрыва в сферической бомбе 18	2084—3207	24	>130

1) Authors
2) year
3) method
4) temperature range
5) number of experiments
6) kcal/mole
7) Ruff, Schmidt
8) Ruff, Konshak
9) Inuzuka, Ageha
10) Brewer, Mastick
11) Porter, Chupka, Inghram
12) Nesmeyanov, Firsova
13) Bergman, Medvedev
14) boiling
15) evaporation on a surface
16) effusion
17) mass-spectrometrical
18) explosion in a spherical bomb.

$\mathrm{SiF_2}$ (gas) and $\mathrm{SiF_3}$ (gas). The heats of formation of $\mathrm{SiF_2}$ and $\mathrm{SiF_3}$, adopted in the present Handbook,

$$\Delta H^{\circ}f_0(\mathrm{SiF_2}, \text{gas}) = -168 \pm 10 \text{ kcal/mole},$$

$$\Delta H^{\circ}f_0(\mathrm{SiF_3}, \text{gas}) = -250 \pm 10 \text{ kcal/mole}$$

were estimated by the Karapet'yants method. The calculation was based on the comparison of the heats of formation of a series of compounds:

SiF_4 and SiF with $SiCl_4$, $SiCl_3$, $SiCl_2$ and SiCl, and also SiF_4 and SiF with CF_4, CF_3, CF_2 and CF.

To the values adopted correspond

$$D_0(SiF_2) = 316 \pm 11{,}2 \text{ kcal/mole},$$
$$D_0(SiF_3) = 416{,}5 \pm 11{,}2 \text{ kcal/mole}.$$

SiF_4 (gas). The values of heats of formation of silicon tetrafluoride, quoted in the most of the contemporary thermochemical Handbooks, are based on measurements of the thermal effects of dissolution of SiF_4 and SiO_2 in hydrofluoric acid, which were carried out as long ago as in the past century. In Truchot's works [4022, 4023], the heat of dissolution (-34.0 kcal/mole) of gaseous silicon tetrafluoride in a solution of hydrofluoric acid was measured. Guntz [1898] found somewhat differing value of the heat of dissolution, equal to -33.5 kcal/mole, on the basis of his own measurements of the heat of dissolution of hydrogen fluoride, the heat of dissolution of silica in hydrofluoric acid, measured by Thomsen [3981], and the heat of hydrolysis of SiF_4, measured by Hammerl [1943]. Bichowsky and Rossini [813] calculated the value $\Delta H^\circ f_{298}$ (SiF_4, gas) = -363 kcal/mole on the basis of these data. The recalculation of this quantity, using more accurate values of the heat of formation of quartz and of the other reactions in the thermal cycles, led to the values -370 kcal/mole [3508], -370.8 kcal/mole [3532] and -373 kcal/mole [420]. These values, however, are not very reliable because the calorimetric technique of the measurements in papers [4022, 4023, 1898, 3981 and 1943] does not meet modern requirements. Moreover, these papers do not contain data about the purity of the initial substances, the concentration of the reaction products, and also about the conditions under which the experiments have been carried out.

Wartenberg and Schutte [4171] measured the heat of the immediate reaction of silicon with elemental fluorine and found $\Delta H^\circ f_{293}$ (SiF_4, gas) = -359.7 ± 2.6 kcal/mole. However, owing to the great difficulties occurring when carrying out a combustion in elemental fluorine (carbon, which gave evidently erroneous results when combusted immediately in fluorine, may serve as an example), the error in the value obtained by Wartenberg and Schutte may be considerably greater than the authors indicate. In particular, Ryss [353, 354, 356] proved that the heat of formation, obtained in this way, may be considerably too low owing to the formation of Si_2F_6, and that the correct value must be 370-373 kcal/mole.

The most accurate determination of the heat of formation of silicon tetrafluoride was carried out by Vorob'yev, Kolesov and Skuratov [34, 39, 129, 129a]. These authors measured the heat of decomposition of silicon tetraflupride (in surplus) by metallic sodium and found $\Delta H_{298,15} = -174,1 \pm 1,4$ kcal/mole. The reaction was carried out in a calorimetric bomb with a movable electrode and was initiated by an electric arc. Assuming on the basis of literature data $\Delta H^{\circ}f_{298,16}$ (NaF, cryst.) = -136, 17 kcal/mole, the authors of [34, 129a] found the heat of formation of silicon tetrafluoride as equal to -370.6 ± 1.5 kcal/mole. The recalculation of this value on the basis of the heat of formation of sodium fluoride adopted in the Handbook gives the value $\Delta H^{\circ}f_{298,15}$ (SiF_4, gas) = -372.3 kcal/mole.

Vorob'yev, Kolesov and Skuratov [39, 129, 129a] also measured the thermal effect of dissolution of silicon tetrafluoride in 19% hydrofluoric acid and found $\Delta Hf_{298,15} = -34,02 \pm 0,04$ kcal/mole. Based on this value and using the thermochemical cycle which includes the heat of dissolution of quartz in hydrofluoric acid, the value $\Delta H^{\circ}f_{298,15}$ (SiF_4, gas) = -372.3 ± 1.5 kcal/mole was found.* Moreover, the heats of dissolution of silicon tetrafluoride in water and in 0.4% hydrofluoric acid were measured in papers [129, 129a], and the values -22.56 ± 0.03

and -33.79 ± 0.05 kcal/mole, respectively, have been found. Starting from these data, the heat of formation of silicon tetrafluoride equal to -372.9 ± 1.5 kcal/mole can be calculated.

On the basis of the measurements by Vorob'yev, Kolesov and Skuratov [34, 39, 129, 129a], the value

$$\Delta H^\circ f_{298.15}(\mathrm{SiF_4},\ \text{газ}) = -372{,}5 \pm 1{,}0 \text{ kcal/mole.}$$

is adopted in the Handbook. To this value corresponds

$$D_0(\mathrm{SiF_4}) = 556{,}168 \pm 5{,}5 \text{ kcal/mole.}$$

SiCl (gas). The linear extrapolation of the wellknown vibrational levels of the $X^2\Pi$ ground state of the SiCl molecule gives the value $D_0(\mathrm{SiCl})=92$ kcal/mole, which is adopted by Herzberg [2020] and in the Handbook [649]. Gaydon [1668] reduced this value by 20% and recommended the value $D_0(\mathrm{SiCl})=76\pm12$ kcal/mole.

A comparison of the dissociation energies of CF, CCl and SiF with the mean energies of the bonds in the CF_4, CCl_4 and SiF_4, molecules proves that the value recommended by Herzberg is more reliable. In the Handbook, the value

$$D_0(\mathrm{SiCl}) = 92 \pm 15 \text{ kcal/mole.}$$

is adopted. To this value corresponds

$$\Delta H^\circ f_0(\mathrm{SiCl},\ \text{gas}) = 47{,}55 \pm 15 \text{ kcal/mole.}$$

$SiCl_2$ (gas). Schafer and Nickl [3601] measured by a static method the partial pressure of $SiCl_2$ generated as the result of the reaction

$$\mathrm{Si}\,(\text{cryst.}) + \mathrm{SiCl_4}\,(\text{gas}) = 2\mathrm{SiCl_2}\,(\text{gas}), \qquad \text{(XXII.6)}$$

they found by the temperature dependence of the logarithm of the equilibrium constant of this reaction within the 1500-1540°K range the thermal effect of the reaction $\Delta H_{1500}=75{,}2$ kcal/mole, to which correspond $\Delta H_0=79{,}8$ kcal/mole and $\Delta H^\circ f_0$ ($SiCl_2$, gas) = -35.3 kcal/mole.

The recalculation of the results obtained by Schafer and Nickl, using the values of the thermodynamic properties of the components of the reaction (XXII.6) adopted in the present Handbook, gives the values $\Delta H_0 = 75{,}6$ kcal/mole and $\Delta H^\circ f_0$ ($SiCl_2$, gas) = -38 kcal/mole. The authors of paper [3601] assume that the error in the measurement of the logarithms of the equilibrium constants of reaction (XXII.6) amounts to ±0.4, which results in an error of the value of the thermal effect of the reaction equal to ±3 kcal/mole.

Antipin and Sergeyev [74] determined the values of the equilibrium constants of the formation of $SiCl_2$ under more complex conditions. In this work, a flow of elemental chlorine passed over elemental silicon, and the generated $SiCl_4$ reacted at temperatures above 1000°C with the surplus of silicon. The equilibrium constants of the reaction (XXII.6) were calculated on the basis of the Si – Cl ratio in the sublimate for the temperature range 1273-1673°K. The calculation proved that a heat of reaction equal to 69.9 ± 0.7 kcal/mole and $\Delta H^\circ f_0$ ($SiCl_2$, gas) = -40.7 kcal/mole corresponds to these constants. It must be mentioned that in contrast to Antipin and Sergeyev [74], Schafer and Nickl [3601] found that no side reactions take place in a considerable degree in the system investigated.

The estimation of the heat of formation of $SiCl_2$ by the Karapet'yants method based on the heats of formation of $SiCl_4$, $SiCl$, CCl_4, CCl_2 and CCl adopted in the Handbook gives $\Delta H^\circ f_0$ ($SiCl_2$, gas) = -43 kcal/ /mole.

In the Handbook, the value

$$\Delta H^\circ f_0(SiCl_2, \text{gas}) = -38 \pm 2 \text{ kcal/mole},$$

is adopted, which is calculated on the basis of the equilibrium constants of reaction (XXII.6) found by Schafer and Nickl. The value calculated on the basis of the measurements by Antipin and Sergeyev [74] conforms to the adopted value within the error limits. To the adopted value of the heat of formation of $SiCl_2$ corresponds

$$D_0(SiCl_2) = 206{,}1 \pm 5{,}5 \text{ kcal/mole.}$$

SiCl$_3$ (gas). The adopted value of the heat of formation of the SiCl$_3$ radical

$$\Delta H^\circ f_0(SiCl_3, \text{gas}) = -87 \pm 10 \text{ kcal/mole,}$$

was estimated by the Karapet'yants method on the basis of the heats of formation of $SiCl_4$, $SiCl_3$, $SiCl$, CCl_4, CCl_3, CCl_2 and CCl. To this value corresponds

$$D_0(SiCl_3) = 283{,}65 \pm 11 \text{ kcal/mole.}$$

SiCl$_4$ (gas). The heat of formation of silicon tetrachloride can be found by the results of measurements of the heat of its hydrolysis and the heat of combustion of silicon in chlorine.

Troost and Hautefeuille [4019, 4020] measured the combustion heat of amorphous silicon in chlorine with formation of liquid silicon tetrachloride and found $\Delta H = -157{,}6$ kcal/mole. The recalculation of these data, taking into account the altered atomic weight of silicon, gives the value $\Delta H = -158{,}1$ kcal/mole. Berthelot [778] revised the data by Troost and Hautefeuille and obtained $\Delta H = -150{,}1$ kcal/mole, after some calorimetrical corrections. This correction, however, cannot be acknowledged as well-grounded: the analogous correction of the heat of combustion of boron in chlorine (see page) found by Troost and Hautefeuille, led to erroneous results. Using the heats of combustion of silicon in chlorine, found by Troost and Hautefeuille and taking into account the heat of conversion of amorphous silicon into crystalline [3508], the authors of the Handbook calculated the value $\Delta H^\circ f_{298}$ (SiCl$_4$, liqu.) = -157.1 kcal/mole. The results of the measurements of Troost and Hautefeuille [4019, 4020] cannot be acknowledged as reliable.

The heat of the hydrolysis reaction

$$SiCl_4(\text{liq.}) + 2H_2O(\text{liq.}) = SiO_2(\text{coll.}) + 4HCl(\text{soln.}) \quad (XXII.7)$$

was measured by Troost and Hautefeuille [4019, 4020], Berthelot [778], Thomsen [3981], Roth and Schwartz [3531] and Andrianov and Pavlov [73]. Values of the hydrolysis heat equal to $-70,0, -69,7, -69,3, -70,1$ and -76.6 kcal/mole, respectively have been obtained in this works [813]. The measurement results of Roth and Schwartz [3531] are the most reliable. Based on the heat of conversion of quartz into the colloidal modification [3508] and the measurement results of Roth and Schwartz, the value $\Delta H^\circ f_{293}$ ($SiCl_4$, liqu.) = -158.1 kcal/mole was calculated.

The heat of evaporation of silicon tetrachloride, $\Delta Hv = 7,0$ kcal/mole, was taken from the data of the Handbook [3508]. Hence, we obtain for the heat of formation of gaseous $SiCl_4$ the value

$$D_0(SiCl_4) = 375,672 \pm 5,1$$

which is adopted in the Handbook. To this value corresponds

$$\Delta H^\circ f_{293,15}(SiCl_4, \text{gas}) = -151 \pm 1 \text{ kcal/mole,}$$

SiN (gas). The linear extrapolation of the vibrational levels of the $X^2\Sigma$ ground state of the SiN molecule gives the value $D_0(SiN) = 143$ kcal/mole. The graphical extrapolation of the wellknown vibrational levels of the $B^2\Sigma$ state of the SiN molecule, carried out by Gaydon [1668] under the assumption that $Si(^1D) + N(^4S)$, correspond to the dissociation limit in this state, gives the value $D_0(SiN) = 101,5$ kcal/mole. Gaydon [1668] recommends the somewhat higher

$$D_0(SiN) = 104 \pm 9 \text{ kcal/mole,}$$

which is adopted in the present Handbook. To this value corresponds

$$\Delta H^\circ f_0(SiN, \text{gas}) = 119,536 \pm 10 \text{ kcal/mole.}$$

SiC (cryst.). Mixter [2926] measured the combustion heats of graphite, silicon and silicon carbide in sodium peroxide and calculated by these data the heat of formation of silicon carbide $\Delta H^\circ f_{298,15} = -3$ kcal/mole. The presence of side reactions and the inaccurate analysis of the combustion products lower the value of this paper. Ruff and Grieger [3553] repeated the measurement by the same method and, after having eliminated some of the errors committed in paper [2926], found the value -26.7 ± 2.1 kcal/mole which was adopted by a series of authors of reviews and Handbooks. However, in spite of the precautions taken by Ruff and Grieger, their method of combusting in sodium peroxide cannot be regarded as reliable.

Wartenberg and Schutte [4171] determined the heat of combustion of silicon carbide, silicon and carbon in fluorine and found by these data the heat of formation of silicon carbide as -31 ± 6 kcal/mole. This value also cannot be regarded as reliable because the heats of combustion of silicon and carbon in fluorine, found by Wartenberg and Schutte, differ considerably from the more accurate modern data.

The value of the heat of formation of SiC can be calculated on the basis of the equilibrium constants of the reaction

$$SiO_2(\text{cryst.}) + 3C(\text{graphite}) = SiC(\text{cryst.}) + 2CO(\text{gas}). \quad (\text{XXII.8})$$

measured by Brunner [998].

The heat of reaction $\Delta H_0 = 147 \pm 8$ kcal/mole and the heat of formation $\Delta H^\circ f_0$ (SiC, cryst.) = -7 ± 8 kcal/mole* correspond to the equilibrium constants found in this paper.

A more accurate value of the heat of formation of silicon carbide can be calculated on the basis of the combustion heat of the cubic (7248.7 cal/g) and hexagonal (7276.1 cal/g) modification of silicon carbide in oxygen, measured by Humphrey, Todd, Caughlin and King [2158] (we cite this paper according to [3434]). Assuming that mainly cristobalite is formed by the combustion of SiC, as it is the fact in the combustion of elemental silicon [2157], we find for the hexagonal modification the value

$$\Delta H^\circ f_{298,15}(SiC, \text{hexag.}) = -11,8 \pm 3 \text{ kcal/mole.}$$

This value is adopted in the Handbook.

The results of measurements of the equilibrium constant of the reaction (XXII.8), obtained in [998], lead to a value which conforms to that adopted within the error limits.

SiC (gas). Ruff and Konshak [3556] investigated the evaporation of silicon carbide in the 2673-2990°K temperature range by determining the boiling points. Assuming that Si(gas) and SiC(gas) are the evaporation products, they calculated the quantity of SiC(cryst.) which evaporates in the form of SiC(gas) and by decomposition into C(graphite) and Si(gas). According to these data and using the values of the thermodynamic properties adopted in the Handbook, the sublimation temperature of SiC equal to 143 kcal/mole was calculated.

The mass-spectrometrical investigation of the composition of silicon carbide vapor, carried out by Drowart, De-Maria and Inghram [1406] (2149-2316°K) proved that besides the gaseous silicon, Si_2C and SiC_2 are the main evaporation products, and the partial pressure of SiC amounts to less than 0.001 of the sum of the partial pressures of Si_2C and SiC_2. Thus, the measurement results by Ruff and Konshak cannot be used to calculate an accurate value of the sublimation heat of SiC. In the paper by Drowart et al [1406] the values of the partial pressures of SiC in silicon carbide vapor were found, and the heat of sublimation

$$SiC(\text{cryst.}) = SiC(\text{gas}), \qquad \text{(XXII.9)}$$

was calculated as equal to $\Delta H_{s0} = 197 \pm 5$ kcal/mole, to which corresponds $D_0(SiC) = 95 \pm 8$ kcal/mole. The recalculation on the basis of the values of thermodynamic properties adopted in the present Handbook, gives the values $\Delta H_{s0} = 190$ kcal/mole and $D_0(SiC) = 102$ kcal/mole.

Drowart et al also found the equilibrium constants of the reaction

$$\mathrm{SiC\,(газ) = C\,(gas) + Si\,(gas)}. \qquad (\mathrm{XXII.10})$$

In addition to their own results, they utilized the measurements of the pressure of saturated monatomic carbon vapor from paper [3894] and calculated by these data $D_0(\mathrm{SiC}) = 103 \pm 5$ kcal/mole. The calculation by means of the values of the thermodynamic functions adopted in the present Handbook gives the value $D_0(\mathrm{SiC}) = 104$ kcal/mole.

In the Handbook, the value of the dissociation energy

$$D_0(\mathrm{SiC}) = 103 \pm 5 \text{ kcal/mole},$$

is adopted, which is the mean between the two values calculated by the data of Drowart et al [1406]. To this value correspond

$$\Delta H^\circ f_0(\mathrm{SiC, gas}) = 177{,}585 \pm 7 \text{ kcal/mole},$$
$$\Delta Hs_0(\mathrm{SiC,\ cryst.}) = 189{,}158 \pm 8 \text{ kcal/mole}.$$

$\mathrm{SiC_2}$ (gas). Drowart, De-Maria and Inghram [1406] determined mass-spectrometrically the composition and the partial pressures of the evaporation products of silicon carbide. They found that the main evaporation products are Si(gas), $\mathrm{SiC_2}$(gas) and $\mathrm{Si_2C}$(gas). Based on the temperature dependence of the $\mathrm{SiC_2^+}$ ionic current, Drowart et al. found for the thermal effect of the reaction

$$\mathrm{SiC\,(крист.) + C\,(графит) = SiC_2\,(gas)}. \qquad (\mathrm{XXII.11})$$

the value $\Delta H_{2000} = 173 \pm 5$ kcal/mole, to which corresponds $D_0(\mathrm{SiC_2}) = 286 \pm 7$ kcal/mole.

Starting from the absolute values of the partial pressure of $\mathrm{SiC_2}$, Drowart et al [1406] found the thermal effect of the reaction (XXII.11) as equal to168 ± 5 kcal/mole, or $D_0(\mathrm{SiC_2}) = 294$ kcal/mole. The recalculation of these values, using the values of the thermodynamic functions of the components of this reaction, adopted in the present Handbook, gives the values $\Delta H_0 = 160{,}3$ kcal/mole and $D_0(\mathrm{SiC_2}) = 300{,}6$ kcal/mole.

On the basis of experimental data, Drowart et al [1406] also calculated the equilibrium constant of the reaction

$$SiC_2\,(gas) = Si\,(gas) + 2C\,(gas) \qquad (XXII.12)$$

and found for the thermal effect of this reaction $D_0(SiC_2)=302$ kcal/mole. Recalculation, based on the thermodynamical properties adopted in the present Handbook, gives a conformable value.

In the Handbook preference is given to the values calculated on the basis of the partial pressures of evaporation products, and is adopted.

$$D_0\,(SiC_2) = 300 \pm 5 \text{ kcal/mole}.$$

To this value corresponds

$$\Delta H^{\circ}f_0\,(SiC_2,\ gas) = 150{,}17 \pm 7 \text{ kcal/mole}.$$

Si_2C (gas). On the basis of a mass-spectrometrical investigation of the evaporation of silicon carbide (see the sections dealing with SiC_2 and SiC), Drowart, De-Maria and Inghram [1406] found the temperature dependence of the Si_2C^+ ionic current and calculated the thermal effect of the reaction

$$2SiC\,(cryst.) = Si_2C\,(ras) + C\,(graphite), \qquad (XXII.13)$$

as equal to $\Delta H_{1000}=170\pm5$ kcal/mole, to which corresponds $D_0(Si_2C)= 241\pm10$ kcal/mole. The calculation of the thermal effect of the reaction (XXII.13), carried out by the authors of paper [1406] on the basis of the measured partial pressure of Si_2C and the values of the thermodynamic functions of the components of this reaction, led to the values $\Delta H_0=181\pm5$ kcal/mole and $D_0(Si_2C)=234$ kcal/mole. Calculation on the basis of the values of thermodynamic functions adopted in the present Handbook led to the essentially differing values $\Delta H_0= 160{,}5$ kcal/mole and $D_0(Si_2C)=254$ kcal/mole.*

Using the found values of the partial pressures of Si and Si_2C, Drowart et al [1406] also found the equilibrium constant of the reaction

$$Si_2C\,(gas) = 2Si\,(gas) + C\,(gas) \qquad (XXII.14)$$

and the dissociation energy $D_0(Si_2C)=250$ kcal/mole. Recalculation of these data by means of the values of thermodynamic functions of the components of reaction (XXII.14) adopted in the present Handbook led to the somewhat higher value, equal to 255 kcal/mole.

TABLE 206

Adopted Values (in cal]mole) of the Thermochemical Quantities of Silicon and Its Compounds

1 Вещество	2 Состояние	D_0 или 3 ΔHs_0	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293.15}$	$\Delta H^\circ f_{298.15}$	$H^\circ_{293.15}-H^\circ_0$	$H^\circ_{298.15}-H^\circ_0$
Si	4 Крист.	111 000[a]	0	0	0	747	770
Si	5 Газ	—	111 000	112 034	112 035	1778	1805
Si_2	»	74 000	148 000	148 873	148 881	2367	2421
SiO	»	191 987	—22 000	—21 720	—21 725	2047	2083
SiO_2	6 Кварц.	135 000[a]	—208 812	—209 995	—210 000	1604	1657
SiO_2	Газ	302 786	—73 812	—74 175	—74 180	2424	2477
SiH	»	74 000	88 632	89 043	89 039	2150	2186
SiF	»	125 000	4 500	4 937	4 935	2220	2260
SiF_2	»	316 000	—168 000	—168 270	—168 280	2550	2601
SiF_3	»	416 500	—250 000	—250 884	—250 896	2973	3041
SiF_4	»	556 168	—371 168	—372 489	—372 500	3572	3660
SiCl	»	92 000	47 550	48 046	48 045	2319	2362
$SiCl_2$	»	206 100	—38 000	—38 062	—38 066	2838	2898
$SiCl_3$	»	283 650	—87 000	—87 322	—87 322	3655	3739
$SiCl_4$	»	375 672	—150 472	—151 000	—150 997	4525	4633
SiN	»	104 000	119 536	119 822	119 818	2051	2088
SiC	Крист., 7 гекс.	189 158[a]	—11 573	—11 799	—11 800	746	777
SiC	Газ	103 000	177 585	178 997	179 018	2384	2437
SiC_2	»	300 000	150 170	151 450	151 463	2477	2531
Si_2C	»	255 000	136 585	137 549	137 554	2683	2743

a) The value of the sublimation heat is given.

1) Substance; 2) state; 3) or; 4) cryst.; 5) gas; 6) quartz; 7) hexagon.

The value

$$D_0(Si_2C) = 255 \pm 5 \text{ kcal/mole},$$

is adopted in the Handbook, calculated on the basis of the partial pressures of the evaporation products of silicon carbide, measured by Drowart et al [1406]. To the adopted value corresponds

$$\Delta H^\circ f_0(Si_2C, \text{gas}) = 136{,}585 \pm 10 \text{ kcal/mole}.$$

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1358	A minute analysis of the evaporation processes of silicon monoxide is given in Schick's review [3622a].
1372	The values of the ω_e frequencies of SiC, calculated by Majumdar and Varshni [2746] and Varshni [4071], are erroneous because the authors of the papers [2746, 4071], used in their estimate the value of $\omega_e(Si_2)$ found by Downie and Barrow [1399] (see page 1360) and the value of $\omega_e(C_2)$ for the $a^3\Pi_u$ state (see page 868).
1375	The bands are obtained in the spectrum of a discharge in a hollow cathode in a mixture of SiF_4 vapor and helium.
1376	The force constants of SiF_2 have been estimated by Johns et al. [2259] on the basis of the wellknown values of the fundamental frequencies of SiF_4 and SiF. The fundamental frequencies of $CF_2 (\nu_1 \sim 1178$ и $\nu_2 \sim 630$ см$^{-1})$ calculated in paper [2259] in an analogous manner, conform satisfactorily to the experimentally observed frequencies (see Table 189).
1377	The bands observed in paper [581] belong to two systems caused by transitions between two excited states which posses excitation energies of about 28,034 and 29,952 cm^{-1} and the ground electron state of $SiCl_2$.
1378	To the adopted values of the fundamental frequencies of $SiCl_2$ conform satisfactorily (within a limit of 10%) the frequencies calculated by Eqs. (P4.28) using the force constants of $SiCl_2$ assumed as being equal to the force constants of $SiCl_4$: $\nu_1 = 490$, $\nu_2 = 235$, $\nu_3 = 670$ см$^{-1}$ (using the constants $f_d = 5.5 \cdot 10^6$, $f_{dd} = 0,10 \cdot 10^6$, $f_\alpha/c^2 = 0,86 \cdot 10^6$, $f_{d\alpha} = 0,80 \cdot 10^6$ см$^{-2}$, calculated by Schneider and Pliva [3645]) and $\nu_1 = 544$, $\nu_2 = 220$ and $\nu_3 = 530$ см$^{-1}$ (using the constants $f_d = 2,575 \cdot 10^5$, $f_{dd} = 0,399 \cdot 10^5$, $f_\alpha/d^2 = 0,296 \cdot 10^5$ and $f_{d\alpha} = 0,029 \cdot 10^6$ dyne$\cdot$$\cdot$$cm^{-1}$, calculated by Pistorius [3250]). The satisfactory conformity of the calculated ν_1 and ν_2 values to the experimentally found values proves the correctness of the interpretation of the $SiCl_2$ spectrum suggested in paper [581].
1382	The work by Best and Tramp was not published.
1385	The value $f_\alpha'' = 0,47 \cdot 10^{-11}$ dyne$\cdot$cm$\cdot$$rad^{-1}$ was assumed for the force constant of the deformation vibration of the C_3 molecule.

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1385	This estimate of the interatomic distance Si = C in SiC_2 on the basis of the interatomic Si – C distance in organosilicon compounds is obviously erroneous because the comparison of the interatomic C – C distances in C_2H_6 and C_3 with the interatomic Si – C distance in SiH_3CH_3 proves that $r_{Si=C}$ in SiC_2 must be equal approximately to 1.55 A and not 1.9.
1386	The calculation of the fundamental frequencies of the asymmetrical molecule Si_2C by Eqs. (P4.27), assuming that $f_{SiC} = 2{,}9 \cdot 10^5$ dyne•cm^{-1} and $f_\alpha = 0{,}5 \cdot 10^{-11}$ dyne•cm•rad^{-1} (Like in SiC_2) and $f_{SiSi} = 2{,}6 \cdot 10^5$ dyne•cm^{-1} [estimated by comparison of the force constants of the C – C bonds in SiC_2 and C_2 (in the $a^3\Pi_u$ state) and the Si – Si bond in the Si_2 molecule (in the $a^3\Pi$ state) gives $\nu_1 = 485,\ \nu_2 = 250,\ \nu_3 = 815\ см^{-1}$. The moment of inertia of the asymmetric Si_2C molecule, which corresponds to the interatomic distances $r_{SiC} = 1{,}75$ and $r_{SiSi} = 2{,}20 A$, is equal to $23 \cdot 10^{-39}$ g•cm^2.
1393	The calculation by means of Eqs. (II.149) and (II.150), which correspond to a bond intermediate between the Hund cases a and b, results in values which conform within the limits of the accuracy of the calculation to the data of Table 238 (II).
1399	The values $S^\circ_{298,16} - S^\circ_{193,96}$ are calculated on the basis of the molecular constants of SiF_4 adopted in the present Handbook.
1404	In solid state, the silicon dioxide can also exist in a vitreous state which is a thermodynamically nonequilibrium phase.
1404	There are references in [1014] that Westrum and Biel measured the specific heat of quartz in the temperature range from 6 to 300°K, however, these data have not been published up to the present. Extrapolation of the specific heat of quartz measured between 2 and 4°K [2296a] to higher temperatures results in data which conform to the data of [551, 3042].
1404	The conversion of quartz II into quartz I is a second-order phase change occurring in the temperature range from 825 to 850°K. The heat of this conversion, calculated by the results of measurements of the specific heat of quartz carried out by Sinel'nikov [376a], amounts to approximately 100 cal/mole.

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The value $\Delta H_{848} = 290$ cal/mole, recommended by Kelley [2364a], is an effective value, coordinated to the equations for the specific heats of the low- and high-temperature quartz modifications, derived by him.

1406 The authors of the Handbook know paper [2158] by Chemical Abstracts. The absolute values of the entropies of silicon carbide modifications are not quoted in the abstract.

1407 The black and green color of SiC samples depends on the different degrees of purity and the different methods by which the silicon carbide is produced.

1410 This value is calculated using the thermodynamic functions of the components of reaction (XXII.1) adopted in the Handbook. A significantly different value $\Delta H_0 = 131 \pm 3$ kcal/mole is quoted in paper [1406]. This difference is incomprehensible because the values of the thermal effects of the same reaction at 298.15 and 2000°K, quoted in [1406] and calculated using the data of the present Handbook conform excellently to one another.

1412 In the paper by Davis et al [1275a], published after this chapter was finished, the vapor pressure of elemental silicon carbide (2117-2171°K) have been measured by the Knudsen method. In this paper, the following values have been obtained: $\Delta Hs_{298.15}$ (Si, cryst.) = 108.4 ± 3 kcal/g-atom (recalculation to 0°K gives $\Delta Hs_0 = 107.4$ kcal/g-atom) and the heat of the reaction (XXII.1) equal to $\Delta H_{298.15} = 126 \pm 3$ kcal/g-atom to which corresponds ΔHs_0 (Si, cryst.) = 113.4 kcal/g-atom.

1412 It must be taken into account that these values were obtained for an electron state of Si_2 which is possibly not the ground state of this molecule (see page 1361).

1422 The small difference between the values of the heat of formation of SiF_4 quoted in the Handbook and those calculated by Vorob'yev et al [129a] on the basis of the measured heats of dissolution may be accounted for by the somewhat different values of the heat of formation of quarts used in the calculations.

1427 This value is calculated using the values of thermodynamic properties the components of the reaction (XXII.8) adopted in the present Handbook. Brunner [998], using the temperature dependence of the logarithm of the equilibrium constant of this reaction, obtained the sharply differing value $\Delta H^\circ f_{298} = -43{,}5$ kcal/mole.

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1430	The difference between the values of the thermodynamic quantities of SiC, SiC_2 and Si_2C, calculated by the authors of the present Handbook on the basis of the data by Drowart et al [1406], and the values quoted in the original paper can be explained by the obviously erroneous values of the thermodynamic properties of SiC(cryst.) used in paper [1406].

Chapter 23

BORON AND ITS COMPOUNDS

(B, B_2, BO, BO_2, B_2O_2, B_2O_3, BH, HBO, HBO_2, H_3BO_3, BF, BF_2, BF_3, FBO, BCl, BCl_2, BCl_3, BN)

In the present chapter boron and several of its compounds with oxygen, hydrogen, fluorine, chlorine and nitrogen will be discussed.

Elementary boron is known to exist in several crystalline modifications [2086, 2687a, 3918a] and in amorphous state. Temperatures and heat values for polymorphous transformations of crystalline boron were not determined; therefore, polymorphism of crystalline boron is not dealt with in this Handbook. Respective data cited in text and in the table of Vol. II pertain to the alpha-rhombohedral modification, which is stable at temperatures up to 1000°K.

Saturated boron vapors consist of boron atoms and diatomic B_2 molecules which were observed in mass-spectroscopic investigations of boron vapors. Discussion of thermodynamic properties of monatomic and diatomic boron is included in the present Handbook. The following should be mentioned: though in mass-spectroscopic analysis of the composition of boron vapors no molecules with more than two atoms have been revealed, the discrepancies between the results for vapor pressures determined by the Knudsen method and those obtained through mass spectroscopy, which are also analogous to those observed in investigations of sublimation heat of carbon, hint at a possible existence of such molecules which do possess low evaporation coefficients (see page).

Until recently, sufficiently reliable data on the existence of only two boron oxygen compounds were available in literature; those on boron oxide (boric anhydride) B_2O_3 and boron monoxide BO. Suggestions have also been made as to the possible existence of the boron oxide dimer B_4O_6 [1523, 376, 8]. In this conjunction, in the first edition of the present Handbook three boron oxygen compounds have been treated with: B_2O_3 (in the crystalline, liquid, and gaseous states), B_4O_6 (in gaseous state), and BO (in gaseous state). Through mass-spectrometric [2171, 2, 3, 4], effusiometric [3611, 3612], and spectroscopic [52, 52a, 54, 351b, 4238] investigations, carried out during the years 1957-1960, it was possible to essentially expand and specify the knowledge about the composition of boron oxygen compounds existing in gaseous state. Above all, it was proven by mass-spectrometric and effusiometric measurements that B_4O_6 molecules were not present in vapors exhaled from boron oxide, while, on the other hand, examinations on the composition of boron oxide vapors under reducing conditions (using a mixture of B_2O_3 + B) lead to the conclusion that under these conditions at temperatures up to 3000°K not the BO molecule is the representative principal compound which is present in the vapors but its dimer B_2O_2. Careful investigations of spectrums of boron oxide vapors heated in atmospheres of various gases inferred the conclusion that the well known "fluctuation bands" appearing in vapor spectrums under oxidizing conditions belong to the BO_2 molecule [54, 289a, 293b]. The suggested existence of molecules of boron dioxide BO_2 in gaseous state was subsequently confirmed by spectral examinations of boron-containing flames [2329a] and explosive mixtures of various boron oxygen compounds [351b]. At the same time it is worthwhile mentioning that preliminary attempts to discover BO_2 molecules by mass-spectrometric investigations of boron oxide vapors under oxidizing conditions, as tried in the study [10a], failed to render positive results.

Thus, at the present time the existence of four gaseous oxygen compounds has been confirmed: of BO, B_2O_2, B_2O_3, and BO_2; all these compounds are discussed in the present Handbook.

Detailed investigations of the composition and stability of boron oxygen compounds in condensed state were not carried out. Suggestions have also been made that in addition to the well known boron oxide B_2O_3, occurring in both the crystalline and amorphous state, the preparation of boron suboxide is possible [see 356a]. Thus, in the study [3612] indirect hints are given as to the possibility of preparing boron suboxides in solid state on heating a mixture of boron oxide with boron.* Since, however, the question of the thermodynamic stability of boron suboxides in condensed state is fore-the-time-being left open and no data on the thermodynamic properties of these compounds are available in literature, in the present Handbook only one boron oxygen compound in condensed state is discussed, the B_2O_3.

Boron is able to form a great variety of compounds of hydrogen; all these compounds are unstable already at moderate temperatures, especially in the presence of oxidizers. In the Handbook only the simplest of this class of compounds, the boron monohydride BH is included.

In the system Boron-Oxygen-Hydrogen two compounds are known to exist in condensed state: the metaboric acid HBO_2 and the orthoboric acid H_3BO_3.** On heating both these compounds decompose in water vapors and boron oxide at such low temperatures as of the order of 400-500°K, and therefore, they are not treated with in the present Handbook. When studying volatility of boron oxide in water vapors several investigators were able to assume that there exist boric acids which are stable in gaseous state. Thermodynamic calculations carried out by Medvedev [295] in 1955 gave also rise to the conclusion that metaboric acid in gaseous state is a rather stable compound at high temperatures. On these grounds, gaseous HBO_2 was included among the boron compounds which were described in the first edition of the present Handbook. Though new investigations (see page 1537) led to the conclusion that stability of HBO_2 at high temperatures is lower than should be expected on the basis of the calculations made in the study [295], this boron compound remains still as one of the most stable in the system Boron-Oxygen-Hydrogen over a broad range of temperatures and pressures.

In literature [2773, 752, 1515] information is available on the existence of the dimer $(HBO_2)_2$ (in gaseous state). Afterwards, however, this information was not confirmed. In recent words [2853b, 3368b, 3369a] small quantities (about 1% at 1000-1500°K) of a trimer type molecule $(HBO_2)_3$ were said to exist. Possibly it could be expected that at even more elevated temperatures the concentration of the trimer will be reduced even more.

In the present Handbook besides HBO_2 two more gaseous compounds of this system are discussed: H_3BO_3 and HBO. At high temperatures, the stability of the orthoboric acid is essentially lower than that of the metaboric acid, however, at moderate temperatures and high water vapor pressures, the H_3BO_3 type acid (gaseous state) may become the principle component of the system under discussion. There are no experimental data on the existence of HBO molecules in literature, however, it can be expected that this acid forms at elevated temperatures in analogy with the isoelectronic type molecules of HCN, which plays an essential part in the Carbon-Nitrogen-Hydrogen system at elevated temperatures.

On the whole, the data presented on the Boron-Oxygen and the Boron-Oxygen-Hydrogen systems in this Handbook may be considered more complete by comparison to those cited in other Handbooks and Reviews.

The errors in the tables on thermodynamic properties of a number of substances are, however, too great for making precise equilibrium calculations of the chemical reactions in which the compounds participate. This holds chiefly for such compounds as B_2O_3, B_2O_2, and H_3BO_3 in gaseous state.

Of the gaseous compounds of the Boron-Fluorine system and of the Boron-Chlorine system the following are described in this Handbook: BF, BF_2, BF_3 and BCl, BCl_2 and BCl_3, respectively. There is no experimental evidence on the stability of BF_2 and BCl_2 molecules in literature.* These compounds were included in the Handbook according to the analogy with corresponding aluminum compounds. On the other hand, there are literature data on such compounds as B_2F_4 and B_2Cl_4 (viz. e.g., [1558a, 1888a]) or $BFCl_2$ and BCl_2F [2068a]. These compounds are not discussed in the Handbook.

There are no data on the boron-oxygen-fluorine system in the literature. In this Handbook only the simplest compound of this system, FBO has been included, since its existence can probably conceived in accord with the analogy to the isoelectronic molecule FCN and also supported by the general concept on the structure of molecules.

Out of the nitrogen compounds of boron the boron nitride has been included herein, with data given for both the condensed and gaseous state. The low stability of boron nitride in the gaseous state should be referred to.

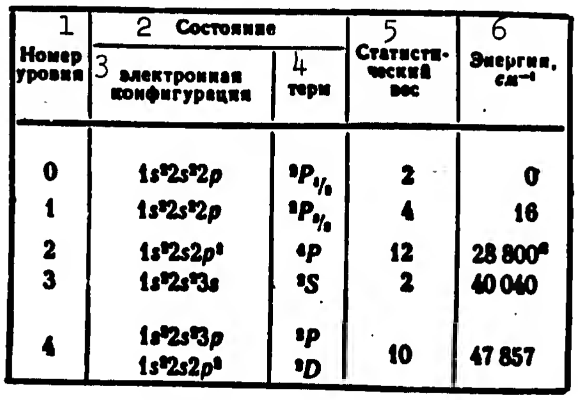
General information on the chemical and physical properties of boron compounds and boron alloys can be found in the monograph by Samsonov, Markovskiy, Zhigach and Valyashko [356a].

§91. MOLECULAR CONSTANTS

B. In its ground state ^2P the boron atom has the electron configuration $1s^2 2s^2 2p$. On excitation of the 2p-electron a group of energy states of the type L = 1 is formed whose ionization range equals 66,930 cm^{-1} with respect to the lower state $^2P_{1/2}$. The excitation energies of this group are big: the first excited state $1s^22s^23s^2S$ has an energy of about 40,040 cm^{-1}, and the second excited state $1s^22s^23p^2$ P has not been observed experimentally until now. In Table 207 the states of this group with excitation energies lower than 50,000 cm^{-1} are listed. There, we find listed also the energy state $2s2p^2\ ^4P$; since in the boron spectrum no intercombinational transitions could be observed, the energy of this state has been accepted in accordance with Edlen's estimate on the basis of the data for C^+ and N^{++} (see [2941]).

TABLE 207

Energy Level of the Boron Atom



1 Номер уровня	2 Состояние		5 Статистический вес	6 Энергия, $см^{-1}$
	3 электронная конфигурация	4 терм		
0	$1s^22s^22p$	$^2P_{1/2}$	2	0
1	$1s^22s^22p$	$^2P_{3/2}$	4	16
2	$1s^22s2p^2$	^4P	12	28 800^a
3	$1s^22s^23s$	^2S	2	40 040
4	$1s^22s^23p$ $1s^22s2p^2$	^2P ^2D	10	47 857

^{a}Estimate

1) Level number; 2) state; 3) electron configuration; 4) term; 5) statistic weight; 6) energy, cm^{-1}.

$\underline{B_2}$. The information on the spectrum of the B_2 molecule is exhausted with the data obtained by Douglas and Herzberg [1376, 1374] who observed the system of the B_2 bands in the region of 3200 A in the emission spectrum of a non-condensed discharge in helium with traces of BCl_3. Based on fine structure band analysis, intensity distribution in the bands and electron state analysis of the B_2 molecule, this system was attributed to the transition $^3\Sigma_u^- - {}^3\Sigma_g^-$. In the work [1374] Douglas and Herzberg assumed the lower state ($^3\Sigma_g^-$) to be the electronic ground state of the B_2 molecule. This suggestion is in agreement with the prediction by Mulliken [2983] on possible types of the ground electron state of the B_2 molecule and is also confirmed by comparative studies on vibration frequencies and interatomic distances of diatomic molecules formed by elements of the second period in their ground electron states, which had been carried out by Douglas and Herzberg.*

On the other hand, quantum-mechanical calculations made by Padgett and Griffing [3162] led to the conclusion that the $^5\Sigma_u^-$ state should be considered the ground electron state of the B_2 molecule. However, resulting from the simplified calculations adopted by these authors, the possibility may not be excluded that the ground electron state of B_2 might be either $^3\Sigma_g^-$ or $^3\Pi_u$. The final solution to the problem of the ground electron state of the B_2 molecule will not be possible until its absorption spectrum will be investigated.

In accordance with the recommendations made by Douglas and Herzberg [1374], in the present Handbook $^3\Sigma_g^-$ is being considered as the ground electron state of the B_2 molecule.

The vibration constants of the B_2 molecule for the electronic states $X^3\Sigma_g^-$ и $A^3\Sigma_u^-$, included in the present Handbook and listed in Table 208, were found by Douglas and Herzberg [1374] in an analysis of the vibration structure of bands formed in the sequence $\Delta v = 0, 1$ с $v' \leqslant 4$ and $v'' \leqslant 3$. The rotation constants were found as the result of fine structure investigations of the P- and R- branches in the 0-0, 1-0 and 1-1 bands.

In the monograph by Herzberg [2020] and in the Handbook [649] the very same values for the molecular constants of the B_2 molecule are recommended.

TABLE 208

Accepted Values for the Molecular Constants of B^{11}_2, $B^{11}O^{16}$, $B^{11}H^1$, $B^{11}F^{19}$, $B^{11}Cl^{35}$, $B^{11}N^{14}$

A Молекула	B Состояние	T_e	ω_e	$\omega_e x_e$	B_e	α_1	$D_e \cdot 10^6$	r_e
		см$^{-1}$						Å
B^{11}_2	$X^3\Sigma^-_g$	0	1051,3	9,4	1,212	0,014	5,35^а	1,590
	$A^3\Sigma^-_u$	30573,4	937,4	2,6	1,160	0,011	6,10^а	1,625
$B^{11}O^{16}$	$X^2\Sigma$	0	1885,44	11,769	1,7803	0,01648	6,29	1,2049
	$A^2\Pi$	23958,85^б	1260,415	10,935	1,4277	0,0196	7,06	1,345
	$B^2\Sigma$	43174,4	1280,69	10,59	1,5192	0,0210	8,4	1,304
$B^{11}H^1$	$X^1\Sigma$	0	2366^в	49^г	12,018	0,412	1220	1,2325
	$a^3\Pi^д$	20000^е	—	—	12,667^ж	—	1220	1,198^з
	$A^1\Pi$	23105,0	2344^и	123^к	12,152	0,521^л	1410	1,221
	$b^3\Sigma$	47060	—	—	12,126^ж	—	1280	1,220^з
$B^{11}F^{19}$	$X^1\Sigma^м$	0	1400,6	11,2^н	1,518	0,017	7,13^а	1,262
	$a^3\Pi^о$	35000^е	1323,64	9,40	1,412	0,0179	—	1,312
	$A^1\Pi^п$	51151,4^р	1271,8	15,0^с	1,423	0,018	7,14^а	1,304
$B^{11}Cl^{35}$	$X^1\Sigma$	0	839,12	5,11	0,6838	0,00646	1,72	1,716
	$A^1\Pi$	36750,92^т	849,04	11,37^у	0,7054	0,00820^ф	1,60^х	1,689
$B^{11}N^{14}$	$X^3\Pi$	0	1514,6	12,3	1,666	0,025	8,1	1,281
	$A^3\Pi$	27851	1317,5	14,9	1,555	0,010	8,7	1,326

a) Calculated by the relation (1.36)

b) $A = 122,36$ см$^{-1}$.

v) Computed by the relation (1.36)
g) Computed by the relation (1.38)

d) $A = 5,95$ см$^{-1}$.

e) Estimate
zh) Reduced to the value B_0

z) Reduced to the value r_0

i) Computed on the basis of the estimated value $\omega_e(X^1\Sigma)$ and the difference magnitude $\omega'_e - \omega''_e$, found in the work [523].

k) Computed on the basis of the estimated value $\omega_e x_e(X^1\Sigma)$ and the difference magnitude $\omega'_e x'_e - \omega''_e x''_e$, found in the work [523].

l) $\alpha_2 = -0,105$ см$^{-1}$.

m) In the study by Onaka [3141] the following constants for the - state are listed $\omega_e = 1402,13$, $\omega_e x_e = 11,84$, $\omega_e y_e = 0,056$, $B_e = 1,5107$, $\alpha_1 = 0,0165$, $\alpha_2 = -0,00015$, $D_e = 7 \cdot 10^{-6}$ см$^{-1}$, $r_e = 1,2652$ Å.

n) $\omega_e y_e = +0,016$ см$^{-1}$.

o) In the work by Barrow et al. [659] the following constants of a $a^3\Pi$ state of the BF molecule are listed: $\omega_e = 1323,86$, $\omega_e x_e = 9,20$, $\omega_e y_e = -0,047$, $B_e =$

$1{,}4413$, $\alpha_1=0{,}0158$, $D_e=6{,}3\cdot 10^{-6}\,см^{-1}$, $r_e=1{,}3079$ A, $A=24{,}25\,см^{-1}$.

p) In the study by Onaka [3141] for the $A^1\Pi$ state of the BF molecule the following constants were found: $T_e=51157{,}48$, $\omega_e=1264{,}96$, $\omega_e x_e=12{,}53$, $\omega_e y_e=-0{,}242$, $B_e^c=1{,}4205$, $B_e^d=1{,}4207$, $\alpha_1=0{,}0165$, $\alpha_2=-0.00057$, $D_e=7\cdot 10^{-6}\,см^{-1}$, $r_e=1{,}3047$ A.

r) It is possible that the $^1\Sigma^-$ state with an excitation energy being close to the energy of the $A^1\Pi$ state exists.

s) $\omega_e y_e=0{,}10$, $\omega_e z_e=-0{,}017\,см^{-1}$.

t) In the scheme of terms of BCl a stable triplet state $a^3\Pi$ should exist. An estimate of the excitation energy of this state gives $T_e\,(a^3\Pi)\sim 24\,000\pm 3000\,см^{-1}$.

u) $\omega_e y_e=-0{,}100$; $\omega_e z_e=-0{,}0271\,см^{-1}$.

f) $\alpha_2=0{,}00050\,см^{-1}$.

ch) $\beta_1=0{,}27\cdot 10^{-6}\,см^{-1}$.

A) Molecule;
B) state.

BO. The ground electron state of the BO molecule is the $X^2\Sigma^+$ state. As a result of investigations of the BO spectrum the existence of three excited electronic states of this molecule has been established: $A^2\Pi$, $B^2\Sigma$ and $C^2\Pi$. Between the four mentioned states the following transitions were observed: $A^2\Pi \leftrightarrows X^2\Sigma$ in the region 3100-12,000 A (α-system of bands),* $B^2\Sigma \rightarrow X^2\Sigma$ — in the region 2000-3600 A (β-system of bands), $B^2\Sigma \rightarrow A^2\Pi$ — in the region 4800-5800 A and $C^2\Pi \rightarrow X^2\Sigma$ — in the region 1600-2100 A.

In the BO spectrum the α-and β- systems of bands were most thoroughly investigated. The molecular constants of BO in the $X^2\Sigma^+$ and $A^2\Pi$ states were determined in the works [2226, 3614, 2235, 289] on the basis of an analysis of an α-band-system. Scheib [3614] obtained values for the rotational constants of BO in the $X^2\Sigma$ and $A^2\Pi$, states when he investigated the fine structure of the 0-1, 0-2, 0-3 and 0-4 bands. The spectrum was excited in a graphite arc, into which boric acid was introduced, and recordings were made in the first order of the diffraction grating (with a dispersion of 1.98 A/mm). Jenkins and McKellar

[2235] measured and analysed a large number of spectral lines which formed nin bands (0—0, 0—1, 0—2, 1—0, 1—1, 1—2, 2—0, 3—0, 4—0). The spectrum was excited by introducing BCl_3 into an atmosphere of active nitrogen containing oxygen traces, and was recorded on an apparatus with a dispersion of 0.95 A/mm. Precision of measurement for the position of the individual lines was 0.01 cm^{-1}. The vibrational and rotational constants of BO in the $X^2\Sigma$ and $A^2\Pi$ states have been recommended in Herzberg book [2020] and in the Handbook [649] and have been adopted in the present Handbook (cf. Table 208). Mal'tsev, Kuzyakov and Tatevskiy recalculated the values for the rotational constants of BO according to the experimental data obtained by Scheib [3614], and those by Jenkins and McKellar [2235]. Thereby it was shown that the calculation made by Scheib was incorrect. The values for the rotational constants of BO in the $X^2\Sigma$ state ($B_e = 1{,}77997$, $\alpha_1 = 0{,}01536$, $\alpha_2 = 0{,}00022$, $D_e = 6{,}4 \cdot 10^{-6}$ $см^{-1}$, $\beta = 0$), found in the study [289] on the basis of Scheib's values, are obviously more correct, since Scheib observed lines with greater values for J than those found by Jenkins and McKellar. The more accurate values as specified by the authors of the study [289] are, however, irrelevant with respect to the goals of the present Handbook.

The molecular constants of BO in the $B^2\Sigma$ state were obtained as a result of investigations on the rotational structure of β-system bands, carried out in the works [1475, 1477, 1631, 289, 2531]. The most careful studies on the β-system were made by Malt'sev, Kuzyakov and Tatevskiy [289] as well as by the authors Lagerqvist, Nilsson and Wigartz [2531]. Mal'tsev, Kuzyakov and Tatevskiy were able to identify β-system bands on an apparatus with a dispersion of 2 A/mm, using for the excitation of the spectrum a discharge tube with a hot cup cathode. As the result of the rotational structure of the bands 0—0, 0—1, 0—2, 0—3, 1—4, 1—5, 2—5, 2—6 and 3-4 the authors [289] found for the molecular constants of BO values in the $B^2\Sigma$ state which are listed in Table 208.

Lagerqvist, Nilsson and Wigartz [2531] also examined the fine structure of nine bands of the β-system: 3—1, 2—0, 2—2, 1—0, 1—4, 0—0, 0—1; 0—2 and 0-3. The bands were observed in spectrum being excited in a graphite arc and the recordings were made on an instrument with a dispersion of 1.3 A/mm. The accuracy of measurement was for the majority of the spectral lines ± 0.05 cm^{-1}. As the result of this analysis, the rotational and vibrational constants for BO in the $B^2\Sigma$: state were found to have the following values: $T_e = 43174{,}05$, $\omega_e = 1281{,}69$, $\omega_e x_e = 10{,}66$, $B_e = 1{,}5171$, $\alpha = 0{,}0210$, $D_e \sim 8{,}5 \cdot 10^{-6}$ см$^{-1}$; these values differed only little from those found in the work [289].

It should be noted that in the study of Lagerqvist, Nilsson and Wigartz [2531] we find a summary of molecular constants for BO in which as the most reliable vibrational and rotational constants in the ground state those constants are recommended, which were found by the authors of the present work as the result of the analysis of bands of the β-system. In the work [289] it is shown, however, that with the same error found when determining the wave length of the spectral lines in the region $\lambda \sim 2500$ Å (β-bands) and in the region $\lambda \sim 5000$ Å (α-bands), the errors in the determination of the wave numbers were four-time larger for the lines of the β-bands than for those of the α-bands. Therefore, the constants for the ground state as obtained from the analysis of the bands of the α-system, listed in Table 208, prove to be more reliable than those obtained from the analysis of the bands of the β-system.

Mulliken [2972] observed in the spectrum of BO besides the α- and β-systems a system of bands located in the region 4800-5800 A, which he referred to the transition $B^2\Sigma - A^2\Pi$. The analysis of the bands of this system yielded vibrational constants for BO in the $B^2\Sigma$ и $A^2\Pi$ states, which were in good agreement with the constants found in the α- and β-system analyses.

When investigating the spectrum of BN Kret'yen discovered in the vacuum ultraviolet a band system in the region 1700-1900 A which he assumably attributed to the transition $C^2\Pi - X^2\Sigma$ of the BO molecule. Subsequently, Mal'tsev, Katayev and Tatevskiy [288a] used as a source for the excitation of the BO spectrum a hot cored cathode. With this feat they were able to obtain in the ultraviolet, in the region 1850-2090 A, intensive bands, which had been masked by BF bands in the studies by Chretien. Analyzing the data, the authors of the study were able to prove that the ultraviolet bands belong indeed to the transition $C^2\Pi - X^2\Sigma$ of the BO molecule and to identify the following values for the vibrational constants in the state $C^2\Pi: T_e = 55369, \omega_e = 1315$ и $\omega_e x_e = 11$ $см^{-1}$. The rotational constants of BO in the state $C^2\Pi$ were $B_e = 1,4759$, $\alpha_1 = 0,0170$ и $D_e = 8,3 \cdot 10^{-6}$ $см^{-1}$ — which were found by Kuzyakov, Tatevskiy and Tunitskiy [270] as a result from an analysis of the rotational structure of the 1-0 and 2-0 bands in the ultraviolet system of $C^2\Pi - X^2\Sigma$. Similar data were obtained by the authors of the work [288a]. Since the excitation energy of the $C^2\Pi$ state exceeds 50,000 cm^{-1} the BO constants in this state have not been included in Table 208.*

BH. The ground electron state of the BH molecule is the state $^1\Sigma^+$. In the emission spectrum of the boron monohydride four band systems could be observed: the singlet systems $A^1\Pi - X^1\Sigma^+$ [2636, 3195, 3989, 523], $C^1\Sigma \rightarrow A^1\Pi, D^1\Sigma \rightarrow A^1\Pi$ [1367], and a band system which was associated with transition between the triplet states $^3\Sigma - {}^3\Pi$ [2636, 523] . In the absorption spectrum, only the most intensive system $A^1\Pi - X^1\Sigma^+$, was obtained, which occurred in the photolysis spectrum of diborane as well as of BCl_3 in the presence of hydrogen [3988a, 3038b].**

The ground electron state of the BH molecule is only associated with the system $A^1\Pi - X^1\Sigma^+$, which had been investigated in the studies [2636, 3195, 3989, 523]. The measurement results for the wave numbers of the lines occurring in the bands 0-0 and 1-1, obtained in the studies [2636, 2193, 3989 and 523], were in good mutual agreement within the limit of errors of the experiment. Almy and Horsfall [523] found in addition to the 0-0 and 1-1 bands also the 2-2 band. The values found by these authors [study 523] for the vibrational and rotational constants of BH in the states $X^1\Sigma$ and $A^1\Pi$ are listed in Table 208 and are used in the present Handbook.

Since in the band system $A^1\Pi \rightarrow X^1\Sigma$ only the bands of the sequence $\Delta v = 0$, could be obtained, the spectrum analysis allowed only to determine the values for the differences between the vibrational states of BH in the states $A^1\Pi$ and $X^1\Sigma$: $\omega'_e - \omega''_e = -21{,}8$ и $\omega'_e x'_e - \omega''_e x''_e = 80{,}2\ см^{-1}$. Using the values $\omega''_e = 2366$ и $\omega''_e x''_e = 49\ см^{-1}$, which have been calculated according to the relations (1.36) and (1.38) respectively,* Almy and Horsfall found $\omega'_e = 2344$ и $\omega'_e x'_e = 129\ см^{-1}$. When comparing the difference values $\Delta\omega_e$ and $\Delta\omega_e x_e$ — with the calculated and experimental values of the corresponding terms for the $X^1\Sigma$ state of the AlH molecule, it is possible to conclude that the possible errors in the values ω_e and $\omega_e x_e$ for the $X^1\Sigma$ state of the BH molecule amount to ±40 and ±1 cm^{-1}.

Besides the $A^1\Pi - X^1\Sigma$ system in the study of Almy and Horsfall also a 0-0 band of a triplet system was discovered, located in the region 3694 A. An analysis of the structure of the P- and R-branches of this band instigated the authors of work [523] to draw the conclusion that the band under consideration should be assigned to the transition $^3\Sigma - {}^3\Pi$, whereby the association with the $^3\Pi$ state was similar to Hund's Case (b). The triplet state constants, as recommended in the work [523] are listed in Table 208. Since in the spectrum of the boron monohydride no intercombinational transitions could be observed, the energy of the triplet states remains unknown. However, it is possible to assume on the basis of the analysis the possible electron configurations of the BH molecule and to demonstrate by the analogy of the energy scheme of the AlH molecule that the lower triplet state of BH should have an excitation energy of the order of 20,000 ± 2000 cm^{-1}, i.e., an energy being smaller than that of the $A^1\Pi$ state.

Besides the band systems of BH which have been so far considered, Douglas [1367] discovered in the spectrum of a noncondensed discharge through helium with traces of BCl_3 and hydrogen, three bands at the wave lengths $\lambda\lambda$ 3415 , 3396 and 3099 A, which he assigned to the transitions $C^1\Sigma^+ \to A^1\Pi$ и $D^1\Sigma^+ \to A^1\Pi$. An analysis of these bands enabled Douglas to estimate the values of the molecular constants in the $C^1\Sigma^+$ and $D^1\Sigma^+$ states, which have not been included in Table 208, as the excitation energies of these states exceed 50,000 cm^{-1} 50 000 $см^{-1}$ ($T_e\,(C^1\Sigma) = 52346{,}6$, $T_e\,(D^1\Sigma) = 55333{,}6$ $см^{-1}$) . It should be noted that the occurrence of energy states of the type $^1\Sigma^+$ in the BH molecule with large excitation energies may be considered as an additional prove for true analogy in the scheme of the electron states of BH and AlH, which was the basis for estimating the excitation energy of the $a^3\Pi$ state of the BH molecule.

The molecular constants for BH, listed in Table 208, and accepted in the present Handbook were also recommended in the book by Herzberg [2020] and Handbook [649].

BF. The ground electron state of the BF molecule belongs to the $^1\Sigma^+$ type. Investigations of the BF spectrum yielded the following results: in the studies, [3890, 3199, 2909, 1414, 1100, 659, 3141, 287a] the existence of five stable excited singlet states ($A^1\Pi$, $B^1\Sigma^+$, $C^1\Sigma$, $D^1\Pi$ and $E^1\Sigma$) and of three triplet states ($a^3\Pi_r$, $b^3\Sigma^+$, $c^3\Sigma^+$) has been established.

The most comprehensive studies of the band systems associated with the transitions between the singlet states of BF and those located in the far ultraviolet (1300-2100 A) were carried out by Chretien and Miescher [2909, 1100, 1100a]. The source of excitation used in these investigations was a glow discharge in a discharge tube with aluminum electrodies, through which helium with a small amount of BF_3 was circulated. The spectrum was obtained in a vacuum spectrograph with a dispersion of 8.3 A/mm. Chretien identified [1100] four systems of bands associated with the transitions between the excited singlet states and the electron ground state $^1\Sigma^+$. The nature of the band structure allowed to determine the type of states participating in the corresponding transitions, and a comparison of the isotopic shifts of the band edges found for $B^{11}F^{19}$ and $B^{10}F^{19}$ by measurement and those found through calculation proved that the spectrum has been correctly assigned to the molecule of BF. The most intensive and distinct system of bands in the BF spectrum proved to be the $A^1\Pi \rightarrow X^1\Sigma$ (2100—1860 Å) system. Kret'yen measured the wave lengths of the edges of the Q-branches (which practically coincide with the initial position of the corresponding bands) of 35 bands of this system, which formed the sequence $\Delta v = 0, \pm 1$ и ± 2 с $v' \leqslant 8$ and $v'' \leqslant 10$. The band structures found as a result of the analysis for the vibrational and rotational constants of BF in the states $X^1\Sigma$ and $A^1\Pi$ are listed in Table 208 and have been adopted in the present Handbook. *

Onaka [3141] re-examined in 1957 the band system $A^1\Pi - X^1\Sigma$, using a vacuum spectrograph with a grating of the "echelle" type whose dispersion was in the region 1900 Å ~ 0,3 Å/мм. In the study [3141] an analysis of the fine structure of 13 bands was carried out, which correspond to the values $v' < 5$ and $v'' < 6$. The molecular constants of BF occurring in the states $X^1\Sigma$ and $A^1\Pi$, as found by Onaka are listed in the remarks to Table 208. They differ only unessentially from the constants adopted in the present Handbook.

The BF constants for the $X^1\Sigma$ and $A^1\Pi$, states as found by Chretien and adopted in the present Handbook for the calculation of thermodynamic functions are cited in Handbook [649]. In Herzberg's monograph [2020] some different values are said to have been recommended according to preliminary information by Miescher and Chretien [2909].

It should be noted that the considerations on various possible electron configurations for the BF molecule encouraged Onaka [3141] to draw the conclusion that in the vicinity of the $A^1\Pi$ state there should exist a $^1\Sigma^-$, state, which so far has not been discovered in the BF spectrum.

The excitation energies of all remaining known singlet states of BF ($B^1\Sigma$, $C^1\Sigma$, $D^1\Pi$ and $E^1\Sigma$) exceed by far 50,000 cm^{-1}. Therefore, the molecular constants for BF as found by Kret'yen [1100] and Mal'tsev [287a] have not been included in the present Handbook's Table 208.

The system of bands associated with the transition between the triplet states and located in the near ultraviolet region, were investigated in the studies [3890, 3199, 1414 and 659]. An analysis of the vibrational structure of the triplet bands had been carried out for the first time by Strong and Noss [3890]. In this study an electrodeless discharge in a BF_3 atmosphere has been used as excitation source. The spectrum was obtained on a Hilger spectrograph and also on the first scale of the grating (at a disperion of 1.2 A/mm). An analysis of 12 bands of the system $b^3\Sigma - a^3\Pi$ and of three bands of the system $c^3\Sigma - a^3\Pi$, carried out on the edges of the P_3-branches enabled the authors [3890] to find vibrational constants for BF in the $a^3\Pi$ and $b^3\Sigma$. states. The rotational constants for BF in the $a^3\Pi$ and $b^3\Sigma$ states were found by Paul and Khauss [3199] when they investigated the fine structure of the band system $b^3\Sigma - a^3\Pi$ with $v' < 1$ and $v'' \leqslant 1$.

In Table 208 the vibrational and rotational constants for BF are listed in Table 208 in the $a^3\Pi$. state as found in the studies [3890, 3199].* Since in the BF spectrum no intercombinational transitions could be observed, the absolute values for the excitation energies of the triplet states are unknown. An attempt to determine the excitation energy of triplet states in BF, as tried in the study [659], failed, since it was not possible to discover any excitation in the rotational structure of triplet bands. The value for T_e for the state $a^3\Pi$, equaling 35,000 ± 2000 cm^{-1}, cited in Table 208, was estimated according to the method suggested in the study [1355] on the basis of the value for the dissociation energy of the BF molecule, on the linear extrapolation of the state levels of $a^3\Pi$ and on the assumption that the states $X^1\Sigma$ and $a^3\Pi$ have a common dissociation limit.

As the excitation energies for triplet and singlet states of the InF and GaF molecules [651, 656] are known, the excitation energy for the state $a^3\Pi$ of the BF molecule has been estimated also according to the relation (1.31) and was found to be equal to 36,000 cm^{-1}.

In a study by Barrow et al [659], published in 1958, the triplet system of bands of the BF molecule has been reinvestigated again. A spectrum with great dispersion in the third and fourth order of a 21-feet grating was obtained. A detailed fine-structure analysis of six bands of the system $b^3\Sigma - a^3\Pi$ and of the 0-0 band of the system $c^3\Sigma - a^3\Pi$ showed that the lower triplet state $a^3\Pi$ proved to be the normal state $^3\Pi_r$, and that the upper states proved to be $^3\Sigma^+$ states. The values for the molecular constants of BF in the states $a^3\Pi_r$ and $b^3\Sigma^+$ found in the study [659] differ only unessentially from the constants obtained in previous works [3890, 3199].

<u>BCl.</u> The ground electronic states of the BCl molecule as well as of other molecules of mono-halides of elements belonging to the third

group is the state $X^1\Sigma^+$. In the emission spectrum of BCl a single band system could be observed, being associated with the transition $A^1\Pi - X^1\Sigma$. The same system was obtained recently by Thrush [3988a] in an absorption spectrum of BCl during a pulse photolysis of BCl_3.

Bands belonging to the BCl molecule and located in the region of 2600-2900 A had been discovered for the first time by Jevons in 1924 [2247] in a spectrum of discharge through BCl_3 vapors. The vibrational structure of these bands has been later on analyzed by Miescher [2904].

The most detailed investigation of the band systemof BCl had been accomplished by Herzberg and Hushley [2034]. The spectrum was excited through non-condensed discharge in a helium atmosphere with small additions of BCl_3, and the photographs were made in the sixth order of a 21-feet grating. In the spectrum well developed sequences of the type $\Delta v = 0, \pm 1$ and ± 2 were observed which were formed by bands with v' and $v'' \leqslant 8$. Due to the presence of P-, Q-, and R-branches in each spectral band it was possible to assign the system under investigation to the transition $^1\Pi \rightarrow {}^1\Sigma$. Furthermore, an analysis of the vibrational structure of the ultraviolet band system of BCl, carried out by Herzberg and Hushley on the edges of the Q-branches of $B^{11}Cl^{35}$ and $B^{10}Cl^{35}$, who took also into account the measurement results of Miescher [2904], made it possible to reveal vibrational structures of BCl in the states $A^1\Pi$ and $X^1\Sigma$. In study [2034] it was shown that the interpretation of the vibrational structure being characteristic for the spectrum of isotope molecules of BCl, as suggested by Miescher [2904] proved to be wrong in a number of cases, and consequently, the constants found by him for BCl are erroneous, too.

The vibrational constants ω_e and $\omega_e x_e$ of the molecule $B^{11}Cl^{35}$ in the $X^1\Sigma$ and $A^1\Pi$ states, as found by Herzberg and Hushley [2034] have been included in the present Handbook. In the same Table the rotational constants for $B^{11}Cl^{35}$, also obtained by Herzberg and Hushley in an analysis of the rotational structures of the P-, Q-, and R-branches of bands with v' and $v''\leqslant 6$. Analogous values for the molecular constants of $B^{11}Cl^{35}$ are recommended in the book [2020] and in the Handbook [649].

The following should be noted: in analogy to other molecules of halides of elements of the third group one should expect for the BCl molecule the existence of a stable triplet state of the type $a^3\Pi$, with its position below the singlet state $A^1\Pi$ which so far could not be observed. An estimate of the excitation energy of this state based on a comparison with excitation energies of the corresponding states of AlCl yields a value $T_e(a^3\Pi)=24\,000\pm3000$ см$^{-1}$.

BN. The first work in which a spectrum for BN has been obtained is that by Douglas and Herzberg [1375]. The spectrum was excited in a discharge tube filled with helium, with a small amount of BCl_3 and traces of Nitrogen added, and photographed on a spectrograph with a 21-feet grating.

In the BN spectrum two band systems could be observed: a triplet system $(^3\Pi - {}^3\Pi)$ and a singlet system $(^1\Pi - {}^1\Sigma)$.

Based on the analogy of the structure of the triplet system of BN with Swan's system of the C_2 molecule, whose lower state $^3\Pi$ previously was considered as the ground state of C_2, Douglas and Herzberg [1375] suggested that the lower state of the triplet system of BN might be the ground electronic state of the molecule. At the present time it has been shown that the ground state of the C_2 molecule is the singlet state $^1\Sigma$, and that the $^3\Pi$ state is located at 717 cm^{-1} above the $^1\Sigma$ state (see page 868). Hence it could be expected that the suggestions made by Douglas and Herzberg on the type of the ground electronic state of BN should be revised. However, on the basis of an absorption spectrum of BN, obtained by Thrush [3988a] during a pulse photolysis of BCl_3 in the presence of nitrogen, it was shown that in the spectrum only bands of the triplet system $^3\Pi - {}^3\Pi$, appeared and that singlet bands were not observed. This is to corroborate the conclusion drawn by the authors of study [1375] that the state $X^3\Pi$ should be considered as the ground state of BN. Thrush tries to explain a similar discrepancy in the scheme of electronic states in isoelectronic molecules of BN and C_2 on the grounds that the boron and nitrogen atoms in ground states (^2P and ^4S) possibly could correspond to the triplet and quintuplet states of BN, while two carbon atoms in the ground electronic state ^3P might lead to the formation of a C_2 molecule in the triplet and quintuplet states as well as in the singlet states. In accordance with the results obtained from an investigation of the absorption spectrum of BN it has been assumed that the state $X^3\Pi$ may be considered the ground electronic state of this molecule.

When analyzing the vibrational structure of the triplet system on the edges of ten bands forming three sequences $(\Delta v = 0, \pm 1 \text{ c } v' \leqslant 3$ and $v'' \leqslant 3)$, Douglas and Herzberg found the constants ω_e and $\omega_e x_e$ to be in the $X^3\Pi$ and $A^3\Pi$ states. In analyzing the structure of the 0-0 band it was shown that both states $^3\Pi$ according to the type of coupling should be close to Hund's case (b). Since R-branches could not be resolved in the bands observed and due to the fact that the Q-branches were in the $^3\Pi - {}^3\Pi$ type transitions of so little intensity that they could practically not be detected in the spectra it proved to be impossible to set up an analysis of the rotational structure through compilation of the combinational differences. Therefore, the authors of study [1375] were able to analyze only the structure permitted P-branches in the following three bands: 0-0, 1-0, and 0-1. The error thus found in value B''_e may probably reach a magnitude of ± 0.05 cm^{-1}.

The vibrational and rotational constants for BN in both states $^3\Pi$, as found in the study [1375], are listed in Table 208 and have been adopted in the present Handbook. In the monograph [2020] and in the Handbook [649] the same values for the molecular constants of BN are recommended. It should only be noted that in the book [2020] for the state $A^3\Pi$ a value for T_e being equal to 27,877.0 cm^{-1} has been cited, while in the Handbook [649] $T_e = 27\,850$ $см^{-1}$. The value T_e cited in Herzberg's book [2020] was calculated for the value ν_∞ of the band edges, while the value T_e cited in the Handbook [649] corresponds to ν_∞ of the initial band. The value T_e listed in Table 208 corresponds to the onset of the 0-0 band.

In addition to the triplet system of bands belonging to the BN spectrum, Douglas and Herzberg [1375] discovered three other bands with an unresolved fine structure and edges at 30,963.3; 32,817.2 and 34,498.8 cm^{-1}. On the basis of the external view the authors assigned them to the singlet system $^1\Pi - {}^1\Sigma$ [1375]. On the assumption that these bands are of the type 0-1, 0-0 and 1-0, this assignment allowed to estimate the following values: $\Delta G''_{1/2} = 1853{,}9$ and $\Delta G'_{1/2} = 1681{,}6$ $см^{-1}$. The authors of study [1375], however, emphasize that similar interpretations of the observed bands should be considered as roughly tentative.

BO_2. All flames containing boron and its compounds have a characteristic green color caused by the so-called fluctuation bands, reaching the spectra of these flames from 3700 to 6800 A. For the first time these bands have been obtained by authors of the work [3575a] and subsequently they have been investigated by a number of authors. However, all attempts to determine the carrier of these bands with a single value, which had been ascribed in various studies to molecules of B_2O_3 [3813] and of BO [3745] have been unsuccessful until 1960.

In 1958 Mal'tsev and Tatevskiy [54] were the first to suggest that these bands belong to the previously unknown molecule of BO_2. The correctness of this suggestion was confirmed by their further investigation of the intensity of the "fluctuation bands" in emission and absorption spectra of boron oxide vapors in an atmosphere of various gases, depending on the temperature of the furnace and the nature of the gas [52a, 289a, 289b], furthermore by investigations of the intensity of these bands in the flame spectra, depending on the oxygen content in the fuel mixture, carried out in the work of Kaskan and Millikan [2329a] and also by the study of Rusin and Tatevskiy [351a] who investigated the spectra of explosions of boron-containing mixtures.

In the studies [52a, 289a, 289b] Mal'tsev, Matveyev and Tatevskiy investigated also the "fluctuation bands" of BO_2 on an apparatus with great dispersion and they performed a preliminary analysis of the vibrational structure of the spectrum. On the basis of the data obtained Tatevskiy and co-workers drew the conclusion that the BO_2 molecule as well as its isoelectronic molecules NCO and N_3 possess a linear structure, and they found ν_2^{π} to be ~ 650 см$^{-1}$.

Having assumed that the two B – O bonds in the BO_2 molecule are inequal (one being a single bond and the second being a double bond) and having accepted the bond energy constants and the bond lengths to be of the same values as those accepted for B_2O_3 ($f_{B-O} = 5{,}3 \cdot 10^5$, $f_{B=O} = 13{,}4 \cdot 10^6$ dyne·cm^{-1}, $r_{B-O} = 1{,}36$ and $r_{B=O} = 1{,}20$ Å), the authors of [52a] found for $B^{11}O_2$ the values ν_1 and ν_3 to be $\nu_1 = 908$ and $\nu_3 = 1932$ cm^{-1}.

The suggestion made on the inequality of the boron-oxygen bonds in the BO_2 molecule by Mal'tsev, Matveyev and Tatevskiy on the basis of the analogy with the inequality of these bonds in the group O – B = O in the molecules B_2O_3 and XOBO cannot be considered as fully justified. It is more probable that in the molecule BO_2 as well as in its isoelectronic molecules CO_2^+ and N_3 both bonds are equivalent and that their properties are intermediate between the single and double boron-oxygen bonds. If this bond proves to be of the sesqui-valent type, and consequently, the bond constants B – O in the BO_2 molecule are approximately equal to the half-sum of the corresponding constants of the single and double boron-oxygen bonds $(f_{B-O} = (10 \pm 2) \cdot 10^5$ dyne$\cdot$cm^{-1} and $r_{B-O} = 1{,}27 \pm 0{,}03$ Å$)$, then the symmetric and antisymmetric valence vibration frequencies should be equal to $\nu_1 = 1000 \pm 100$ and $\nu_3 = 1900 \pm$ $\pm$ 200 cm^{-1}. A comparison of the ground frequency values for BO_2 obtained on the assumption that both bonds are either nonequivalent or equivalent, of course by taking into account averaged values for the bond energy constants may lead to the conclusion that the values of the ground frequencies ν_1 and ν_3 are preserved in both cases as practically constant.

It should be noted, however, that in the CO_2^+ molecule being isoelectronic with BO_2 the bond energy constant, the bond length and the bond interaction constant possess magnitudes which are close to the constants of this type in the CO_2 molecule (f_{C-O} and f_{dd} are equal (in 10^{-5} dyne$\cdot$cm^{-1}) to 14.5 and 0.9 for CO_2^+ and 15.5 and 1.3 for CO_2, respectively.). This means that the detachment of one of the eight shared valence electrons from the CO_2 molecule does not result in a noticeable weakening of the C – O bond, which in the CO_2^+ type molecule remains practically a double one. Therefore, it can be assumed that, if the bonds in the BO_2 molecule are considered to be equivalent, the properties of these bonds formed by seven electrons, which is also the case in the CO_2^+ molecule, should approach those of the double bond type boron-oxygen. Apparently, this suggestion is confirmed when the values of the bond dissociation energies of BO are compared with those of BO_2 (see §94 and Table 219), since according to data obtained by Rusin and Tatevskiy [52a and 351b] the dissociation energy of BO_2 (of the order of 14 ev) exceeds $D_0(BO)$ almost by a factor of two. If we assume the coupling constant f_d in BO_2 to have a value of the order of $12 \cdot 10^5$ dynes·cm^{-1} (i.e. somewhat less than the constants of the double bonds in BO and B_2O_2, which are equal to $13.3 \cdot 10^5$ dynes·cm^{-1} and $13.5 \cdot 10^5$, respectively) and if we consider the constant $f_{dd} = 1 \cdot 10^5$ dynes·cm^{-1}, then we obtain for the symmetric and antisymmetric vibration frequencies $\nu_1 \sim 1100$ and $\nu_3 \sim 2050$ см$^{-1}$.[1] .*

TABLE 209

Accepted Values for the Molecular Constants of BO_2, B_2O_2, HBO and FBO

Молекула[1]	ν_1	ν_2	ν_3	ν_4	ν_5	I	σ
	см$^{-1}$					10^{-40} г·см^2	
BO_2 [a]	1070	464 (2)	1322	—	—	8,502	2
B_2O_2	2100	650	1890	500 (2)	250 (2)	23	2
HBO	2450	700 (2)	1800	—	—	2,1	1
FBO	1000	400 (2)	2100	—	—	8,5	1

Note: a) $A = -148.6$ cm^{-1}.

1) Molecule.

<u>Amendments to the proof</u>. After the manuscript of the Handbook was sent to the press, a work by Johns [2256b] was published, in which an analysis of the absorption spectrum of BO_2, obtained by pulse photolysis of a mixture of BCl_3 and oxygen, has been described. The spectrum was photographed on an apparatus with great dispersion; it was formed by a number of band groups in the region 3800-6800 A.

Owing to the fact that the spectrum was obtained by pulse type photolysis and not in flames or King's furnace the rotational structure of the bands was relatively simple, thus considerably facilitating the analysis and making separation of the bands, belonging to the $B^{11}O_2$ and $B^{10}O_2$ molecules possible. The band groups with the red shade, previously known as "fluctuation bands" have been attributed to the transition $A^2\Pi - X^2\Pi$, while the group of doublet bands in the region 4070 A has been assigned to the transition $B^2\Sigma - X^2\Pi$. As the result of the analysis intended to determine the rotational structure of the band system $A^2\Pi - X^2\Pi$ Johns was able to show that the BO_2 molecule is a symmetric linear molecule in both electronic states $B''_0 = 0.3292$; $B'_0 = 0.3106$ cm^{-1}, $r''_0 = 1.2653$ and $r'_0 = 1.3025$ A). The values for the ground frequencies and for the spin-orbital coupling constant of BO_2 in the $X^2\Pi$ state found by Johns are equal to $\nu_1 = 1070$; $\nu_2 = 464$; $\nu_3 \sim 1322$*; $A = -148.6$ cm^{-1}. The constants for BO_2 in the $A^2\Pi$ state have according to the data of Johns the following values (in cm^{-1}): $T_0 = 18291.59$; $\omega_1 = 994$; $\omega_2 = 502$; $\nu_3 = 2357$; $A = -101.3$ см^{-1}. The analysis cf the group of bands of the $B^2\Sigma - X^2\Pi$ system allowed to determine only the values $T_0 = 24507.9$ см^{-1}, $\nu_2 = 505$ and $B_0 = 0.3250$ см^{-1}. Since the values for the constants of BO_2 found by Johns are considerably more accurate than those estimated by the authors of the Handbook and those listed in the works [52a, 289a, 289b] they have been adopted for the subsequent calculations. The corresponding values for the BO_2 constants in the $X^2\Pi$ state are given in Table 209.

HBO and FBO. The spectra of the HBO and FBO molecules could not be observed until the present time and their constants are unknown in the literature so far. It is, however, possible to estimate the values of these constants with a sufficient great precision on the basis of the general concepts on the orientation of chemical bonds, resorting to their analogy with their isoelectronic molecules HCN and FCN. When the present Handbook was drawn up, it has been accepted that both molecules do have in the group electronic state $^1\Sigma$ a linear structure (the point group being $C_{\infty h}$) and that the bond energy constants and bond lengths in the HBO and FBO molecules have the same values as the constants for the following molecules: BH($k_e = 3.04 \cdot 10^5$ dyne·cm^{-1},

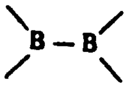
r_e = 1.255 A); BF(k_e = 8.16·10^5 dyne·cm^{-1}, r_e = 1.262 A); BO(k_e = = 13.3·10^5 dyne·cm^{-1}, r_e = 1.205 A). The values f_α/d_1d_2, which are indispensable for the calculation of the ground frequencies for the deformation vibrations of the HBO and FBO molecules have been accepted as being equal to 0.2·10^5 dyne·cm^{-1} on the basis of the corresponding values which are valid for the isoelectronic molecules HCN and FCN.*

The values for the ground frequencies of the HBO and FBO molecules were calculated according to the Eqs. (P4.27) using the accepted values for the bond energy constants given in Table 209. The error of the cited values is ±10%. In Table 209 also the moments of inertia of these molecules are given, which have been calculated according to the above accepted parameters for the molecular structure; the error of the latter does not exceed 0.03 A.

$\underline{B_2O_2}$. There are no experimental data on the structure of the B_2O_2 available in the literature. Through comparison of the properties of the isoelectronic molecule C_2N_2 and using the general concepts on the orientation of the chemical bonds of the boron it is possible to assume that the B_2O_2 molecule should have a linear structure and should belong to the point group $D_{\infty h}$. Tetratomic molecules of this type possess five normal vibrations two of which (the deformation vibrations ν_4 and ν_5) show a twofold degeneracy.

The only experimental investigation of the B_2O_2 spectrum ever made was carried out by White, Walsh and Mann [4240]. The emission spectrum was obtained on heating a mixture of magnesium oxide with elementary boron at a temperature of 1550°K, i.e., under conditions which are described by Searcy and Myers [3673] as favorable for the formation of B_2O_2 in the vapors. In the region from 1200 to 3000 cm^{-1} the authors of the study [4240] were able to detect only a single band at a frequency of 1890 cm^{-1} which was interpreted by them as a valence vibration of the $- B = O$ bond type.

The structural parameters and the ground frequencies for the B_2O_2 molecule may be estimated with the aid of indirect data. Such an estimate was carried out for the first time by Inghram, Porter and Chupka [2171] on the basis of the interatomic distances and bond energy constants of the B_2 and BO radicals, three years before the study [4240] had been published. The bond lengths $= B - B =$ and $- B = O$ in the B_2O_2 molecule have been assumed to be equal to the interatomic distances in the mentioned radicals (1.589 and 1.205 A, respectively) and the vibration frequencies have been calculated using the Eqs. (P4.36). The force constants of the bonds $= B - B =$ and $- B = O$ were assumed to be equal to the force constants of B_2 and BO ($3.58 \cdot 10^5$ and $13.65 \cdot 10^5$ dyne$\cdot$cm^{-1}), and the constant of the deformation vibrations was estimated in analogy to the corresponding constant of C_2N_2 to be $0.135 \cdot 10^5$ dyne$\cdot$cm^{-1}. The values for the ground frequencies found in this manner in the work [2171] for $B_2^{11}O_2$ were equal (in cm^{-1}) to: $\nu_1 = 2070$, $\nu_2 = 610$, $\nu_3 = 1885$, $\nu_4 = 435$ and $\nu_5 = 215$.*

Mal'tsev et al [54] tried to re-estimate the constants for B_2O_2. In this work the bond length $= B - B =$ was assumed to be equal to 1.70 A, based on the value of the corresponding interatomic distance in the molecules B_2F_4 (1.67 A) [4017] and B_2Cl_4 (1.75 A) [588] and the force constant of this bond was assumed to be equal to the coupling constant  in the B_2Cl_4 molecule [2757] ($2.6 \cdot 10^5$ dyne$\cdot$cm^{-1}). For the interatomic distance and the force constant of $- B = O$ and for the constant of the deformation vibrations of B_2O_2 the authors [54] adopted values being close to those selected by Inghram, Porter and Chupka (1.20 A, $13 \cdot 10^5$ and $15 \cdot 10^5$ dyne$\cdot$cm^{-1}). The ground frequencies of the molecule $B_2^{11}O_2$, calculated in the study [54] from the Eqs. (P4.

.36) are equal to the following values (in cm^{-1}): $\nu_1 = 1975$, $\nu_2 = 533$, $\nu_3 = 1840$, $\nu_4 = 462$ and $\nu_5 = 198$, i.e., rather close to the results obtained by the calculation in [2171].

It should be noted, however, that the alteration of the force constant and bond length of = B – B = as outlined in the study [54] is not justified with respect to the corresponding values which have been adopted by Inghram, Porter and Chupka. From data on hydrocarbons and from general considerations, developed in the studies of Tatevskiy (see e.g., [409])., it follows that the bond length of = X – X = should be considerably smaller and the force constant should be considerably larger than the analogous constants for the bond >X–X<. Therefore, the estimated values for the constants of the B_2O_2 molecule according to the B_2F_4 and B_2Cl_4 molecules are false. The bond lengths – B = 0 and = B – B = in the B_2O_2 molecule could possibly be expected to be somewhat smaller and the force constants somewhat larger than those in the molecules BO and B_2.* If we assume the force constants of the bond types B – B and B = 0 in the B_2O_2 molecule to be equal to $4\cdot10^5$ and $14\cdot10^5$ dyne·cm^{-1}, and the interatomic distances to be equal to 1.55 and 1.20 A, then the values of the fundamental frequencies of B_2O_2 are found to be equal to: $\nu_1 = 2120$, $\nu_2 = 670$, $\nu_3 = 1920$, $\nu_4 = 540$ and $\nu_5 = 270$ cm^{-1} (when $f_\alpha/d_1d_2 = 0.2\cdot10^5$ dyne·cm^{-1}).

From the given data it is apparent that the values of the fundamental frequencies of B_2O_2 being obtained through calculation from various values of the force constants vary within the limit of errors originating from the use of a simplified field of force for this molecule and from neglecting the constants of interaction.

The values for the fundamental frequencies of the B_2O_2 molecule used in this Handbook are those given in Table 209, where for ν_3 a value has been accepted, which was found experimentally in the work

[4240], while for all other frequencies the values chosen were close to averaged values from those calculated in the study [2171] and those by the authors of the Handbook. The rate of errors in these values is 10-15%. The moment of inertia of the B_2O_2 molecule, listed in Table 209, was calculated to be for $r_{B-B} = 1{,}57 \pm 0{,}03$ and for $r_{B-O} = 1{,}20 \pm 0{,}03$ Å.

Since the B_2O_2 molecule has an even number of electrons, its ground state has been accepted in this Handbook to be of the $^1\Sigma$ type.

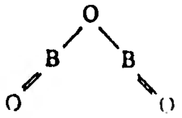
After the calculations of the thermodynamic functions of the B_2O_2 molecule had been completed a study by White, Mann, Walsh and Sommer [4238] was published in which IR emission spectra of B_2O_3 and B_2O_2 have been investigated. In the spectrum of B_2O_2 in the region 700--3000 cm^{-1} only one frequency could be observed at 1890 cm^{-1} which was attributed to the vibration ν_3. The values for the other frequencies of B_2O_2 were obtained on the basis of estimates and were assumed to be equal to: $\nu_1 = 2000$, $\nu_2 = 750$, $\nu_4 = 600$ and $\nu_5 = 300$ cm^{-1}. The value for ν_1 was calculated by the authors of the work [4238] through comparison of the values ν_1 and ν_3 in C_2N_2 with the value ν_3 for B_2O_2, given above. Value ν_2 was calculated in accordance with the Eqs. (P4. 36), assuming that $f_{B-B} = 4 \cdot 10^5$ and $f_{B-O} = 13{,}5 \cdot 10^5$ dyne•cm^{-1}, and the values ν_4 and ν_5 were obtained through comparison of these frequencies in C_2N_2 with frequencies of deformation vibrations of B_2O_3.

The values ν_1, ν_4 and ν_5 obtained in the study [4238] on the basis of qualitative considerations, in general are in satisfactory agreement with those accepted in the present Handbook, though they are seemingly less precise. As to value ν_2 obtained in this study, the authors of [4238] obviously commited in their calculation an arithmetical error, since when assuming $f_{B-B} = (4 \pm 0{,}5) \cdot 10^5$ and $f_{B-O} = (13{,}5 \pm 0{,}5) \cdot 10^5$ dyne•cm^{-1}, $\nu_2 = 640 \pm 30$ см$^{-1}$.

$\underline{B_2O_3}$. During the last 10-15 years great attention was given to the determination of the structure, structural parameters and fundamental frequencies of the boron oxide. Until the middle of the 1950-ties these investigations were limited to various estimates based on the general connotations of the theory of oriented valences and to results obtained from investigations of spectra of combinational scattering observed in vitreous boron oxide. In all studies made the conclusion was drawn that the B_2O_3 molecule has a dypiramidal structure (with the point group D_{3h}). The entropy of gaseous boron oxide at $T \sim 1600° K$, calculated according to these data with the help of statistical methods were found to be in satisfactory agreement with the value calculated according to the Eqs. (17) (see page 36) from results of calorimetric measurements of the specific heat and enthalpy of the boron oxide in the solid and liquid states and from data on saturated vapor pressures obtained by Speiser, Naidich and Johnston [3817]. Since analogous calculations based on molecular constants of B_2O_3, estimated for the angular model of this molecule (with the point group C_{2v}) resulted in sharp discrepancies for the entropy values, the conclusion on the dipyramidal structure of the boron oxide molecule appears to be sufficiently well established.

It should be noted, however, that the attempts to determine the fundamental frequencies of the B_2O_3 molecule from absorption spectra of vitreous boron oxide proved to be unfounded. Through subsequent careful investigations of spectra appearing in the vitreous and also in the liquid form of boron oxide, carried out in the studies by Sobolev and co-workers [280, 375, 376]* it was shown that in the bands a great number of bands could be observed which by no means whatsoever could be interpreted as to be representative of some sound model of the B_2O_3 molecule, even with an allowance for intermolecular interaction. For this reason Stepanov (see [28]) as well as Sidorov as Sobolev [375, 376] attempted to interpret the spectra which they obtained from vitreous boron oxide, after correlating their findings with the work [1523] as if the latter would exist of the B_4O_6 molecule (point group T_d). The values for the frequencies of the molecule B_4O_6 this way are given in the study [376]. However, later on Geerin came to the conclusion that in accordance with his theory of vibrations of finite crystal lattices [152a] the frequencies in the spectra of vitreous boron oxide cannot be assigned to any molecular vibrations, but are caused by vibrations of the crystal lattice [152b]. Thus, the results from the investigations of spectra of boron oxide in the condensed state cannot be used to draw any conclusion on the structure and constants of the B_2O_3 molecule.

A careful study of the structure and structural parameters of the boron oxide molecule was carried out in the works by Akishin and Spiridonov [8, 10, 67b] using the electron diffraction method. The results of these investigations proved to be incompatible with the dipyramidal model of the B_2O_3 molecule. At first Akishin and Spiridonov [8] who took into account the results obtained from investigations of spectra of the vitreous boron oxide in the studies [375, 376] attempted to interpret the electron diffraction pattern obtained by them as being due to electron scattering from B_4O_6 molecules. This, however, proved to be possible only for an asymmetric model of the molecule, though the authors of the works [275, 276] had conceived for the B_4O_6 molecule a model of high symmetry. Besides that it was shown by mass-spectrometric and effusionometric investigations of the composition of boron oxide vapors (see page 1437) that in these vapors there are no molecules of the type B_4O_6 present.

Akishin and Spiridonov [10, 67b] having re-investigated the structure of the boron oxide molecule using rotating sectors and microphotometric measurement of the electron diffraction pattern (electronograms), came to the conclusion that the only structure of the B_2O_3 molecule which could be explained by the diffraction pattern observed should be that represented by the angular model  (point group C_{2v})* with the following structural parameters: $r_{B=O}$ = = 1.20 ± 0.03, r_{B-O} = 1.36 ± 0.03 A, $\angle$B)B = 95°. These values are in good agreement with those to be expected for the angular model of the B_2O_3 molecule according to theoretical connotations.**

The IR-emission spectrum of boron oxide vapors has been studied in the works by Dawes and Porter [1401], White, Walsh and Mann [4240], White, Mann, Walsh and Sommer [4238] and Tatevskiy, Mal'tsev et al [54, 52a]. To determine the size of the isotope shift of bands in the B_2O_3 molecule, in these investigations in addition to the normal boron oxide also the B^{10}-enriched oxide has been examined.

In the work by Dawes and Porter [1401] in the infrared spectrum only a single band could be observed in the region 2013 cm^{-1} (for $B_2^{10}O_3$ in the region 2114 cm^{-1}); in the presence of water vapors an additional weak band could be revealed in the region 3770 cm^{-1}. On the basis of the size of the isotope shift observed Dawes and Porter suggested for the B_2O_3 to have a dipyramidal structure (group D_{3h}). However, subsequently, Taylor [3956] was able to show that this conclusion is erroneous and that the isotope shift as observed by Dawes and Porter is incompatible with the dipyramidal and linear models of the B_2O_3 molecule.

White et al [4240, 4238] investigated the emission spectrum of boron oxide vapors in the region from 650 to 4000 cm^{-1} on heating B_2O_3 in a vacuum furnace in an argon atmosphere at a temperature of 1350 -

1400°K. In the spectrum three bands were observed which were located (for the natural mixture of the isotopes B^{10} and B^{11}) at 2040, 1302, and 742 cm^{-1}. According to the data of [4240, 4238] the isotope shift for these bands was equal to 60, 35, and 22 cm^{-1}, respectively. On the basis of the analysis of the spectrum obtained and in accordance with the general concepts on the orientation of the boron atom valences the authors of these works came to the conclusion that the B_2O_3 molecule should have an angular structure (of the type of the C_{2v} symmetry). The molecule of this type should have nine normal vibrations eight of which are active in the infrared spectrum. White et al identified the band at 2040 cm^{-1} with valence vibrations of the double bond B = O (by the frequency of the symmetric vibration ν_1 and the anti-symmetric vibration ν_6), which should be close to each other according to their values, and the band in the region 1300-1400 cm^{-1} with the valence vibrations of the single bond B – O (by the frequencies ν_2 and ν_7, respectively). The band in the region 742 cm^{-1} was assigned to the deformation vibration ν_8 of the group OBO. In order to confirm the suggested interpretation of the boron oxide vapor spectrum and in order to determine the values for the rest of the frequencies, the authors of the work [4238] calculated the vibration frequencies for B_2O_3 according to their estimated values of the force constants. The values of the fundamental frequencies found for the B_2O_3 molecule this way were equal to*: $\nu_1 = 2035$, $\nu_2 = 1411$, $\nu_3 = 873$, $\nu_4 = 310$, $\nu_5 = 758$, $\nu_6 = 2035$, $\nu_7 = 1300$, $\nu_8 = 740$, $\nu_9 = 869\ \text{см}^{-1}$.

Tatevskiy and Mal'tsev [52a, 54] investigated the emission and absorption spectra of boron oxide vapors in atmospheres of He, N_2, H_2, O_2 and water vapors. In all cases the infrared spectrum showed in the region up to 2500 cm^{-1} only a single band at about 2100 cm^{-1}, while in the visible region in the presence of oxygen a green luminescence was revealed, which was absent in the atmospheres of inert gases, hydrogen and water vapors, and which was identified with the spectrum of BO_2. Aiming at the determination of the frequencies of the B_2O_3 molecule the authors of the work [54] estimated the force constants for the angular model of this molecule as being equal to (in 10^5 dyne·cm^{-1}) $5 \leqslant f_{B-O} \leqslant 6$; $13 \leqslant f_{B=O} \leqslant 14$; $f_{B-O-B} = 0{,}71$ and $0{,}45 \leqslant f_{O-B=O} \leqslant 0{,}67$; they also calculated the following values for the fundamental frequencies of B_2O_3: $\nu_1 = 2050 \pm 80$, $\nu_2 = 1020 \pm 80$, $\nu_3 = 700 \pm 80$, $\nu_4 = 190 \pm 30$, $\nu_5 = 700 \pm 80$, $\nu_6 = 2050 \pm 80$, $\nu_7 = 980 \pm 60$, $\nu_8 = 620 \pm 60$, $\nu_9 = 630 \pm 80$ см^{-1}.

Due to the fact that the results of these calculations only badly agree with the data obtained in the study by White et al [4238], Tatevskiy and Mal'tsev checked and re-examined these calculations in the work [52a] and recalculated them for various isotope modifications of the B_2O_3 molecule on the basis of various sets of force constants, including those which were assumed in the work [4238]. Thereby it was found that the frequency of the order of 1300 cm^{-1} cannot be obtained with any rational set of force constants, including those assumed by White et al. This led the authors [290a, 52a] to the conclusion that in the work [4238] in the calculation of the fundamental frequencies for the B_2O_3 molecule an error was tolerated and that the bands observed in the spectrum of boron oxide vapors in the regions 1302 and 742 cm^{-1} do not belong to free B_2O_3 molecules, but to fine particles of the liquid boron oxide formed as a dispersed cloud at the ends of the heater.* On the basis of the calculations carried out by Tatevskiy, Koptev and Mal'tsev [52a, 410a] they recommended for the molecule $B_2^{11}O_3$ the following values for the fundamental frequencies (in cm^{-1}): $\nu_1 = 2015$, $\nu_2 = 815$, $\nu_3 = 749$, $\nu_4 = 160$, $\nu_5 = 753$, $\nu_6 = 2029$, $\nu_7 = 933$, $\nu_8 = 658$ and $\nu_9 = 673$.

Although the objections raised in the works [52a, 290a] against the interpretation of the infra-red spectra of boron oxide vapors, as suggested by White, Mann, Walsh and Sommer, may not be considered as proven until new investigations of the infrared spectra of boron oxide vapors will be carried out, the data obtained in the studies [4238, 52a] allow to give preference to the values for the fundamental frequencies of B_2O_3 calculated by Tatevskiy, Koptev and Mal'tsev, except for the frequency of the deformation vibration ν_4. The value ν_4 obtained in the work [52a] is underestimated, since it leads to an increased discrepancy between the values S°_{T} calculated by statistical methods and those obtained from results of calorimetric measurements.

The molecular constants for boron oxide as accepted in the present Handbook are listed in Table 210. The corresponding product of the chief moments of inertia is calculated according to formula (3.43) and the structural parameters found in the work of Akishin and Spiridonov [67b]. The values for the fundamental frequencies, with the exception of ν_4 have been accepted on the basis of the calculation made by Tatevskiy and Mal'tsev [52a] and by taking into account the rounding off of the values obtained by them, which they made due to the isitope constitution of boron. The value ν_4 has been accepted according to the work [4238]. The errors for the accepted values of the fundamental frequencies, in particular of the deformation vibrations of B – O – B (ν_4) and also of the valence vibrations of the single bond B – O may be rather considerable.

<u>HBO_2</u>. In the literature there are no experimental data available on the structure of the HBO_2 molecule. However, using the general concepts on the orientation of the chemical bonds of the boron atom and the results from electron diffraction pattern investigations of the salts of the metaboric acid (see [67]) it can be undoubtedly assumed that the HBO_2 molecule should have an angular structure in analogy to

its isoelectronic molecules HN_3, HNCO, HOCN, with three atoms (O – B = = O) lying in one straight line. Molecules of this type belong to the point group C_s and do have six normal vibrations. The only investigation ever made on the HBO_2 spectrum had been carried out in 1960 by White, Mann, Walsh, and Sommer [4239] who obtained an infrared emission spectrum from the vapors of $HB^{11}O_2$, $HB^{10}O_2$, $DB^{11}O_2$ and $DB^{10}O_2$ on heating B_2O_3 in an atmosphere of water vapors. In the spectrum of HBO_2 the following three frequencies were observed: 3680, 2030 and 1420 cm^{-1}, which were identified by the authors with the fundamental frequencies for the valence vibrations of the bonds $—O—H\,(\nu_1)$, $—B=O\,(\nu_2)$ and $=B—O—\,(\nu_3)$ respectively.* Frequencies of the three deformation vibrations could not be observed in the spectrum, although in the region 1300 cm^{-1} a weak band, shifted in the spectrum of DBO_2 towards the region 1000 cm^{-1}, has been observed where one actually would expect a band which corresponds to the deformation vibration B – O – H (ν_4). However, an unambiguous assignment of this band to the molecule of the metaboric acid proved to be unfeasible due to the bands of H_2O and D_2O located in this region. The authors of the study [4239] accepted ν_4 = = 1250 cm^{-1}. The fundamental frequencies of the vibrations O = B – O of the deformation type (of the in-the-plane type ν_5 and out-of-the-plane type ν_6) were estimated to be equal to 600 and 700 cm^{-1} on the basis of the fundamental frequencies of analogous vibrations occurring in the molecules HN_3 and B_2O_3.

In the preparation of the first edition of the present Handbook the fundamental frequencies of the HBO_2 molecule have been estimated at an earlier period from the frequency values of isoelectronic molecules and have been accepted to be equal to 3680, 2200, 1300, 1000, 610 and 700 cm^{-1}, correspondingly, which were in excellent agreement with the data obtained in the study [4239].

The values of the fundamental frequencies for HBO_2 which have been accepted in the present Handbook on the grounds of results from infrared spectroscopic investigations of the metaboric acid and on the basis of approximated estimates are given in Table 210. There, we find also the product of the principal moments of inertia of HBO_2 which was calculated by assuming $r_{B=O} = 1{,}20, r_{B-O} = 1{,}36, r_{O-H} = 0{,}96$ Å and $\angle HOB = 105°$. The errors for the accepted values of the frequencies ν_1, ν_2 and ν_3 seemingly do not exceed ± 10 cm^{-1}; in the values of the frequencies ν_4, ν_5 and ν_6 the errors are essentially greater and cannot be accurately estimated. Possibly one can assume that they do not exceed ± 100 cm^{-1} in ν_5 and ν_6, and ± 150 cm^{-1} in ν_4.

$\underline{H_3BO_3}$. The spectrum and molecular structure of the orthoboric acid in the gaseous state has not been experimentally investigated. However, there is a rather large number of works dedicated to the study of the infrared spectrum of a variety of isotopic modifications of the crystalline boric acid (boracic acid) and of the Raman spectrum diagram of its solutions, which allows to make an approximate estimate of the molecular constants of H_3BO_3.

By x-ray diffraction studies [4372a] and electron diffraction studies [1207a, 1207b] it has been shown that the boracic acid in its crystalline state consists of two-dimensional plane layers separated by a comparatively large distance one from the other (3.18 A) and bound by the weak van der Waals forces. In the plane layer the group $B(OH)_3$ has the symmetry C_{3h}.

Landsberg and Baryshanskaya [272a] investigated the Raman spectrum of the boracic acid and were able to show that the valence frequency OH is subject to considerable shifting and broadening. This proved to be good evidence for the suggestion made earlier by Bernal and Megaw [758c] as to the existence of hydrogen bonding between the groups $B(OH)_3$ in the boracic acid. Since the forces of hydrogen bonding are by one order smaller than the forces acting between atoms within the range of a molecule, it is possible to consider the H_3BO_3 group of the crystalline boracic acid with sufficient approximation as an isolated molecule and to interpret the frequency observed in the spectrum of the crystalline boracic acid as associated with the vibrations of the H_3BO_3 molecule.

TABLE 210

Accepted Values for the Molecular Constants of B_2O_3, HBO_2, H_3BO_3

Молекула 1	2 ν_1	3 ν_2	4 ν_3	5 ν_4	6 ν_5	7 ν_6	8 ν_7	9 ν_8	10 ν_9	11 ν_{10}	$I_AI_BI_C$	σ 13
	$см^{-1}$ 12										10^{-117} $(г \cdot см^2)^3$	
B_2O_3	2030	820	750	310	760	2040	935	660	680	—	3425	2
HBO_2	3680	2030	1420	1250	610	700	—	—	—	—	11,3	1
$H_3BO_3^a$	3250	880	1060	650	800	3150 (2)	1440 (2)	550 (2)	1190 (2)	210 (2)	1115	3

Note: a) $I_{pr} = 1.3 \cdot 10^{-40}$ $g \cdot cm^2$, V = 2000 kcal/mole.
1) Molecule; 2) ν_1; 3) ν_2, 4) ν_3; 5) ν_4; 6) ν_5; 7) ν_6; 8) ν_7; 9) ν_8; 10) ν_9; 11) ν_{10}; 12) 10^{-117} $(g \cdot cm^2)^3$; 13) σ .

Zachariasen [4372a] determined on the basis of x-ray diffraction measurements the following values for the bond lengths and bond angles in the crystalline boracic acid: $r_{B-O} = 1{,}362$, $r_{O-H} = 0{,}88$ Å, $\angle OBO = 120°$ and $\angle BOH = 114°$. When Cowley [1207a, 1207b] studied later on the hydrogen bonding in crystalline boracic acid he found the following values: $r_{B-O} = 1{,}36$ and $r_{O-H} = 1{,}00–1{,}05$ Å . The latter values, being by far superior to those found by Zachariasen, are in good agreement with results obtained from investigations of the interatomic distance O – H in various crystalline compounds with hydrogen bonding, which distorts the interatomic distance O – H and the angle XOH (ss [3248a]).

It can be possibly assumed that the structure of the H_3BO_3 group in the crystalline boracic acid should be preserved on the whole in the isolated molecule H_3BO_3. However, the values for the interatomic distance O – H in the H_3BO_3 molecule should be close to the O – H bonds in other compounds (0.95 ± 0.02 A) and also the angle BOH should be close those occurring between oxygen bonds (of the order of 105 ± ± 10°). In this conjunction it has been assumed in the present Handbook that the molecule H_3BO_3 is plane, belongs to the point group of the symmetry C_{3n} and is characterized by the following structural parameter values: $r_{B-O} = 1{,}36 \pm 0{,}02$, $r_{O-H} = 0{,}95 \pm 0{,}02$ Å, $\angle OBO = 120°$ and $\angle BOH = 105 \pm 10°$. The value corresponding to these parameters for the product of the principal moments of inertia of the H_3BO_3 molecule is given in Table 210.

The plane molecule H_3BO_3 should have three non-degenerate vibrations of the type A'(where ν_1 is the valence vibration O – H, ν_2 is the valence vibration B – O , ν_3 is the deformation vibration BOH), two non-degenerate vibrations of the type A" (where ν_4 is the deformation vibration of the structure BO_3, ν_5 is the rotation vibration O – – H), four two-fold degenerated vibrations of the type E' (where ν_6 is the valence vibration O – H, ν_7 is the valence vibration B – O, ν_8 is the deformation vibration of the structure OBO, ν_9 is the deformation vibration of the structure BOH) and a two-fold degenerate vibration of the type E" (where ν_{10} is the rotation vibration O – H). The A', E' and E" types vibrations are active in the spectrum of combination scattering while the A" and E' types vibrations are active in the infrared spectrum. The results from the investigations of the infrared spectrum [2810a, 2913a, 3688] and from those of the combination scattering spectra [272a, 544a, 2065a, 2316a, 2500, 2924b, 2688a, 4078a, 372a, 800a, 1430a] of the crystalline boracic acid and its aqueous solutions, its solutions in methanol and other solvents are in good agreement one with another. The existing discrepancies occur mainly due to the fact that some investigations were made on spectra of the crystalline boracic acid while others were carried out on solution of the boracic acid. Besides that, a certain difference in the frequencies is caused by a considerable band width in the infrared spectrum and by difficulties arising in the determination of the band peaks.

The most detailed investigations of infrared spectra and Raman spectra for various isotopic modifications of the boracic acid were carried out by Bethell and Shephard [800a], Servoss and Clark [3688] and Sidorov and Sobolev [372a]. The data obtained in the cited works are verified by earlier and less extensive investigations [544a, 1430a 2065a, 2316a, 2500, 2810a, 2913a, 2924b, 4078a]. Based on an analysis of measurement results given in the works [800a and 3688] Pistorius [3251] recommended the following values of fundamental frequencies (in cm^{-1}) for the molecule H_3BO_3: $\nu_1 = 3250$, $\nu_2 = 1060$, $\nu_3 = 881$, $\nu_4 = 648$, $\nu_5 = 824$, $\nu_6 = 3150$, $\nu_7 = 1428$, $\nu_8 = 544$, $\nu_9 = 1183$, $\nu_{10} = 209$. The force constants calculated by Pistorius on the basis of these values yield a rather good description of the field of force of the H_3BO_3 molecule (the calculated frequencies are in good agreement with the experimental frequency values within the limits of 3-5%).*

In the work [372a] done by Sidorov and Sobolev, which apparently remained unknown to Pistorius, they investigated infrared spectra of the boracic acid with a natural mixture of isotopes and boracic acid enriched with the isotope B^{10} (in the frequency region 450-4000 cm^{-1}) and on the basis of the data received and from analysis of previously published works they recommended the following frequency values (in cm^{-1}): $\nu_1 = 3170$, $\nu_2 = 886$, $\nu_3 = 1169$, $\nu_4 = 658$, $\nu_5 = 729$, $\nu_6 = 3240$, $\nu_7 = 1448$, $\nu_8 = 550$, $\nu_9 = 1198$, which are in good agreement with the values selected by Pistorius.**

In the present Handbook the values listed in Table 210 have been accepted for the fundamental frequencies of the H_3BO_3 molecule. They are rounded off and close to the average values found in the works [800a, 3688, 372a]. The possible rate of errors for the accepted frequency values amounts to 5-10%.

Since in the H_3BO_3 molecule three groups are linked to the boron atom through the single bonds B – O, in this molecule a rotation of the group OH around the bond B – O should occur. The cited moment of inertia for H_3BO_3 has been calculated according to the formula (II.234) which by first approximation is true for the case of several tops [3255]. For each top a value $I_{pr} = 1.297 \cdot 10^{-40}$ $g \cdot c,^2$ was found, which after rounding off was included in Table 210 containing the accepted values of the molecular constants of H_3BO_3.

The magnitude of the potential barrier for the internal rotation in the molecule H_3BO_3 is unknown. An estimate on the basis of the most common notations with an allowance for the spatial relations and a comparison of the potential barrier magnitudes in various molecules with an analogous top (chiefly in alcohols) yielded a value $V_0 = 2000 \pm 1000$ kcal/mole (see Table 210) (for the condition that the potential curve has two peak minima, i.e., n = 2). It should be mentioned that such a value for the magnitude of the potential barrier had been adopted in the work of Evans, Prosen and Wagman [1515] in thermodynamic calculations of the functions of H_3BO_3.

BF_2 and BCl_2. In the literature there are no experimental data available on the molecular constants of BF_2 and BCl_2. The vibration frequencies and the structural parameters of these molecules have been approximately estimated in the works of Tatevskiy, Veits (Weiz) and Gurvich [51]. In the estimate it was suggested that BF_2 and BCl_2 do have a non-linear symmetry structure and do belong to the point group C_{2v}.* Assuming that the bondage in these molecules is established by two p-electrons of the boron atom, the authors of the work [51] came to the conclusion that the angle X – B – X should have a size within the limit from 90 to 120°; they considered the same to be equal to 110 ±10°. The interatomic distances in the molecules BF_2 and BCl_2 have been assumed to be equal to those occurring in the molecules BF_3 and BCl_3: $r_{B-F} = 1,30 \pm 0,03$ and $r_{B-Cl} = 1,73 \pm 0,03$ Å. On the basis of the accepted values for the structural parameters the moments of inertia were calculated for the cited compounds which are given in Table 211.

Triatomic molecules belonging to the point group of the symmetry C_{2v} have three fundamental frequencies. The fundamentals of the BF_2 and BCl_2 molecules have been calculated in the work [51] in three different ways on the basis of different values of the force constants. The calculation was carried out according to the Eqs. (P4.30) and (P4.29), assuming that the force constants of BX_2 are equal to force constants of BX_3, which were calculated correspondingly: a) without taking into consideration the interaction of the angles one with another and of the angle with the bond and b) by taking into consideration such interactions. Due to the fact that the suggestion for the equality of the force constants of BX_2 type molecules with the force constants of BX_3 type molecules has been made on a rather arbitrary basis, in the work [51] the fundamental frequencies of BX_2 type molecules were calculated according to the Eqs. (P4.29), taking into consideration force constants of the bond type B – X, which have been accepted as being equal to the force constants of the corresponding diatomic molecules of the type BX and also to the deformation constant and force constants of bond interactions satisfying the relations

$$\frac{l}{f_{B-X}}(BX_2)=\frac{l}{f_{B-X}}(BX_3).$$

On the basis of the results obtained from a comparison of the above mentioned calculations carried out in the work [51] the fundamental frequency values for the BF_2 and BCl_2 molecules recommended are those listed in Table 211, which have also been accepted in the present Handbook.* Since the discrepancies between the frequency values, calculated by different methods, do not exceed 10%, the errors in these magnitudes can possibly assumed to be of the same order. Since in the BF_2 and BCl_2 molecules there is an unpaired electron, there ground electronic states should be of the doublet type.

TABLE 211

Accepted Values for the Molecular Constants of BF_2, BCl_2, BF_3 and BCl_3

1 Молекула	2 ν_1	3 ν_2	4 ν_3	5 ν_4	$I_A I_B I_C$	7 σ
	см⁻¹				6 10^{-117} (г·см²)³	
BF_2	1260	420	1420	—	45	2
$B^{10}F_3$	888	718,23	1504,8 (2)	482,0 (2)	999	6
$B^{11}F_3$	888	691,45	1453,5 (2)	480,4 (2)		
BCl_2	800	210	900	—	915	2
$B^{10}Cl_3$	471	480	995 (2)	244 (2)^a	36915	6
$B^{11}Cl_3$	471	460	956 (2)	243 (2)		

Note: a) Calculated according to the rule of the Teller-Redlich products

1) Molecule; 2) ν_1; 3) ν_2; 4) ν_3; 5) ν_4; 6) 10^{-117} $(g \cdot cm^2)^3$; 7) σ .

BF_3. By an analysis of spectroscopic data [554, 620, 619, 1637, 4363, 3070, 2710, 290], furthermore from results of electron diffraction patterns [910, 2600] and also from results of dipole moment measurements [2620, 3047] it was possible to reveal that the BF_3 molecule is plane, symmetric, has the form of a true triangle with the fluorine atoms positioned at its vertices, in the center of which the boron atom is located. Such a molecule is assigned to the point group of the symmetry D_{3h} and possesses four fundamental frequencies which correspond to the types A' (ν_1), A" (ν_2) and E' (ν_3 and ν_4). In the infrared spectrum the ν_1 frequency is inactive, while in the Raman spectrum the ν_2 frequency is inactive. The two-fold degenerate vibrations ν_3 and ν_4 are active in both the infrared spectrum and the Raman spectrum.

The Raman spectrum of BF_3 had been investigated for the first time by Anderson, Lassettr and Jost [554]. In 1938, Jost, De-Volt, Anderson and Lassettr [4363] who carried out a more elaborate measurement of the Raman spectrum of gaseous boron trifluoride (boron fluoride) were able to show that the only strong line related to the molecule BF_3 in the spectrum was that with the frequency of 888 cm^{-1}, which was interpreted by the authors of the work [4363], as linked to the full-symmetric vibration ν_1. This interpretation was confirmed by the absence of an isotopic shift in the band when B^{10} has been replaced by the isotope B^{11}. The low-frequency band, located in the region 439-513 cm^{-1}, which the authors of the work [4363] were able to observe has been assigned by them to the vibration ν_4.

An infrared absorption spectrum of gaseous BF_3 in the region from 10,000 to 667 cm^{-1} (1-15μ) has been obtained on prism spectrometer for the first time by Bailey, Hale and Thompson [620, 619]. However, due to the presence of a large number of bands caused by insufficient purity of the investigated substance the interpretation of the results was rather difficult.

Gage and Barker [1637] investigated the infrared spectrum of BF_3 on a device with a crystal lattice and expanded the region under investigation to 500 cm^{-1} (20μ). In the spectrum six bands were disclosed, being associated with the fundamental vibrations ν_2, ν_3 and ν_4 and also the first overtone of the vibration ν_3. In the study [1637] the values ν_2, ν_3 and ν_4 are listed correspondingly for $B^{10}F_3$ and $B^{11}F_3$ It should be noted that the accurate measurement of the band peaks was impeded by the bands of water and carbon dioxide, masking the structure of the spectrum studied.

Nielsen [3070] tried to scavenge the casing of the spectrometer with dry nitrogen in order to eliminate the influences of the atmospheric bands. In the spectrum obtained he measured very carefully the rotational structure of the band ν_2, proceeded to analyze the rotational structure on the basis of the data obtained and determined the wave numbers for the onsets of the ν_2 frequencies for $B^{10}F_3$ and $B^{11}F_3$ (as being equal to 718.23 and 691.45 cm^{-1} correspondingly) as well as the values for the rotational constants as being equal to $B'' = 0.35272$, $B' = 0.35288$ and $D'' = D' = 13.72 \cdot 10^{-7}$ cm^{-1}. Using the value found for the rotational constant in the ground state it was possible to calculate the moment of inertia for the BF_3 molecule with respect to the axis located in the plane of the same to be $I_B = 79.34 \cdot 10^{-40}$ $g \cdot cm^2$ and also the value for the interatomic distance $r_{B-F} = 1.295$ A, which is in good agreement with results obtained from electron diffraction pattern measurements ($r_{B-F} = 1.30$ A).

The values of the fundamental frequency ν_3 for the isotopic molecules of BF_3 were rendered more accurately in the works by Lindeman and Wilson [2617], by McKeen [2710], by Mal'tsev, Moskvitina and Tatevskiy [290], and finally by Wanderrin [4056]. Lindeman and Wilson obtained for $B^{11}F_3$ and $B^{10}F_3$ ν_3 values, being equal to 1453.5 and 1504.7, respectively. The study of McKeen was dedicated to intensity measurements of infrared absorption bands of the BF_3 molecule. The spectrum was recorded on a double-beam spectrometer with prisms consisting of CaF_2 and KBr. The values ν_3 ($B^{10}F_3$) = 1504.7 and ν_3 ($B^{11}F_3$) = 1453.6 cm^{-1} are in excellent agreement with the results obtained by Lindeman and Wilson and prove to be more accurate than those cited in the work by Gage and Barker [1637]. Using the rule of the Teller-Redlich products and the relation $x_i' = x_i (\nu_i'/\nu_i)^2$, being true for isotopic molecules, and also the values of the ν_2 frequencies found in the work of Nielsen [3070], furthermore the value for ν_4, found in the work of [1637], McKeen calculated the following constants of anharmonicity and the zero frequency vibrations ω_2^0, ω_3^0 and ω_4^0 for the molecules $B^{10}F_3$ and $B^{11}F_3$*:

$$B^{10}F_3\begin{cases}\omega_2^0 = 760{,}00 & x_2 = 0{,}058 & \nu_2 = 718{,}13\\ \omega_3^0 = 1607{,}5 & x_3 = 0{,}068 & \nu_3 = 1504{,}7\\ \omega_4^0 = 510{,}9 & x_4 = 0{,}06 & \nu_4 = 482{,}1\end{cases}$$

$$B^{11}F_3\begin{cases}\omega_2^0 = 730{,}17 & x_2 = 0{,}056 & \nu_2 = 691{,}54\\ \omega_3^0 = 1549{,}6 & x_3 = 0{,}066 & \nu_3 = 1453{,}6\\ \omega_4^0 = 509{,}2 & x_4 = 0{,}06 & \nu_4 = 480{,}4\end{cases}$$

In the work of Mal'tsev, Moskvitina and Tatevskiy, intended for the study of the isotopic effect and for obtaining a more accurate infrared spectrum of BF_3 the spectrum of natural BF_3 mixed with the enriched isotope B^{10} (85%) has been investigated in the region from 10,000 to 1000 cm^{-1} (1-10 μ). The authors of this work obtained for the frequency ν_3 values (1504.8 and 1453.2 cm^{-1}) which were identical with those found by McKeen [2710] and Lindeman and Wilson [2617], and additionally a number of combination bands and overtones in the region from 10,000 to 2000 cm^{-1} (1-5 μ). The constants of anharmonicity were not calculated in the work [290].

Another work dedicated to obtain more accurate values for the combination frequencies of bands and overtones in the infrared spectrum of BF_3 was that of Wanderrin [4056] in which the spectra of a natural boron isotope mixture with BF_3, containing approximately 96% B^{10}, were studied. The frequencies in the region 1500 cm^{-1} were measured with a precision of up to ±1 cm^{-1} and the accuracy in measurement in the region 3000 cm^{-1} amounted to 2-3 cm^{-1}. The values for the frequencies $\nu_1 + 2\nu_4$, $\nu_3 + \nu_4$, $2\nu_1 + \nu_4$, $\nu_1 + \nu_3$, $2\nu_3$ and $2\nu_1 + \nu_3$ found by Wanderrin coincided within the limits ±5 cm^{-1} with those cited in the work of Mal'tsev, Moskvitina and Tatevskiy [290]. The values ν_3 ($B^{10}F_3$) = 1504.8 and $\nu_3(B^{11}F_3)$ = 1453.9 found by Wanderrin differ from those obtained in the works [290, 2617] by tenths of a reciprocal centimeter.

A review of the results listed in the above mentioned works shows clearly that the available data on the overtone and combination band frequencies are insufficient for calculating a complete set of constants of anharmonicity, being part of the expression for the vibration energy of the molecule BF_3. Therefore, in the present Handbook we find recommended for the calculation of the thermodynamic functions of BF_3 the values of the fundamental frequencies, which were found in the works [1637, 4363, 3070, 2710, 290, 4056, 2617] and which are also given in the Table 211. In the same table we find also listed the value for the product of the moments of inertia of BF_3, calculated on the basis of the interatomic distance r_{B-F} obtained by Nielsen [3070] as the result of an analysis of the fine structure of the ν_2 band.

The ultraviolet absorption spectrum of gaseous boron trifluoride has been investigated by Kaufman [2335]. On the basis of the data obtained he was able to draw the conclusion that the first stable excited state had its position approximately at 49,600 cm^{-1}, above the ground electronic state of the BF_3 molecule.

$\underline{BCl_3}$. From electron diffraction measurements [2600], spectrum studies [554] and also from dipole moment measurements [755] it could be shown that the BCl_3 molecule as well as the BF_3 molecule has the form of a plane equilateral triangle with the boron atom in its center and that it belongs to the point group of the D_{3h} symmetry.

A Raman spectrum of liquid BCl_3 had been obtained for the first time by Bagavantam [809]. In the spectrum under investigation two frequencies have been observed: 470 and 255 cm^{-1}. Subsequently, Vankatesvarlu [4084] who studied the spectrum of liquid BCl_3 found frequency bands corresponding to the following frequencies: 472, 255 and 947 cm^{-1}. (In the work [4084] it is noted that the intensity of the last two frequencies mentioned is small and that they are very probably doublets). The most exhaustive investigation of the Raman spectrum of BCl_3 has been carried out by Anderson, Lassettr and Jost [554]. The spectrum of BCl_3 was obtained at room temperature. The results from polarization measurements which were carried out simultaneously facilitated the interpretation of the observed spectrum. The authors of this work assigned the band with the frequency 471 cm^{-1} to the vibration ν_1, the bands at 946 and 989 cm^{-1} to the frequency ν_3 of the $B^{11}Cl_3$ and $B^{10}Cl_3$ molecules, respectively, and the sharp band found at 902 cm^{-1} was interpreted by them as an overtone of the deformation vibration $2\nu_2$.

An infrared spectrum of gaseous BCl_3 has been obtained for the first time by Cassey [1071] in the region ranging from 3300 to 670 cm^{-1} (3-15 μ). In the spectrum, nine bands were observed which were attributed by Cassey to fundamental and Raman frequencies and overtones. As it was shown in a later work by Anderson, Lassettr and Jost [554] this assignment proved to be incorrect. At a later period, Scruby, Lacher and Park [3668a] reinvestigated the infrared spectrum of gaseous BCl_3 again in the same region as studied by Cassey, and they were able to measure 15 bands, belonging to the $B^{10}Cl_3$ and $B^{11}Cl_3$ molecules. Measurements and calculations carried out by authors of [3668a] confirmed the interpretation of the spectrum as outlined in the work [554] and allowed to obtain more accurate values for the frequencies γ_2 and γ_3. From our own data and from an analysis of previous works Scruby, Lacher and Park were able to recommend certain values for the fundamental frequencies of the $B^{10}Cl_3$ and $B^{11}Cl_3$ molecules, which also have been accepted in the present Handbook and which have been included in Table 211.

Levy and Brokway [2600] found from electron diffraction studies the interatomic distance B – Cl in the BCl_3 molecule to be equal to 1.73 ± 0.02 A and the angle Cl – B – Cl to be equal to 120 ± 3°. The product of the moments of inertia of the BCl_3 molecule, calculated for the angle $\angle Cl - B - Cl = 120°$ and for the interatomic distance $r_{B-Cl} = 1.73$ A, is given in Table 211.

Since it has not been possible until present to reveal in the spectrum of BCl_3 an isotope effect caused by the isotopes Cl^{35} and Cl^{37}, the molecular constants listed in Table 211 are considered to be linked to the natural mixture of chlorine isotopes. In the monograph by Herzberg [152] for the fundamental frequencies of BCl_3 those values are being recommended which were found in the works by Cassey [1071] and in those by Anderson, Lassettr and Jost [554].

§92. THERMODYNAMIC FUNCTIONS OF GASES

Thermodynamic functions of boron and its compounds of oxygen, hydrogen, fluorine, chlorine and nitrogen, in the state of an ideal gas, have been calculated for temperatures from 293.15 to 6000°K from constants accepted in the preceding section and listed in the Tables 267-271, 273-284 and also in the Table 286 contained in Volume II of this Handbook. In the calculations of the thermodynamic functions for diatomic and several multiatomic boron compounds (viz. below) the difference between the isotopic modifications of their molecules was taken into account. In the present Handbook, data for two gases (BF_3 and BCl_3), allowing for the influence of intermolecular interaction on thermodynamic functions, have been included [see Supplement 5 and Tables 422 (II) and 423 (II)].

B. The translational components in values of thermodynamic functions of monatomic boron have been calculated according to formulas (II.8) and (II.9), assuming $A_{\Phi} = -0{,}1849$ and $A_S = 4{,}7833$ cal/g-atom·degree; the electronic components have been calculated according to Eqs. (II.20) and (II.21) on the basis of the energy levels listed in Table 207. The basic errors in the calculated values of thermodynamic functions of boron are characterized by the lack of experimental data on the excitation energy of the state $2ssp^2\ ^4P$ and by excluding states with excitation energies above 50,000 cm^{-1} from consideration. Nevertheless, at temperatures up to 6000°K the errors in the values Φ_T^* and S_T° do not exceed ± 0.01 cal/g-atom·degree.

Thermodynamic functions of monatomic boron have been calculated by Kol'skiy et al [2462] (Φ_T^* for $T < 8000°$ K), Huff, Gordon and Morrell [2142] and by Wilkins and Altman [4269] ($T < 6000°$ K); in the summary of Stoll and Zinke [3894] the table for thermodynamic functions of boron has been accepted according to data by [2142]. The discrepancies between the values listed in Table 267 (II) and in the work [2462] do not exceed 0.01 cal/g-atom·degree and arise chiefly from the difference in the accepted values for the physical constants; the discrepancies with respect to the data of [2142] amount to 0.03 cal/g-atom·degree in the value S_{6000}°, which are explained in addition to the dissimilar values for the physical constants by the negligence of the excited states of the boron atom in the work [2142].

The values of thermodynamic functions for monatomic boron listed in the first edition of the present Handbook and in the work of Wilkins and Altman agree with the data listed in Table 267 (II) within the limits of 0.001 cal/g-atom·degree.

B_2 and BO. Thermodynamic functions of diatomic boron and boron monoxide as listed in the Tables 268 (II) and 269 (II) have been calculated according to Eqs. (II.161) and (II.162). The values in Σ and

$T\frac{\partial}{\partial T}\ln\Sigma$ in these equations have been calculated according to the method of Gordon and Barnes [using the relations (II.137), (II.138) for a natural mixture of boron isotopes. The calculations were carried out using averaged values of the molecular constants for B_2 and BO found according to Eqs. (1.45) on the basis of constants listed in Table 208. The calculations were made without limitation of the number of rotational states of the molecules B_2 and BO. Although the molecules B_2 and BO possess multiplet ground electronic states, the values $\ln\Delta$ and $T\frac{\partial}{\partial T}\ln\Delta$ in Eqs. (II.161) and (II.162) have been accepted as being equal to zero, as the spin-orbit couplings are unknown. In Table 212 the following values are listed: C_Φ and C_S for the calculation of the components of translational motion and the rigid rotator in the thermodynamic functions of these gases, θ and $\underline{x}$ for the interpolation according to the tables of the anharmonic oscillator and also the coefficients used in Eqs. (II.137) and (II.138); corresponding values have been calculated from "effective" values of molecular constants. Since the molecules B_2 and BO do have the ground electronic states $^3\Sigma$ and $^2\Sigma$, in the values C_Φ and C_S of these gases the addends R ln 3 (for B_2) and R ln 2 (for BO) have been included. When the thermodynamic functions of BO were calculated the components of state $A^2\Pi$ of the molecules of this gas were computed according to relations (II.126) and (II.127); more elevated electronic states of BO (see Table 208) have not been considered in the calculation.* The constants of the state $A^3\Sigma$ of the B_2 molecule were calculated according to Eqs. (II.120), (II.121), i.e., without taking into consideration the difference between the constants of B_2 in the states $X^3\Sigma$ and $A^3\Sigma$.

The basic errors in the calculated values for thermodynamic functions of B_2 and BO are due to the lack of data on the energy of elevated vibrational and rotational levels of the corresponding molecules in the ground state. In the case of B_2, whose bond dissociation energy is not large, the rate of errors is augmented by some other fault due to the neglected necessity of introducing into the calculation corrections for the limitation of the number of rotational levels of the molecule, which leads to an error of the order of 0.1 cal/mole·degree in the value Φ^*_{6000}. The general errors in the calculated values of Φ^*_T at 298.15, 3000 and 6000°K for diatomic boron and its monoxide amount to approximately ±0.02, ±0.1 and ±0.2 (B_2), and to ±0.01, ±0.03 and ±0.1 (BO) cal/mole·degree, respectively.

Earlier, thermodynamic functions of B_2 and BO have been calculated by Walker, Woolley and Fire (the work has become known from the summary of Huff et al [2142]) for a temperature of up to 6000°K and by Wilkins and Altman [4269] ($T \leqslant 6000°$ K, in approximation to the rigid rotator-harmonic oscillator model, thereby introducing corrections which were calculated according to the method by Pennington and Cobb). Thermodynamic functions of BO have also been calculated by Evans, Prosen and Wagman [1515] ($T \leqslant 2500°$ K).

TABLE 212

Values of Constants for the Calculation of Thermodynamic Functions of Gaseous B_2, BO, BH, BF, BCl, and BN

1 Вещество	θ	$x \cdot 10^3$	$\beta_1 \cdot 10^3$	$\beta_2 \cdot 10^4$	$\frac{q_0}{T}$	$\frac{d_0 \cdot 10^6}{T}$	C_Φ	C_S
	2 град				3 град$^{-1}$		4 кал/моль·град	
B_2	1525,7	9,0523	1,1416	1,35	0,567022	6,17	1,5604	8,5159
BO	2726,3	6,2742	0,9348	0,90	0,38827	2,78	2,0184	8,9739
BH	3403,5	20,710	3,4785	13,55	0,058853	12,16^a	−5,5476	1,4079
BF	2026,0	8,0233	1,1134	1,29	0,455400	4,36	1,2743	8,2298
BCl	1213,1	6,1186	0,9541	0,94	1,01130	5,30	4,1700	11,1255
BN	2178,8	8,1210	1,5112	2,39	0,420422	4,07	4,1300	11,0855

Note: a) $\frac{f_0}{T^2} = -1{,}85 \cdot 10^{-10}$ deg^{-2}

1) Compound; 2) deg; 3) deg^{-1}; 4) cal/mole·degree.

In the case of BO, the discrepancies between the values of thermodynamic functions listed in Table 269 (II) and those given in the work [2142] agree with the magnitude of the components of the state $A^2\Pi$ of this molecule (up to 0.15 cal/mole·degree in the value S°_{6000}). On this account it possibly may be assumed that in the calculation of Walker, Woolley and Fire the excited electronic states of BO have not been taken into consideration

In the case of B_2, the values Φ^*_T and S°_T, given in the summary of [2142] for $T = 298.15^\circ$ K, exceed the data given in Table 268 (II) by 0.42 cal/mole·degree. With rising temperatures the discrepancies decrease to 0.05 cal/mole·degree in the value Φ^*_{6000}, and in the entropy, passing through zero, they increase again reaching approximately 0.5 cal/mole·degree in the value S°_{6000}, with the entropy of B_2 at elevated temperatures being smaller, according to the data of [2142], than that listed in the present Handbook. For this reason it can be possibly assumed that the calculation of Walker et al for B_2 had been carried out in approximation to the rigid rotator-harmonic oscillator model. The discrepancies between the values of the functions in question at 298.15°K cannot be explained. However, due to the identical discrepancies in the values $\Phi^*_{298.15}$ and $S^\circ_{298.15}$, it seems to be obvious that in the work of the American authors an arithmetic error of the order of 0.4 cal/mole·degree has been committed in the computation of the translational and rotational components.

The thermodynamic functions of BO, calculated by Wilkins and Altman, are close to those given in the summary of [2142]. At high temperatures they are in good agreement with the data listed in Table 269 (II); at high temperatures the discrepancies increase and reach approximately 0.2 cal/mole·degree in S°_{6000}. From the magnitude of the discrepancies it becomes evident that in the work [4269] and in the calculation the state $A^2\Pi$ of the BO molecule had not been considered.

The thermodynamic functions of B_2, calculated in the work [4269], are at $T < 3000°K$ in good agreement with those given in Table 268 (II). However, with rising temperatures the discrepancies do increase rapidly and reach 0.07 and 0.3 cal/mole·degree in the values Φ°_{6000} and S°_{6000} correspondingly. These discrepancies are obviously due to the inaccuracy of the method of Pennington and Cobb used in the work [4269] for the calculation of corrections for the deviation of the B_2 molecule from the rigid rotator-harmonic oscillator model.

The thermodynamic functions of B_2 and BO as listed in the first and present edition of this Handbook are identical.

BH. The thermodynamic functions of gaseous boron monohydride listed in Table 274 (II) have been calculated according to Eqs. (II.161) and (II.162). The values $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ in these equations were calculated by the method of Gordon and Barnes (using the relations (II.137) and (II.138)) and by introducing corrections for the limitation of the number of rotational states of BH in the ground electronic state $X^1\Sigma$. The calculation has been carried out using the molecular constants given in Table 208. In view of the lack of reliable data on the vibrational constants of BH in the ground state $X^1\Sigma$ the difference between the constants of the molecules $B^{10}H$ and $B^{11}H$ was not accounted for.

In Table 212 the following values are listed: C_Φ and C_S in Eqs. (II.161) and (II.162), the values of the coefficients used in Eqs. (II.137) and (II.138), and also the values θ and x, calculated from the accepted values for the molecular constants of BH. The components of the excited electronic states $a^3\Pi$ and $A^1\Pi$ have been calculated without taking into consideration the difference of the molecular constants of BH in these states and in the ground state $X^1\Sigma$ [using Eqs. (II.120) and (II.121)]. The application of a more accurate method for considering the excited states is unwarranted in view of the lack of reliable data on the energy of the state $a^3\Pi$.

The basic errors in the calculated values for the thermodynamic functions of boron monohydride are caused by the following reasons: a) by the lack of experimental data on the vibrational constants of BH (the error being up to 0.05 cal/mole•degree in Φ_T^*); b) by the lack of information on the energy of high vibrational and rotational levels of the ground state of this molecule (the error being up to 0.1 cal/mole•degree in Φ_T^*); c) by the negligence of the difference between the constants of the isotopic modifications of BH (of the order of 0.01 cal/mole•degree) and d) due to the approximated calculated of the components of the excited states. The errors in the values $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000}, listed in Table 274 (II) have magnitudes of the order of 0.01, 0.1 and 0.3 cal/mole•degree, respectively.

Thermodynamic functions of boron monohydride have been calculated by Walker, Woolley and Fire (viz., the summary of [2142]) for $T \leq 6000°K$, by Ward and Husse [4149] (from 2000 to 5000°K) and by Wilkins and Altman [4269]. The first two calculations obviously have been carried out in approximation to the rigid rotator-harmonic oscillator model, leading thus to an essential difference between the values obtained through these calculations and those listed in the present Handbook. Corresponding discrepancies with the data obtained by [2142] at $T = 6000°K$ exceed 1.3 cal/mole•degree in the value for the entropy.

The values Φ_T^* for $T < 5000°K$, being close to those cited in the works [2142, 4149] are recommended by Margrave in the book of [2775].

In the work of Wilkins and Altman [4269] thermodynamic functions of BH have been calculated for $T < 6000°K$. The discrepancies between the data of Wilkins and Altman and those listed in Table 274 (II) amount to 0.14 cal/mole•degree in Φ^{*}_{T} and 0.57 cal/mole•degree in S°_{T} at 6000°K. These discrepancies obviously may result from the application of a less elaborated method of calculation (the method of Pennington and Cobb being used) and from disregarding the excited electronic states of BH.

The discrepancies between the values of functions for BH given in the first edition and those given in the present edition of this Handbook (up to 0.07 cal/mole•degree) are attributed to additional consideration of the state $a^{3}\Pi$ and to the introduction of corrections for the limitation of the number of rotational levels of the ground state.

BF and BCl. The thermodynamic functions for boron monochloride and monofluoride listed in Table 278 (II) and 282 (II) have been calculated in accordance with Eqs. ((II.161) and (II.162). The values $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ in these equations were calculated by the method of Gordon and Barnes (using the relations (II.137) and (II.138)) without introducing corrections for the limitation of the number of rotational states in the molecules of both gases.

The calculation was carried out for a natural mixture of the isotopes B^{10} and B^{11} as well as for Cl^{35} and Cl^{37} (in the case of BCl) by using "effective" values of the molecular constants computed on the basis of the constants given in Table 208 and with the aid of the relations (1.45).

In Table 212 we find listed values for C_{Φ} and C_{S} in Eqs. (II.161) and (II.162), the values for the coefficients in Eqs. (II.137) and (II.138) and also the values θ and $\underline{x}$ calculated from the "effective" constants of both molecules. The molecules BF and BCl have excited electrons of the state $a^{3}\Pi$ with energies of the order of 35,000 and 24,000 cm^{-1}, respectively; however, there are no experimental data available on the energies of these states. In this connection, the components of the state $a^3\Pi$, and also of the state $A^1\Pi$ of the BCl molecule was computed by the simplest method feasible [using Eqs. (II.120) and (II.121), i.e., without considering the difference of constants in the ground state and in the excited state. As to the excited states of the BF molecule it should be stated that they have not been considered in the calculation of the thermodynamic functions of this gas; the errors due to this simplification do not exceed 0.005 cal/mole•degree in the values Φ_T^*.

The basic errors in the calculated thermodynamic functions of boron monofluoride and boron monochloride are chiefly due to the lack of experimental data on the energy of high vibrational and rotational levels of the ground electronic states for both molecules and also due to the fact that the accepted values of the vibrational constants in the binomial equations lead to a convergence of the vibrational levels of the ground state markedly below its dissociation limit. However, owing to the large magnitude of the vibration frequencies and the dissociation energies in the molecules of the gases under consideration, these reasons as well as the negligence of the necessity to limitate the number of the rotational constants of the molecules do not lead to remarkable errors in the results of calculations. The general errors in the values Φ_T^* are of the order of 0.05 cal/mole•degree at T = 3000°K and 0.1 cal/mole•degree at $T = 6000°$ K .*

Thermodynamic functions of boron monofluoride have been cited earlier in the summary of Huff et al [2142] for $T \leqslant 6000°$ K and in the work of Ward and Husse [4149] for temperatures from 2000 to 5000°K. The calculation carried out in the latter was based on false values for the constants of BF and its results differ from the data of the present Handbook by 3.5-3.8 cal/mole•degree. The discrepancies as to the data of [2142] do not exceed 0.2 cal/mole•degree in Φ_T^* and 0.5

cal/mole·degree in S°_T and are obviously due to the fact that the calculation in the work [2142] had been carried out in approximation to the rigid rotator-harmonic oscillator model.

In a work by Altman [526], published recently, the thermodynamic functions for BF and BCl have been calculated for $T \leqslant 6000° K$. The discrepancies between the results of this work and the data given in the present Handbook amount to 0.05 cal/mole·degree in S°_T for BF and to 0.46 cal/mole·degree correspondingly for BCl. These discrepancies may be attributed to the fact that in the work [526] a less accurate calculating method has been used and that the excited electrons of the state of BCl have not been taken into account.

The thermodynamic functions for boron monofluoride given in the first edition and in that of the present Handbook are identical; the functions of BCl differ by one order of magnitude, not exceeding 0.04 cal/mole·degree in the value of Φ^*_T and 0.25 cal/mole·degree in the value of S°_T; the differences arise from additional consideration of the state $a^3\Pi$ of this molecule.

The thermodynamic functions of boron nitride given in Table 286 (II) have been calculated according to Eqs. (II.161) and (II.162). The values of $\ln\Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations have been calculated by the method of Gordon and Barnes [using the relations (II.137) and (II.138) without introducing corrections for the limitation of the number of rotational states. The values $\ln\Delta$ and $T\frac{\partial}{\partial T}\ln\Delta$ in Eqs. (II.161) and (II.162) have been assumed of being equal to zero, since the constant of spin-orbit coupling for BN is unknown. The calculation was performed on the basis of the molecular constants as listed in Table 208. The difference in the constants of the isotopic molecules $B^{10}N$ and $B^{11}N$ has not been considered in the calculation in view of the insufficient accuracy of the known constants. In Table 212 we find listed the values of C_Φ and C_S, of θ and $\underline{x}$ and also of the factors used in Eqs. (II.137) and (II.138), which have been calculated according to the accepted molecular constants for BN.

Since the BN molecule has a ground electronic state of the type $^3\Pi$, in the values of C_Φ and C_S the addends R ln 6 have been included. The components of the state $A^3\Pi$ of the BN molecule have been calculated according to Eqs. (II.120) and (II.121).

The basic errors in the calculated values of thermodynamic functions for boron nitride at low temperatures follows from the approximate estimate of multiplicity for the rotational levels of BN in the ground state $^3\Pi$. This uncertainty may amount up to 1-1.5 cal/mole•degree. At more elevated temperatures this type of error decreases while another type becomes more essential because there are no data available on the energy of high vibrational and rotational levels of the state $X^3\Pi$ and because the necessity of introducing corrections for the limited number of rotational levels is being neglected. It should also be noted that, in analogy to C_2, in BN the occurrence of a number of electronic states with low excitation energies can possibly be assumed. The general error in the values of Φ°_{3000} and Φ°_{6000} is of the order of 1-1.5 cal/mole•degree.

The thermodynamic functions for boron nitride given in the first edition and in the present edition of this Handbook are identical

In the book [2775] Margrave quotes values of Φ^*_T for $T \leqslant 3000°$ K, based on unknown data. These values exceed those given in Table 286 (II) by 2.76 cal/mole•degree and are obviously erroneous. Kelley [2363] quotes values of $S^\circ_T - S^\circ_{298}$ for $T < 2000°$ K , however, without indicating the value of S°_{298}.

$\underline{BO_2}$. The thermodynamic functions for boron dioxide given in Table 270 of the Second Volume (Vol.II) of this Handbook have been calculated according to Eqs. (II.241) and (II.242). The calculation was performed in approximation to the rigid rotator-harmonic oscillator model on the basis of the molecular constants for BO_2 listed in Table 209. In Table 213 we find listed the values of C_Φ, C_S and θ_n, which had been calculated on the basis of values accepted for the constants. Since the BO_2 molecule has the ground electronic state of the type ${}^2\Pi_g$, in the values of C_Φ and C_S the addends R ln 4 have been included; splitting of the components ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$ of this state has been accounted for by using Eqs. (II.151) and (II.152) on the basis of the spin-orbit coupling constant found by Johnson (cf. Table 209). The values of $R\ln\Delta_M$ and $R\ln\Delta_M + RT\frac{\partial}{\partial T}\ln\Delta_M$ have been added to the magnitudes calculated according to Eqs. (II.241) and (II.242). The BO_2 molecule has 2 excited low-energy electronic states. The components of these states have been calculated according to Eqs. (II.120) and (II.121), i.e., without considering the difference between the constants of BO_2 in the states $X^2\Pi$, $A^2\Pi$ and $B^2\Sigma$.

The basic errors in the calculated values of thermodynamic functions for BO_2 have been introduced due to the fact that it is impossible to consider the deviations of the BO_2 molecule from the rigid rotator-harmonic oscillator model and also due to the low accuracy of the accepted value for ν_3. The errors are estimated to amount to ± 0.2, and ± 1 and ± 2 cal/mole·degree in the values of Φ^*_T at 298.15, 3000 and 6000°K. It should be noted that the discrepancy between the values of thermodynamic functions for BO_2 listed in Table 270 (II) and those computed from the constants as estimated by the authors of this Handbook (cf. page 1457) amounts to 0.26 cal/mole·degree in $\Phi^*_{298.15}$ and up to 2 cal/mole·degree in S°_{6000}.

Other calculations of thermodynamic functions for BO_2 have not been published in the literature.

TABLE 213

Constants for Calculation of Thermodynamic Functions for Gaseous BO_2, B_2O_2, B_2O_3, HBO, HBO_2, H_3BO_3, FBO, BF_2, BF_3, BCl_2, BCl_3

1 Вещество	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7	θ_8	θ_9	C_Φ	C_S
	2 град									3 кал/моль·град	
BO_2	1539,5	667,6(2)	1902,1	—	—	—	—	—	—	6,7781	13,7336
B_2O_2	3021,5	935,2	2719,3	719,4(2)	—359,7(2)	—	—	—	—	6,6724	13,6279
B_2O_3	2920,7	1179,8	1079,1	446,02	1093,5	2935,1	1345,3	949,6	978,38	9,0598[a]	17,0089[a]
HBO	3525	1007,2(2)	2589,8	—	—	—	—	—	—	1,3371	8,2926
HBO_2	5294,7	2920,7	2043,1	1798,5	877,66	1007,2	—	—	—	3,3794[a]	11,3285[a]
H_3BO_3	4676,1	1266,1	1525,1	935,21	—	4532,5(2)	2071,9(2)	791,3(2)	1712,2(2)	6,7851[a]	14,7342[a]
FBO	1438,8	575,52(2)	3021,5	—	—	—	—	—	—	5,6021	12,5576
BF_2	1812,9	604,29	2043,1	—	—	—	—	—	—	5,0740[a]	13,0231[a]
BF_3	1277,7	1002,8	2104,7(2)	691,63(2)	—	—	—	—	—	5,5731[a]	13,5222[a]
BCl_2	1151	302,15	1294,9	—	—	—	—	—	—	9,6026[a]	17,5517[a]
BCl_3	677,67	667,60	1385,6(2)	349,63(2)	—	—	—	—	—	10,7911[a]	18,7402[a]

Note: a) Given are the values of C'_Φ and C'_S.

1) Compound; 2) degree; 3) cal/mole·degree.

B_2O_2. The thermodynamic functions of the dimer of boron monoxide listed in Table 271 (II) have been calculated according to Eqs. (II.241) and (II.242) in approximation to the rigid rotator-harmonic oscillator model. The calculation was performed with the aid of the constants as accepted in Table 209. In Table 213 we find listed values of C_Φ and C_S for the calculation of the components of the progressive motion (translation) and of the rigid rotator and also values of θ_n for the calculation of components of the harmonic oscillator. The latter have been calculated without considering the difference in the frequencies of the individual isotopic modifications of the B_2O_2 molecule.

The basic errors in the calculated values of the thermodynamic functions of B_2O_2 result from the lack of experimental data on the fundamental frequencies and the structure of this molecule (approximately ±2 cal/mole·degree in the value of Φ^*_{3000}) and also from the fact that it is impossible to consider the deviations of the B_2O_2 molecule from the rigid rotator-harmonic oscillator model (approximately 2 cal/mole·degree in the value of Φ^*_{3000}). The general errors in the calculated values of $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} do have magnitudes of the order of ±1; ±4 and ±6 cal/mole·degree.

During the recent years Tables of thermodynamic functions for B_2O_2 have been calculated in the works of Evans, Prosen and Wagman [1515] **($T \leqslant 2500°$ K)**, of Wilkins and Altman [4269] **($T \leqslant 6000°$ K)** and of White et al [4238] **($T \leqslant 6000°$ K)**. All calculations were accomplished on the basis of estimated values for the constants of the B_2O_2 molecule; in the works [1515, 4269] values have been accepted for these constants which had been suggested by Inghram and co-workers [2171], while in the work [4238] constants have been selected, which had been obtained by the authors themselves (see page 1464). The discrepancies between all calculations performed in these works and listed in Table 271 (II) on the values of thermodynamic functions amount in Φ^*_T and S°_T to about 1.2-1.5 cal/mole·degree; thereby, the results of calculations obtained in [1515, 4269] are larger than the data listed in Table 271 (II) while those results obtained in the calculations of [4238] are smaller than the latter. The discrepancies between the results from all calculations are almost entirely caused by the differences existing in the values which had been accepted for the calculations of the fundamental frequency values for the deformation vibrations ν_4 and ν_5 occurring in B_2O_2.

In the book [2775] Margrave quotes values of Φ^*_T for the dimer of boron monoxide at several temperatures. These data obviously are based on approximated calculations performed in a work which remained unknown to the authors of this Handbook; they differ essentially from data obtained in other works.

HBO and FBO. The thermodynamic functions for boron hydrideoxide and boron fluoro oxide listed in Tables 275 (II) and 281 (II) have been calculated according to Eqs. (II.241) and (II.242) in approximation to the rigid rotator-harmonic oscillator model. Calculations were carried out from constants listed in Table 209. In Table 213 values are quoted of C_Φ and C_S in Eqs. (II.241) and (II.242) and also of θ_n for the calculation of the vibrational components according to the Tables of the harmonic oscillator.

The basic errors in the calculated values of the thermodynamic functions for HBO and FBO are due to the lack of experimental data on the constants of these molecules and also due to the fact that it is impossible to consider the deviations of the molecules of both gases from the rigid rotator-harmonic oscillator model. These errors show magnitudes of the order of 0.5, 1.5 and 3 cal/mole·degree in the values of Φ_T^* at 298.15, 3000 and 6000°K, respectively.

Thermodynamic functions of both gases have been published in the literature for the first time.

<u>B_2O_3</u>. The thermodynamic functions of boron oxide listed in Table 273 (II) have been calculated on the basis of the constants of the B_2O_3 molecule which were accepted above (see Table 210). The calculation was performed according to Eqs. (II.243) and (II.244) in approximation to the rigid rotator-harmonic oscillator model. In Table 213 we find listed the values of the constants C'_Φ and C'_S used in Eqs. (II.243) and (II.244) and also of the magnitudes θ_n needed for the calculations according to the Tables of the harmonic oscillator.

The basic errors in the calculated values of thermodynamic functions for boron oxide are due to the lack of reliable data on the fundamental frequencies of B_2O_3 and also due to the fact that it is impossible to consider the deviations of this type molecule from the rigid rotator-harmonic oscillator model. A precise estimate of the magnitude of these errors cannot be made at the present time; it can be assumed that they are equal by the order of magnitude to the discrepancies between the functions which were calculated from the constants as suggested in the works [4238, 52a]. In conjunction with that, the errors in the values of $\Phi_{298.15}^*$, Φ_{3000}^* and Φ_{6000}^* have been assumed to be equal to ±1, ±3 and ±5 cal/mole·degree, respectively.

Thermodynamic functions of gaseous boron oxide were calculated during the recent years in a number of **works** (see [2142, 1515, 4238, 2775]). The first calculation obviously was carried out in the work by Walker, Woolley and Fire which was not published in the periodical literature and became known only from references in a number of American publications. In this work, for B_2O_3 molecules a dipyramidal structure had been accepted and an approximate estimate of the fundamental frequencies of this type molecule had been made. The thermodynamic functions for B_2O_3 calculated by Walker, Woolley and Fire are listed in the summary of Huff, Gordon and Morrell [2142]; they were considered to be sufficient accurate and have been therefore accepted in the first edition of this Handbook. The discrepancies between the values of thermodynamic functions of boron oxide listed in Table 273 (II) and those quoted in the publications mentioned are practically independent of the temperature and do have a magnitude of the order of 6.5 cal/mole•degree. They are chiefly due to the difference in the numbers of symmetry and the products of the moments of inertia between the dipyramidal and angular model of the B_2O_3 molecule.

In the works [4238, 1515] the thermodynamic functions for boron oxide have been calculated for temperatures up to 6000 and 2500°K in accordance with the suggestion that the B_2O_3 molecule possesses an angular structure. The calculation of White et al [4238] was carried out on the basis of the interpretation of the spectrum of B_2O_3 vapors as proposed by them; the results of this calculation are smaller than the values listed in Table 273 (II) by a magnitude of from 0.3 cal/mole••degree in the value of $\Phi^*_{298.15}$ and up to 3 cal/mole•degree in S°_{6000}. The values for the molecular constants of B_2O_3, which have been accepted in the work of Evans, Prosen and Wagman [1515], are unknown; the values of thermodynamic functions obtained by them are in good agreement (within the limits of 0.5 cal/mole•degree in Φ^*_T and S°_T) over the whole temperature range with the data of the present Handbook.

The thermodynamic functions listed by Margrave in the book [2775] are close to those quoted in the summary by Huff et al [2142]; they have been obviously obtained on the basis of an approximate estimate, assuming for B_2O_3 a dipyramidal model, or by recalculation from the data of Walker, Woolley and Fire.

$\underline{HBO_2}$. The thermodynamic functions for gaseous metaboric acid as listed in Table 276 (II) have been calculated according to Eqs. (II. 243) and (II.244). The calculation was carried out in approximation to the rigid rotator-harmonic oscillator model, using the molecular constants which were accepted in the preceding section (see Table 210). In Table 213 we find listed values of the constants C'_{Φ} and C'_{S} used in Eqs. (II.243) and (II.244) and also the values of θ_n for the calculation of the vibrational components of HBO_2, computed from the accepted values of the molecular constants.

The basic errors in the thermodynamic functions for the metaboric acid as listed in Table 276 (II) are due to the lack of experimental data on the fundamental frequencies ν_4, ν_5 and ν_6 of the HBO_2 molecule, furthermore due to the lack of anharmonicity constants, of centrifugal stretching constants, etc., (of the order of 0.5 and 1 cal/ /mole•degree in Φ^*_{3000} correspondingly). The general errors in the calculated values of Φ^*_T at 298.15, 3000 and 6000°K may be estimated to be equal to ±0.2; ±2 and ±4 cal/mole•degree, respectively.

The first calculation of thermodynamic functions for metaboric acid has been carried out during the preparation of the first edition of the present Handbook on the basis of the same values of the structural parameters which had been accepted in the given publications, and on the basis of the close values of fundamental frequencies (see page 1471). The discrepancies between the results from these calculations and the data listed in Table 276 (II) do not exceed 0.5 cal/ /mole•degree. They are chiefly due to the change in the value of frequency ν_4 as compared to the values which had been accepted in the first edition.

White et al [4239] calculated the values of thermodynamic functions for temperatures up to 6000°K on the basis of molecular constants being close to those accepted in this Handbook. The results from both calculations agree within the limits of 0.1 cal/mole·degree. Evans, Prosen and Wagman [1515] calculated thermodynamic functions of HBO_2 up to 2500°K on the basis of estimated values of the molecular constants. The data obtained by these authors essentially differ from those listed in Table 276 (II); thereby the discrepancies rise with increasing temperatures and reach about 1 cal/mole·degree in S°_{2500}.

In the book [2775] Margrave quotes values of Φ^*_T of metaboric acid for several temperatures, without indicating the work in which they have been obtained. These data are false and at a temperature of $T = 1000$°K they differ from those obtained by other authors by 6 cal/mole··degree.

$\underline{H_3BO_3}$. The thermodynamic functions for gaseous ortho-boric acid, listed in Table 277 (II), have been calculated for temperatures of 293.15-6000°K according to Eqs. (II.243) and (II.244) in approximation to the rigid rotator-harmonic oscillator model. The values of θ_n, C'_Φ and C'_S (cf. Table 213), needed for the calculations when using these equations, have been computed on the basis of the molecular constants of H_3BO_3, listed in Table 210. The components of hindered internal rotation of the values $\Phi^*_{vn.\,vr}$ and $S_{vn.\,vr}$ have been calculated according to Eqs. (II.236) and (II.237), in which the expressions $(\Phi^*_{sv.\,vr} - \Phi^*_{vn.\,vr})$ and $(S_{sv.\,vr} - S_{vn.\,vr})$ were found, according to Pitzer's and Quinn's Tables [3259] to be functions of the type $\frac{1}{Q_{\text{св.вр}}} = \frac{6{,}28725}{\sqrt{T}}$ and $V_0/RT = \frac{2000}{RT}$. For the calculation of $Q_{sv.\,vr}$ according to Eq. (II.231) it was assumed that $n = 2$; the value σ_1 in Eqs. (II.236)-(II.237) was assumed to be equal to 1. Since in the H_3BO_3 molecule there are three tops, the values of $\Phi^*_{vn.\,vr}$ and $S^\circ_{vn.\,vr}$ in Eqs. (II.243) and (II.244) were triplicated. At the same time, the components of the twisting (torsional) vibrations (ν_5 and ν_{10}) have been assumed to be equal to zero.

The errors in the values of the thermodynamic functions of ortho-boric acid, listed in Table 277 (II), are due to different factors: at low temperatures, they are due to the lack of experimental data on the magnitude of the potential barrier for internal rotation, and at high temperatures, they are due to the lack of data on the fundamental frequencies for the H_3BO_3 molecule (the fundamental frequencies being assumed on the basis of spectral investigations of the acid in its solid state). As to the above mentioned errors in the value of the potential barrier (±1000 cal/mole) we find analogous errors in Φ_T^* at 298.15; 3000 and 6000°K to be equal to ±1.5, ±0.8 and ±0.2 cal/mole··degree, correspondingly.* The errors resulting from a possible inaccuracy in the assumed structural parameters and fundamental frequencies of the H_3BO_3 molecule are equal to ±0.2; ±1.5 and ±3 cal/mole··degree, respectively, while the errors resulting from not considering the anharmonicity of vibrations and other deviations of the H_3BO_3 molecule from the rigid rotator-harmonic oscillator model do have a magnitude of the order of 0.1; 1.5 and 3 cal/mole·degree, respectively. The general errors in the calculated values of $\Phi_{298.15}^*$, Φ_{3000}^* and Φ_{6000}^* have been estimated to equal ±2' ±4 and ±6 cal/mole·degree, respectively.

The thermodynamic functions of gaseous ortho-boric acid were previously calculated in the work of Evans, Prosen and Wagman [1515] for temperatures up to 2500°K. The results of these calculations are in agreement within limits of 0.5 cal/mole·degree with the values listed in Table 277 (II). In the book [2775] Margrave quotes for H_3BO_3 several values of Φ_T^* (for $T \leq 1500°K$) without indicating the source whence the data have been obtained. The data given by him are smaller than the data listed in Table 277 (II) by 3-3.5 cal/mole·degree.

BF_2 and BCl_2. The thermodynamic functions of boron difluoride and boron dichloride, listed in Tables 279 (II) and 283 (II), have been calculated according to Eqs. (II.243) and (II.244) in approximation to the rigid rotator-harmonic oscillator model according to the molecular constants, which have been accepted in Table 211.

In Table 213 we find listed the values of C'_Φ and C'_S, according to which the components of progressive motion (translation) and of the rigid rotator as well as the values of θ_n, for the interpolation according to the Tables of the harmonic oscillator, were found. Since in the previous section it had been assumed that the molecules BF_2 and BCl_2 have doublet ground states, in the values of C'_Φ and C'_S the addends R ln 2 have been included.

The basic errors in the calculated values of the thermodynamic functions are connected with the lack of experimental data on the molecular constants of the gases under consideration, primarily due to the lack of the vibrational constants. The general magnitude of errors in the values of Φ^*_T at 298.15, 3000 and 6000°K is of the order of 0.5, 2.0 and 4.0 cal/mole•degree.

The discrepancies between the values of the discussed functions given in the first edition and those given in the present edition of this Handbook, amount to 0.005 and 0.002 cal/mole•degree for BF_2 and BCl_2 and which arise from rounding off the products of the moments of inertia of these molecules, which are accepted in the present edition.

Other calculations of thermodynamic functions for BF_2 and BCl_2 are not known in the literature.

BF_3 and BCl_3. The thermodynamic functions for boron trifluoride and boron trichloride, listed in Tables 280 (II) and 284 (II), have been calculated according to Eqs. (II.243) and (II.244) in approximation to the rigid rotator-harmonic oscillator model on the basis of constants accepted in the previous section. For the allowance of the difference between the constants of the individual isotopic modifications of the BF_3 and BCl_3 molecules the calculation was performed by employing averaged values of their vibrational constants and of their products of moments of inertia. In Table 213 we find listed the values of C'_Φ, C'_S and θ_n used in the calculations.

The basic errors in the calculated values of the thermodynamic functions for BF_3 and BCl_3 are due to the fact that there is no possibility for considering the anharmonicity of vibrations in the molecules of these gases as well as for considering other corrections to be made which are typical for their deviation from the rigid rotator-harmonic oscillator model because of lacking experimental data on the magnitude of the corresponding constants. In the case of BCl_3, at low temperatures also the inaccuracy of the accepted value for the interatomic distance (of the order of 0.07 cal/mole·degree) comes into being. The general errors in the calculated values of Φ^*_T at 298.15, 2000 and 6000°K, respectively, show magnitudes of the order of 0.1, 1.5 and 3.0 cal/mole·degree for BF_3 and of 0.2, 2.0 and 4 cal/mole·degree for BCl_3.

The thermodynamic functions for boron trifluoride and boron trichloride have been calculated previously by Spencer [3819] from close values of the molecular constants for $T \leqslant 1000°$ K. Subsequently, Altshuller [529] introduced a correction into the results of Spencer's calculation aiming at a greater precision for the value of interatomic distance B – F in the BF_3 molecule.

In the work of Evans, Prosen and Wagman [1515] the thermodynamic functions for BF_3 and BCl_3 have been calculated for temperatures up to 2500°K; finally, in the summary of Huff, Gordon and Morrell [2142] the values of the functions for BF_3 have been obtained for temperatures up to 6000°K. The results of all these calculations, including those given in the present Handbook, agree with one another within the limits of 0.02 cal/mole·degree.*

The standard entropy of gaseous boron trifluoride has been determined for the first time in the work of Aiken and Schroeder [1505] as a result from heat capacity measurements of BF_3 from 12 to 173°K. The authors of this work found $S^\circ_{298} = 61.17$ cal/mole·degree. Spencer [3819] reqorked and specified the experimental data obtained by Aiken and Schroeder; however, the discrepancy between the value found by them, i.e., $S^\circ_{298} = 60.80 \pm 0.5$ cal/mole·degree and the above mentioned magnitude lies within the limits of errors occurring in experimental data.

In 1954, Strelkov and co-workers [46] repeated the measurement of the heat capacity of BF_3 at temperatures from 12.6 to 162.8°K as well as the measurement of the melting heat and heat of evaporation of BF_3. The value of 60.67 ± 0.04 cal/mole·degree agrees excellently with the value of 60.716 cal/mole·degree listed in Table 280 (II).

§93. THERMODYNAMIC PROPERTIES OF B, B_2O_3 AND BN IN THE SOLID AND LIQUID STATE

The Tables of thermodynamic functions for elementary boron, the boron oxide B_2O_3 and boron nitride BN in the solid and liquid state [Tables 266 (II), 272 (II) and 285 (II) have been calculated according to Eqs. (III.9)-(III.11) on the basis of thermodynamic quantities listed in Table 214. The errors in the calculated values of Φ^*_T at temperatures of 298, 1000, 1500, 2000 and 3000°K which were estimated on the basis of an analysis for determining the possible errors of the initial data are listed in Table 215.

B. Solid boron is known to exist in the crystalline and amorphous state.** Crystalline boron is capable of forming a number of different polymorphic modifications. According to the data by Chord and Newkirk [2086] up to 1300°K the α-rhombohedral modification proved to be thermodynamically stable, in the temperature range of 1400-1600°K the tetragonal modification behaved in the same manner and above 1800°K the β-rhombohedral modification remained stable. However, since the transition points and heats for various boron modifications had not been determined, the polymorphism of crystalline boron has not been considered in the calculation of thermodynamic functions.

TABLE 214

Accepted Values of Thermodynamic Quantities for Boron and Its Compounds in the Solid and Liquid State

1 Вещество	2 Состояние	$H^\circ_{298.15}-H^\circ_0$	$S^\circ_{298.15}$	$C^\circ_{p298.15}$	3 Коэффициенты в уравнении для C°_p а			4 Интервал температур	Tm	ΔHm
		5 кал/моль	6 кал/моль·град		a	$b\cdot10^3$	$c\cdot10^{-5}$	°K	°K	кал/моль 7
B	8 Крист.	292	1,403	2,65	4,013	2,165	1,787	298,15—1100	—	—
B	»	—	—	—	5,42	0,752	—	1100—2500	2500	6000
B	Жидк.	—	—	—	7,5	—	—	2500—5600	—	—
B_2O_3	Крист.	2218	12,87	14,83	8,73	25,4	1,31	298,15—723	723	5500
B_2O_3	9 Жидк.	—	—	—	30,5	—	—	723—3300	—	—
BN	Крист.	641	3,673	4.78	5,034	6,154	1,854	298,15—1000	—	—
BN	»	—	—	—	9,5	1,5	—	1000—3000	3000	18000
BN	Жидк.	—	—	—	16,0	—	—	3000—4500	—	—

Note: a) $C^\circ_p = a + bT - cT^{-2}$ (cal/mole·degree).

1) Substance; 2) state; 3) coefficients used in the equation for $C^{\circ a)}_p$; 4) temperature range; 5) cal/mole; 6) cal/mole·degree; 7) cal/mole; 8) cryst.; 9) liqu.

The heat capacity of pure crystalline boron at low temperatures (17-300°K) has been measured by Johnston, Hersch and Kerr [2279]. The values of $S^\circ_{298.15}$ and $H^\circ_{298.15} - H^\circ_0$ (see Table 214) obtained by these authors are of high accuracy (±0.01 cal/g-atom·degree, respectively); this fact can be explained by the adequate accuracy of the heat capacity measurement (±0.3% at T > 200°K and ±1% at 20°), by the high Debye temperature for crystalline boron (of the order of 1200°K) and by the small value of the entropy obtained through extrapolation of the heat capacity to 0°K (S°_{17} = 0.0014 cal/g-atom·degree).

The data on the average heat capacity of solid boron over a temperature range from room temperature to 400-500°K, already obtained by a number of researchers at the end of the XIXth century (see for references given by Kelley [2363] are unreliable in view of the lack of information on the state of the investigated samples and on their contamination with metal borides. The data by Magnus and Danz [2734] on the enthalpy of amorphous boron in the temperature range 298-1174°K do not seem to be authentic either due to the impurity of the investigated sample (grade of purity 97%) and due to some inadequate working procedures in the method of investigation (the slow establishment of thermal equilibrium because of the poor thermal conductivity of boron and also the interaction between the material of the ampul with boron at temperatures about 1100°K; see [1515]). Evans, Prosen and Wagman [1515] used in the calculation of thermodynamic functions for crystalline boron the data of Robertson [3454] on the heat capacity of B (cryst.) over a range from room temperatures to 373°K*; extrapolation of the heat capacity up to 2000°K has been carried out by the authors [1515] by assuming that $C^\circ_{p_{2000}}$ = 7.0 cal/g-atom·degree.

The only work performed on measuring the enthalpy of sufficiently pure boron over a broad temperature range (298-1103°K) has been carried out in 1960 by Wise, Margrave and Altman [4299a]. The authors investigated two samples of crystalline boron: one of grade I having a purity of 99.6% and the other of grade II having a purity of 99.5%, and also a sample of "amorphous" boron (with a total of metal impurities of 0.2%). X-ray diffraction pattern analysis revealed in all three samples a certain amount of a high-temperature β-rhombohedral modification of boron. The discrepancies between the values of enthalpy obtained for samples I and II, amounting to an average of 2%, has been explained by Wise et al [4299a] by the inequality in the state of the samples being investigated. Sample II had been prepared through recrystallization of amorphous boron and could have contained a considerable quantity of the amorphous phase, what should result in an overrated value of the heat capacity. In the present Handbook in the temperature range 298--1100°K the data obtained by Wise, Margrave and Altman [4299a] for sample I (see Table 214) have been accepted, since sample I was found to be in a better crystalline equilibrium state than sample II.*

In the literature there are no reliable data on the melting point of boron; different authors quote values ranging from 2273 to 2773°K. According to determinations made by Cayeron [1230, 1231] the melting point of boron lies in the range between 2273-2348°K. However, Szerzy and Mayers [3673] were able to show that heating of boron up to a temperature of 2420°K does not lead to its melting. In this Handbook the melting point of boron has been accepted as being equal to 2500 ± 200°K. The melting point for boron $\Delta H_{2500} = 6{,}0 \pm 2$ kcal/g-atom has been calculated on the basis of the approximated value of entropy for the melting of boron $\Delta S = 2{,}4 \pm 0{,}5$ cal/g-atom·degree, which was obtained from the comparison of the melting entropies for a number of common substances having a close-packed crystalline lattice (see [2439]). The heat capacity of liquid boron has been estimated to equal 7.5 cal/g--atom·degree (see page 261).

The values calculated in the present Handbook for the thermodynamic functions of crystalline and liquid boron [Table 266 (II)] differ essentially from those given in the first edition of this Handbook and in a number of summaries [3894, 1515, 2364a] in view of the inequalities of the accepted initial data on heat capacity, melting point and melting heat for crystalline boron. The discrepancies in the entropy values in the temperature range 1000-3000°K amount to 0.2 to 0.6 cal/g-atom·degree, and in the values of Φ_T^* up to 0.4 cal/g-atom·degree (at 2300°K).

The values of thermodynamic functions for boron in its solid and liquid state, calculated for temperatures of 293.15-5600°K, are listed in Table 266 (II). The size of errors in the calculated values of Φ_T^* are listed in Table 215.

$\underline{B_2O_3}$. Solid boron oxide is known to exist in the crystalline and vitreous state. At low temperatures, the heat capacity of crystalline B_2O_3 has been measured by Kelley [2361] (53-295°K) and by Kerr, Hersch and Johnston [2374] (18-297°K). The data obtained by these authors are in good agreement with one another and helped to obtain the values of $S^\circ_{298.15}$ and $H^\circ_{298.15} - H^\circ_0$, listed in Table 214.

Extrapolation of the heat capacity below 18°K yields a value of $S^\circ_{18} = 0{,}027$ cal/mole·degree [2374]. The accuracy in the value of $S^\circ_{298.15}$ according to the estimate of the authors of [2374], amounts to ±0.10 cal/mole·degree, and of the value $H^\circ_{298.15} - H^\circ_0$ according to the estimate made by the authors of this Handbook,* to ±10 cal/mole.

Measurement of the enthalpy of vitreous and crystalline boron oxide at temperatures below the melting point of B_2O_3 has been carried out by Sautard [3814] with an accuracy of about 1%. He also determined the dissolution heats of crystalline and vitreous boron oxide and calculated the transition heat for the transition of vitreous boron oxide into the crystalline form at 298.15°K to equal $\Delta H^\circ_{298.15} = 4{,}36 \pm 0{,}02$ kcal/mole. A recalculation of this value towards the melting point of B_2O_3, assumed to be equal according to the data by Kracek et al [2470c] to 723 $\pm$2°K,** yields a value for melting heat of $\Delta H_{723} = 5{,}27$ kcal/mole, [3814]. Kelley [2363] reexamined the measurement results of Sautard

[3814] and arrived at some different equations for the heat capacity of crystalline and vitreous B_2O_3 and obtained somewhat higher values for the melting heat $(\Delta H_{723} = 5,5 \pm 0,3$ kcal/mole). These data were accepted in the present Handbook. The size of errors in the value for the melting heat of crystalline B_2O_3 should be considered as large as ±1 kcal/mole in view of the fact that errors might also be due to the indeterminacy of the phase transition state in vitreous boron oxide which strongly depends on its thermal treatment [1515].

The enthalpy of liquid boron oxide has been measured by Sautard [3814] (791-1777°K), by Voskresenskaya and Banashek [12] (800-1400°K) as well as by Krasovitskaya, Kutsyna, Kantor, Fomichev and Kandyba [261] (874-2128°K).

The data obtained are in good agreement with one another and yield the following heat capacity values for liquid B_2O_3: 30.45 [3814], 30.0 [12] and 30.54 cal/mole·degree [261]. The value of 30.5 ± 0.5 cal/mole··degree, accepted in this Handbook, is an average value between those obtained in the works [3814 and 261] and coincides with the values recommended by Kelley [2363]. This value has also been utilized for the calculation of thermodynamic functions of liquid boron oxide at temperatures above 2100°K.

Values of thermodynamic functions for boron oxide in both the solid and liquid state, calculated for temperatures of 293.15-3300°K, are given in Table 272 (II). The size of errors in the calculated values of Φ_T^* are given in Table 215.

The tables of the thermodynamic functions of B_2O_3 given in the first and the present editions of the Handbook are identical. The deviations from the values of the thermodynamic functions of B_2O_3, calculated by Huff, Gordon and Morrell [2142] up to 2500°K do not exceed 0.25 and 0.3 cal/mole·degree with the values of Φ_T^* and S_T°, respectively. The deviations from the values of the thermodynamic functions of B_2O_3, obtained by Evans, Prosen and Wagman [1515] for temperatures up to 2000°K are greater and amount to 0.7 and 1.1 cal/mole·degree with Φ^*_T and S°_T at 2000°K, respectively. The causes of these deviations are not clear since the authors of paper [1515] do not give all thermodynamic quantities they had used in order to calculate the thermodynamic functions.

BN. Boron nitride has a hexagonal structure, analogous to the structure of graphite.* The low-temperature specific heat of boron nitride was measured by Dworkin, Sasmor and Artsdalen [1432] (19-301°K) and Westrum and Biel (cf. [4222a]) (5-300°K). A systematic deviation can be observed with the results of the measurements which is greatest at temperatures of 110-120°K. This deviation was explained by Westrum and Biel [4222a] by considerable magnetite impurities in the sample investigated in paper [1432], which, in this temperature interval, shows an anomalous specific heat. According to data of Dworkin et al [1432], $S^\circ_{298,15} = 3,673 \pm 0,02$ cal/mole·degree and $H^\circ_{298,15} - H^\circ_0 = 641$ cal/mole. According to data of Westrum and Biel, $S^\circ_{298,15} = 3,537$ cal/mole·degree. In paper [4222a], however, there are no numerical values of the specific heat and the quantity $H^\circ_{298,15} - H^\circ_0$ for BN. Since the measurements of Westrum and Biel must be published in next to no time, the authors of the Handbook did not recalculate the tables of the thermodynamic functions of boron nitride which have been calculated on the basis of the values of $S^\circ_{298,15}$ and $H^\circ_{298,15} - H^\circ_0$, obtained by Dworkin et al [1432] (see Table 214). The accuracy of these values may be estimated as amounting to ±0.15 cal/mole, respectively.

The enthalpy of boron nitride in the temperature interval of 298-1174°K was measured by Magnus and Danz [2734]. Kelley [2363] estimated the accuracy of these measurements as amounting to ±2%. Based on the values of $H^{\circ}_{700} - H^{\circ}_{298.15} = 2900$ cal/mole and $H^{\circ}_{1000} - H^{\circ}_{298.15} = 5900$ cal/mole, calculated by Kelley [2363] from data of [2734] and the value of $C_{p_{298.15}} = 4{,}783$ cal/mole·degree [1432] the authors of the Handbook derived an equation for the specific heat of boron nitride in the interval 298-1000°K, given in Table 214.*

At the temperatures from 1000 to 3000°K the specific heat of solid boron nitride was estimated with the help of a linear equation (see Table 214], derived on the basis of the value $C^{\circ}_{p_{1000}} = 11.00$ cal/mole·degree and the approximate value of the specific heat of solid BN at the melting point, $C^{\circ}_{p_{3000}} = 14{,}0$ cal/mole·degree.

The melting point of boron nitride was taken as equal to 3000°K, on the basis of insufficiently reliable data of Fiederich and Sittig [1614] (the error of the value used amounts to ±200 – ±300°K.** The melting entropy of boron nitride was assumed as equal to 6 ± 2 cal/mole·degree, according to an approximate estimation (see [267]), which leads us to a value of the melting heat of $\Delta H_{3000} = 18 \pm 6$ kcal/mole. The value of the specific heat of liquid boron nitride was estimated as equal to 16 cal/mole·degree (cf. page 261).

TABLE 215

Errors (in cal/mole·degree) of the Φ^{*}_{T} of Boron and Its Compounds in Solid and Liquid States

T°, K	298	1000	1500	2000	3000
B	±0,01	±0,07	±0,15	±0,3	±0,6
B_2O_3	±0,1	±0,3	±0,5	±0,8	±1,5
BN	±0,15	±0,25	±0,4	±0,6	±1,2

The values of the thermodynamic functions of boron nitride in solid and liquid states, calculated in the interval of 293.15-4500°K, are given in Table 285 (II). The values of the errors of the calculated values of Φ_T^* are given in Table 215.

The tables of the thermodynamic functions of BN, given in the first and in the present editions of the Handbook, are identical.

§94. THE THERMODYNAMIC QUANTITIES

The standard state of boron is B (cryst.)

Most of the thermodynamic investigations were made with boron in amorphous state. The value of the heat of transition, B(cryst) → B (amorph.), $\Delta H_{298,15} = +0,4$ kcal/g-atom, necessary to calculate the standard heats of formation, was taken from the Handbook [3508]. The method of determination and the error of this value are not known so that the estimated values of the errors of the thermodynamic quantities of boron compounds do not include the error of determining the heat of transition of B (cryst.) → B (amorph.).*

B (gas). The values of the heat of sublimation of boron, $\Delta Hs_{291} = 115$ kcal/g-atom [813], $\Delta Hs_{2800} = 75$ kcal/g-atom [1093], and also $\Delta Hs_{298.16} = 97,2$ kcal/g-atom [3508], recommended in the editions of the Handbook, are based on approximate estimates.

Table 216 gives the values of the heat of sublimation of boron, calculated on the basis of experimental measurements of vapor pressures by means of effusion and mass-spectrometrical methods, under the supposition that the vapor consists of boron atoms alone. In the penultimate column of the table the values of the ratio of evaporation area to the area of the effusion opening (α) are given. The values of the heat of sublimation of boron given in the last column of the table differ somewhat from those calculated by the authors of experimental investigations, which is explained by the small difference of the values of the thermodynamic functions of boron in gaseous and condensed states, used in the calculations.

Very careful measurements of the boron vapor pressure were made by Priselkov, Sapozhnikov, Tseplyayeva and Nesmeyanov [22, 338a]. In this paper it was observed that the pressure measured decreases strongly as the relative size of the effusion opening is increased and correspondingly the heat of sublimation of boron rises from 100.6 to 124.5 kcal/g-atom. The authors of papers [22, 338a] recken that in the evaporation of boron from effusor chambers with large openings the boron vapor consists of nonsaturated monatomic boron (the evaporation coefficient of boron is smaller than 10^{-3}), and recommend a value of $\Delta Hs_0 = 101 \pm 2$ kcal/g-atom, which is obtained with the smallest openings.

Mass-spectrometrical measurements of boron vapor pressures were carried out by Akishin, Nikitin and Gorokhov [3, 1, 63a]. Molybdenum and tantalum effusor chambers, lined with pressed boron, were used as boron vapor sources. The authors of this paper could not notice a change in vapor pressure of atomic boron depending on the relative size of the effusion opening (see Table 216). The measurements of boron vapor pressure in evaporation from an open surface, carried out by Akishin et al., together with the results of measurements obtained in evaporation from effusor chambers, permitted the calculation the value of the coefficient of evaporation of boron, being equal to 0.2-0.3 at 1600-2000°K.* Almost the same value of the coefficient of evaporation was obtained for carbon (see page 945).

As may be seen from Table 216, the vapor pressures measured with the help of Knudsen's method yield a value of the heat of sublimation of boron equal to 101 ± 2 kcal/g-atom, the heat of sublimation increasing sharply as the relative size of the effusion opening is increased, reaching values of up to 124.5 kcal/g-atom [22] and 138 kcal/g-atom [3673]. Mass-spectrometrical measurements yielded values of

130.6 kcal/g-atom [3, 63a] and 129 kcal/g-atom [3622b, 1105a],* which do not depend on the size of the effusion opening. It is possible that these deviations, just as the analogous deviations in the case of carbon, can be explained by the existence of associated molecules (for example, B_4) in the saturated boron vapor, molecules which have a very small coefficient of evaporation.** If this supposition is true, the mass-spectrometrical measurements refer to equilibrium partial pressure of monatomic boron, and the effusion measurements in chambers with small openings to saturated boron vapor pressure, with associated molecules of B_n as its main component.

According to this interpretation, the following value is accepted in the Handbook:

$$\Delta Hs_0(\mathrm{B}, \text{cryst.}) = \Delta H^\circ f_0(\mathrm{B}, \text{gas}) = 130 \pm 5 \ \text{kcal/g-atom}.$$

This explanation of the results of experimental measurements of boron vapor pressure cannot be viewed as undisputable.

B_2 (gas). Douglas and Herzberg [1374] estimated the B_2 dissociation energy with the help of a linear extrapolation of the vibrational energy levels of the $X^3\Sigma$ ground state of the B_2 molecule. The value of $D_0(B_2) = 83$ kcal/mole they obtained is given in the Handbook [649] and in Herzberg's book [2020]. As also for a series of other molecules, Gaydon [1668] reduced this value by 20% and recommended a value of $D_0(B_2) = 69 \pm 12$ kcal/mole.

Inghram and Drowart [2170a] give the following value of the dissociation energy

$$D_0(B_2) = 62{,}3 \pm 10 \ \text{kcal/mole},$$

calculated on the basis of mass-spectrometrical measurements of the composition of the boron evaporation products [1105a]. This value is accepted in the Handbook; the following value corresponds to it:

$$\Delta H^\circ f_0(B_2, \text{gas}) = 197{,}7 \pm 14 \ \text{kcal/mole}.$$

TABLE 216

Results of Calculations of the Heat of Sublimation of Boron (in kcal/g-atom)

1 Авторы	2 Год	3 Метод	Интервал температуры, °K 4	5 Число измерений	α	ΔH_{s_0}
6 Серси, Майерс [3673]	1957	Кнудсена 11	2115—2413	9	<40	138 ᵃ
7 Приселков, Сапожников, Цепляева, Ан. Н. Несмеянов [22, 338a]	1958	Кнудсена	1693—1764	5	91427	100,6
			1654	4	45996	98,8
			1651—1734	6	17612	101,2
			1686	1	10800	102,8
			1693	2	9258	102,0
			1663	1	3745	105,4
			1665—1710	3	887	109,6
			1668—1702	2	42	124,5
8 Акишин, Никитин, Горохов [3, 1, 63a]	1958	Масс-спектрометрический, испарение из эффузионной камеры 12	2027—2233	12	7000	130,8
			2024—2231	13	3000	130,6
			1765—1990	11	700	130,5
Акишин, Никитин, Горохов [3, 1, 63a]	1958	Масс-спектрометрический, испарение с открытой поверхности 13	1973—2166	24	—	137,5
9 Чупка [1105a]	1957	Масс-спектрометрический, испарение из эффузионной камеры	1600—2330	—	—	129
10 Шиссель, Вильямс [3622б]	1959	То же 14	1600—2330	—	—	129

Note: a) Previously, values of 133 kcal/g-atom [917] and 140.9 kcal/g-atom were given in literature for the heat of sublimation of boron, making reference to unpublished papers of Searcy and Myers. Obviously, the authors of paper [3673] revised twice the value of the heat of sublimation they had obtained.

1) Authors; 2) year; 3) method; 4) temperature interval, °K; 5) number of measurements; 6) Searcy, Myers [3673]; 7) Priselkov, Sapozhnikov, Tselyayeva, An. N. Nesmeyanov [22, 338a]; 8) Akishin, Nikitin, Gorokhov [3, 1, 63a]; 9) Chupka [1105a]; 10) Schissel, Williams [36aab]; 11) Knudsen; 12) mass-spectrometrical, evaporation from effusor chamber; 13) mass-spectrometrical, evaporation from open surface; 14) ditto.

BO (gas). Gaydon [1668], based on thermodynamic data [3669] and the results of a linear extrapolation of the vibrational levels of the $X^2\Sigma^+$ ground state and the first excited state $A^2\Pi$, recommends a value of $D_0(BO) = 175 \pm 9$ kcal/mole (7.6 ± 0.4 ev).

Lagerquist, Nilsson and Wigartz [2531] extrapolated the vibrational levels of the states $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma$ and, under the supposition that BO in the states $X^2\Sigma^+$ and $A^2\Pi$ dissociates into the atoms

$B(^2P) + O(^3P)$, and in the state $B^2\Sigma$ into the atoms $B(^2P) + O(^1D)$, obtained values of 212, 171 and 188 kcal/mole respectively, for the quantity $D_e(BO)$.

In the paper by Mal'tsev et al [288a] a linear extrapolation was carried out with the vibrational levels of the states $X^2\Sigma, A^2\Pi, B^2\Sigma$ and $C^2\Pi$. If for the states $X^2\Sigma, A^2\Pi$ and $B^2\Sigma$ the same corelation is used as in paper [2531] and BO in the $C^2\Pi$ state is assumed to dissociate into the atoms $B(^2P) + O(^1S_g)$, the authors of [288a] obtained the values of 217, 104, 96 and 113 kcal/mole, respectively, for the BO dissociation energies in the various states. Since the BO molecule in the states $X^2\Sigma$ and $A^2\Pi$ has one and the same dissociation limit, the following relations may be written down:

$$T_e(A^2\Pi) = D(X^2\Sigma) - D(A^2\Pi), \qquad \text{(XXIII.1)}$$

$$T_e(B^2\Sigma) - A_1 = D(X^2\Sigma) - D(B^2\Sigma), \qquad \text{(XXIII.2)}$$

$$T_e(C^2\Pi) - A_2 = D(X^2\Sigma) - D(C^2\Pi), \qquad \text{(XXIII.3)}$$

where A_1 and A_2 denote the excitation energies of the states ^1D and ^1S_g of the oxygen atom. In paper [288a] it was found that the right-hand sides of these relations have values which are higher by about 2 ev (46 kcal/mole) than the left-hand sides which are known exactly. Since the right-hand sides contain the value of $D(X^2\Sigma) = 217$ kcal/mole, it was natural to conclude that this value must be too high by 2 ev and that, consequently, $D(X^2\Sigma) = 171$ kcal/mole. This value is in good agreement with the value recommended by Gaydon [1668]. A value of $\Delta H^\circ f_0(BO) = 19$ kcal/mole corresponds to it.

Searcy and Myers [3669] studied the evaporation of a mixture of elementary boron with beryllium oxide. Assuming that in the evaporation boron monoxide BO is formed, the authors of paper [3669] obtained $\Delta H^\circ f_{298.15}(BO) = +4.5 \pm 3$ kcal/mole. Paper [3669] is referred to in the review of Brewer [917] and the article by Soulen and Margrave [3812].

Searcy and Myers [3671, 3672] used the same method to investigate the evaporation of a mixture of boron with magnesium oxide and found that $\Delta H^\circ f_{298,15} = -5,5 \pm 6$ kcal/mole (cited from [3812] and [1193]). Thereafter Searcy and Myers [3673], based on the results of mass-spectrometrical investigations, recalculated their previous results of measurements with magnesium oxide, under the assumption that B_2O_2 molecules constitute the main product of evaporation.

On the basis of measurements of the vapor pressure above a mixture of boron with beryllium oxide, carried out by Searcy and Myers [3669], Soulen and Margrave [3812] determined the limiting value of the heat of formation of boron monoxide as $\Delta H^\circ f_0(BO) \geqslant 5,3$ kcal/mole. Soulen and Margrave [3812] assumed that higher temperatures in experiments with beryllium oxide favored the production of large quantities of boron monoxide, compared with the magnesium oxide experiments.

In the Handbook a value of

$$\Delta H^\circ f_0(BO, \text{gas}) = 5 \pm 10 \text{ kcal/mole},$$

has been accepted for the heat of formation of boron monoxide; the value of

$$D_0(BO) = 183,987 \pm 11 \text{ kcal/mole}.$$

corresponds to it.

A similar value of the BO dissociation energy has been recommended by Berkowitz [756], referring to a private communication by Chupki.

BO_2 (gas). The heat of formation of BO_2 may be calculated on the basis of equilibrium studies. Mal'tsev, Tatevskiy and Matveyev [52a, 293a] investigated the temperature dependence of the intensity of the fluctuating bands of BO_2 (5500 and 5200 A) in the absorption spectrum under such conditions that the boron oxide is heated in an oxygen atmosphere. From these data the value of the heat effect of the reaction

$$B_2O_3(\text{liq.}) + {}^1/_2O_2(\text{gas}) = 2BO_2(\text{gas}), \qquad \text{(XXIII.4)}$$

was obtained as equal to $\Delta H_{1700} = 159.4 \pm 3.5$ kcal/mole (this value was calculated in paper [293a] with certain corrections, not taken into account in the previous paper [52a]). The values of $\Delta H_0 = 169.8$ kcal/mole and $\Delta H^\circ f_0$(BO$_2$, gas) = -67.2 ± 1.7 kcal/mole correspond to it.

In an analogous paper of Kaskan, MacKenzie and Millikan [2329a] a value of $\Delta H_{1800} = 140$ kcal/mole was found. $\Delta H^\circ f_0$(BO$_2$, gas) = -76.7 kcal/mole corresponds to this value.

In the papers of Rusin, Tatevskiy and Ponkrat'yev [351a, 52a, 329a, 351b] the equilibrium

$$HBO_2\,(gas) + OH\,(gas) = BO_2\,(газ) + H_2O\,(gas) \qquad (XXIII.5)$$

was investigated and also a series of other equilibrium reactions involving BO$_2$.

In these papers the dependence of the intensity of absorption of the fluctuation band (5470 A) of BO$_2$ on the concentrations of oxygen, hydrogen, hydroxyl and water vapor was investigated. The experiments were made in a spherical bomb.

As a result of these works the values of the equilibrium constant of reaction (XXIII.5) were obtained as equal to 0.47 ± 0.05 (at 3027°K). The values of the (XXIII.5) reaction heats, equal to $\Delta H_0 = 6.0$ and 3.6 kcal/mole and of the heats of formation, $\Delta H^\circ f_0$ (BO$_2$, gas) = -61.8 and -64.2 kcal/mole correspond to these values (the values of the thermodynamic parameters of the components of the reaction (XXIII.5) accepted in the present Handbook were used in the calculations).

Similar values of $\Delta H^\circ f_0$(BO$_2$, gas), equal to -65.2 and -65.8 kcal/mole, were calculated from the equilibrium constants of other reactions obtained in paper [351a]. The mean value for the three reactions is equal to -64.2 kcal/mole.

The values of the heat of formation of BO$_2$, calculated on the basis of data from papers [293a, 351a] are in good agreement with one another. In the Handbook we accept the value

$$\Delta H^\circ f_0(BO_2, gas) = -65 \pm 5 \text{ kcal/mole},$$

to which

$$D_0(BO_2) = 312{,}974 \pm 7 \text{ kcal/mole}.$$

corresponds.

B_2O_2 (gas). The gaseous products in the system B – B_2O_3 at temperatures of 1300-1500°K were investigated by Inghram, Porter and Chupka [2171]. In these investigations a mixture of boron and boron oxide (ration $B:B_2O_3 > 1$) was heated in an effusion cell and the vapor emerging was analyzed by means of a mass-spectrometer. It could be observed that under these conditions the main product of evaporation was the B_2O_2 molecule. From the temperature dependence of the $B_2O_2^+$ ion current intensity the authors of paper [2171] determined the value of the reaction heat of

$$\frac{2}{3}B(\text{cryst.}) + \frac{2}{3}B_2O_3(\text{liq.}) = B_2O_2(\text{gas}), \qquad (XXIII.6)$$

and obtained $\Delta H_{1400} = 94 \pm 8$ kcal/mole, to which $\Delta H_0 = 100{,}5 \pm 8$ and a heat of formation of $\Delta H^\circ f_0(B_2O_2) = -102.3$ kcal/mole correspond, if the composition of the condensed phase does not vary on heating.*

Inghram et al used the evaporation of a given quantity of silver from an effusor vessel to determine the absolute values of the partial vapor pressures from the ion currents of Ag^+, $B_2O_2^+$ and $B_2O_3^+$ and calculated the values of the equilibrium constant of the reaction

$$\frac{2}{3}B(\text{cryst.}) + \frac{2}{3}B_2O_3(\text{gas}) = B_2O_2(\text{gas}). \qquad (XXIII.7)$$

The authors of [2171] assumed that in this way the indeterminacy connected with the possible formation of a new condensed phase could be eliminated since in the initial composition of the mixture boron was always present in abundance. However, as mentioned by Searcy and Myers [3673], it is then possible that the results are slightly distorted (by up to 2 kcal/mole) because of the reduction in activity of elementary boron as a consequence of its complete dissolution in boron oxide. Using the estimated values of the reduced thermodynamic potential of B_2O_2, the authors of paper [2171] calculated the thermal effect of the reaction (XXIII.7) and obtained $\Delta H_0 = 35{,}65 \pm 3{,}5$ kcal/mole. A recalculation of the constants found by Inghram et al with the help of the values of the thermodynamic functions of the reaction components accepted in the present Handbook yielded the values of $\Delta H_0 = 27{,}9$ and $\Delta H^\circ f_0\ (B_2O_2) = -109{,}7$ kcal/mole.*

Searcy and Myers [3673] investigated the equilibrium of

$$2B\,(\text{cryst.}) + 2MgO\,(\text{cryst.}) = B_2O_2\,(\text{ra3}) + 2Mg\,(\text{gas}). \quad (XXIII.8)$$

in the temperature interval of 1337-1436°K. The mixture of boron and magnesium oxide was heated in an effusor vessel of tungsten. The partial pressures of B_2O_2 and of magnesium vapor were calculated from the loss in weight. The authors of [3673] used these data to calculate $\Delta H^\circ f_{298.15}\ (B_2O_2,\ \text{gas}) = -100 \pm 5$ kcal/mole. The considerable scatter of the values obtained for the heat of formation of B_2O_2 may, according to Searcy and Myers, be explained by the insufficient surface of contact between boron and magnesium oxide, i.e., by the presence of nonequilibrium conditions (under the conditions of experiment both substances remained in solid state). In one of the experiments the initial mixture of boron and magnesium oxide was pressed and the area of the hole in the effusor chamber was reduced, which resulted in a considerable growth of the partial pressures of B_2O_2 and Mg measured. In this experiment a value of $\Delta H^\circ f_{298.15}\ (B_2O_2,\ \text{gas}) = -107$ kcal/mole (or $\Delta H^\circ f_0 = -107{,}5$ kcal/mole) was obtained. Searcy and Myers assumed that this value was more reliable than the mean value taken from all experiments.

A recalculation of the data obtained by Searcy and Myers [3673], using the values of the thermodynamic parameters of the reaction components of (XXIII.8) accepted in the Handbook yields a mean value of the reaction's thermal effect, $\Delta H_0 = 254 \pm 5$ kcal/mole, or $\Delta H^\circ f_0$ (B_2O_2, gas) = -102 kcal/mole. A calculation of the experiment, carried out with the reduced effusor opening led to the value of $\Delta H^\circ f_0$(B_2O_2, gas) = -109 kcal/mole which must be viewed as more accurate.

The molecular composition and the vapor pressure above the B – B_2O_3 system were investigated by Scheer [3612]. In this paper the quantity of the substance evaporated from the effuser vessel and the torsional stress arising owing to the efflux of vapor from the two openings were determined. It was shown that in the range of 1340-1410°K the molecular weight of the emanating vapor amounts to 55 ± 3 (molecular weight of B_2O_2 equal to 53.6). Based on 14 measurements of the torsional stress arising as a result of efflux of vapor produced above the B – B_2O_3 mixture. Scheer found an equation representing the temperature dependence of the equilibrium constant of the reaction (XXIII.6) to which a value of $\Delta H_{1375} = 72{,}4$ kcal/mole or $\Delta H_0 = 78{,}9$ kcal/mole and $\Delta H^\circ f_0$ (B_2O_2, gas) = -124 kcal/mole corresponds. These values are not in agreement with the results of the papers considered above. Scheer assumed that this deviation is due to the fact that in the system he had investigated it is difficult to maintain the equilibrium so that the values, obtained in the papers [3612, 2171], may contain serious errors. Moreover, Scheer [3612] gives a series of convincing arguments which speak in favor of the formation of a condensed phase of $(BO)_x$ in the effusion cell. If this assumption is true, the values of the heat of formation of B_2O_2 given above, which are based on the results of investigations in [3612] and [2172] must be too low.

A recalculation of the data obtained by Scheer [3612], using the values of the thermodynamic functions of boron and its compounds accepted in the Handbook, yielded a value of $\Delta H_0 = 92 \pm 0{,}5$ kcal/mole for the thermal effect of the reaction (XXIII.6); a value of $\Delta H^\circ f_0$ (B_2O_2, gas) = -111 kcal/mole corresponds to it. The heat of formation of B_2O_2 may also be calculated from the rates of loss in weight of the effusion vessel containing the mixture of B and B_2O_3, measured by Scheer [3612] (the author of paper [3612] used the results of these measurements to determine the molecular weight of the emanating vapor). From these data a value of $\Delta H^\circ f_0 (B_2O_2) = -111$ kcal/mole was found which is in perfect agreement with the results of calculations, based on the measurements of the torsional moment, and with the results obtained in the recalculation of the data from [2171, 3673]. The results of calculations of the experiments of [3612, 2171, 3673] prove convincingly the superiority of the method of experimental data processing with the help of the thermodynamic potentials of the reaction components (according to the 3rd law of thermodynamics), compared to the calculations based on the determination of the temperature dependence of the equilibrium constants (according to the 2nd law of thermodynamics).

The reactions of interaction of liquid boron anhydride with graphite

$$B_2O_3(\text{liq.}) + 3C(\text{graphite}) = 3CO(\text{ra3}) + 2B(\text{cryst.}), \qquad (XXIII.9)$$

$$B_2O_3(\text{liq.}) + C(\text{graphite}) = CO(\text{ra3}) + B_2O_2(\text{gas}) \qquad (XXIII.10)$$

were investigated by Rentzepis, White and Walsh [3422a] in the interval of 1376-1656°K. At a temperature below 1550°K the reaction mainly takes place according to Eq. (XXIII.9). Above 1600°K in accordance with the equation of reaction (XXIII.10) a noticeable quantity of B_2O_2 is formed in the vapor. The authors of paper [3422a] evaporated entirely the known quantity of boron anhydride from the graphite effusion chamber, containing graphite powder and determined the quantity of CO that was formed, in order to determine the ratio of the partial pressures of CO and B_2O_2 at temperatures of 1603-1656°K. This ratio is in fact an equilibrium constant of the reaction

$$C(\text{graphite}) + B_2O_2(\text{gas}) = \frac{1}{3}B_2O_3(\text{liq.}) + \frac{4}{3}B(\text{cryst.}) + CO(\text{gas}). \quad (XXIII.11)$$

Rentzepis et al [3422a], using the values of the thermodynamic functions of the components of reactions (XXIII.9) and (XXIII.10), available in literature, obtained $\Delta H^\circ f_0(B_2O_2, \text{gas}) = -110.7 \pm 1.5$ kcal/ /mole.

A recalculation of the values obtained in paper [3422a] with the help of the values of the thermodynamic functions of the components of reaction (XXIII.11), accepted in the present Handbook, yielded a value of $\Delta H^\circ f_0(B_2O_2, \text{gas}) = -108.7$ kcal/mole. The authors of paper [3422a] assumed that the ratio of partial pressures of CO and B_2O_2 they had obtained might be too low. In this case the true value of $\Delta H^\circ f_0(B_2O_2, \text{gas})$ must be somewhat smaller than the calculated one.

The results of measurements of the heat of formation of B_2O_2 are in good agreement with one another. In the Handbook we accept a mean value

$$\Delta H^\circ f_0(B_2O_2, \text{газ}) = -109 \pm 3 \text{ kcal/mole},$$

to which

$$D_0(B_2O_2) = 486{,}974 \pm 8 \text{ kcal/mole},$$

corresponds.

B_2O_3 (cryst.). The results of measuring the heat of formation of vitreous boron oxide are given in Table 217.* A determination of the heat of formation of boron oxide by direct combustion of elementary boron is rendered difficult by its incomplete combustion, the difficulties of obtaining sufficiently pure initial samples and the insufficient accuracy of the analysis of such samples and the products of their combustion. In the combustion of boron in the presence of substances containing hydrogen (paraffin oil, benzoic acid and the like), the final state of the combustion products becomes indefinite to a high degree because of a partial hydration of the boron oxide being formed.

In the boron samples used by Roth et al [3523, 3521, 3516] and Todd and Miller [3992] hydrogen must have been contained which caused an increase of the values obtained (the spectroscopic analysis of boron carried out in paper [3992] could not yield any information on the presence of hydrogen). The accuracy of these studies was also reduced because the samples were burnt together with paraffin oil [3516, 3521, 3523] or benzoic acid [3992] so that the final results had to be corrected in a very indefinite manner for hydration. Eggersgluess et al [1469] burned boron together with soot. The value obtained in this paper was much lower than the other values to be found in literature, and the cause of this deviation is not clear.*

A careful determination of the heat of combustion of boron was carried out by Gal'chenko, Kornilov and Skuratov [139a, 36, 140, 248]. The initial boron was heated in a calorimetric bomb by means of a special microfurnace which made it possible to obtain a high percentage of boron combustion (35-40%) without auxiliary burning substances. The quantity of boron oxide formed in the combustion was determined from the increase in weight of the quartz cup with the boron.** Using this method the authors obtained a value of -299.5 ± 1.8 kcal/mole. A combustion of boron together with benzoic acid, described in the same paper, yielded a less accurate result, namely -298.3 ± 6.6 kcal/mole.

Eckstein and Artsdalen [1450] burned boron without adding a substance to facilitate the combustion. The same authors [1450] consider their own value of -304.6 ± 4.2 kcal/mole as less accurate than those calculated on the basis of the heat of hydrolysis and the thermal disintegration of diborane [3338].

The paper by Stegman and Nathan [3842] was not published, it is referred to in papers [1276, 2655].

Based on the most accurate measurements of the heat of combustion at elementary boron [139a, 36, 140, 248] (combustion without benzoic acid) and [1450] the value of $\Delta H^\circ f_{298.15}$ (B_2O_3, vitr.) = -302 ± 2 kcal/ /mole was calculated.

Table 217 gives the values of the heat of hydrolysis of boron trichloride, according to the equation

$$BCl_3(\text{liq.}) + 2403H_2O(\text{liq.}) = (H_3BO_3 + 3HCl)\cdot 2400H_2O\ (\text{soln.}). \quad (XXIII.12)$$

The values of the heat of formation of vitreous boron oxide, given in Table 217, last column, were calculated with the help of the values of the heat of dissolution of B_2O_3 [3338, 572], the heat of dilution of boric acid solutions [3769], the heat of mixing of solutions of H_3BO_3 and HCl [1888] the heat of formation of HCl solutions [3508] and the heat of formation of BCl_3 (liqu.) equal to -102.9 ± 0.6 kcal/mole.*

The measurements of Troost and Hautefeuille [2040] contain a systematic error [2267]. The measurements of the heat of hydrolysis of gaseous BCl_3 by Kapustinskiy and Samoylov [211] are, obviously, also incorrect. The most accurate measurements of the heat of hydrolysis of BCl_3 (liqu.) were carried out by Skinner and Smith [3761] and Gunn and Green [1888]. Based on these papers a value of $\Delta H^\circ f_{298.15}$ (B_2O_3, vitr.) = -302.1 ± 1 kcal/mole can be calculated. A similar value was calculated on the basis of measurements of Laubengayer and Sears [2570], the accuracy of this quantity is, however, much lower since Laubengayer and Sears measured at 0°C and the recalculation for 25°C can only be performed in an approximate way [2267].

TABLE 217

Results of Determining the Heats of Formation of Vitreous Boron Oxide From Amorphous Boron and Oxygen (in kcal/mole)

1 Авторы	Год 8	$\Delta Hf_{299,15}$ (B_2O_3)
2 Рот, Бёргер, Бертрам [3516, 3521, 3523] . . .	1946	—340±3
3 Тодд, Миллер [3992]	1946	—335,8±0,8
4 Стейджмен, Натан [3842]	1948	—299,7
5 Эггерсглюс, Монро, Паркер [1469]	1949	—281,1±3,1
6 Гальченко, Корнилов, Скуратов [139а, 36, 140, 248]	1958 1958	—299,5±1,8 —298,3±6,6
7 Экштейн, Артсдален [1450]	1958	—304,6±4,2

Б. Измерение теплоты гидролиза BCl_3 (жидк.)[a]

1 Авторы	8 Год	9 $\Delta H_{298,15}$ гидролиза BCl_3 (жидк.)	$\Delta Hf_{298,15}$ (B_2O_3)
2 Труст, Отфей [4020]	1876	—79,93	—324,2
3 Бертло [779]	1878	—68,13	—300,6
4 Лаубенгейер, Серс [2570]	1945	—69,23	—302,8
5 Капустинский, Самойлов [211] . . .	1952	—75,03	—314,4
6 Скиннер, Смит [3761]	1953	—69,1±0,15	—302,5
7 Гани, Грин [1888]	1960	—68,68±0,06	—301,7

В. Измерение теплоты гидролиза B_2H_6 (газ)[б]

1 Авторы	5 Год	6 $\Delta H_{298,15}$ гидролиза B_2H_6 (газ)	$\Delta Hf_{298,15}$ (B_2O_3)
2 Рот, Бергер [3516, 3521, 3523] . .	1946	—110±2	—300,3
3 Прозен, Джонсон, Пергиль [3338]	1959	—111,46±0,54	—301,78
4 Гани, Грин [1888]	1960	—112,22±0,1	—302,54

Г. Измерение теплоты сгорания BN (крист.) в кислороде

1 Авторы	2 Год	3 $\Delta H_{298,15}$ сгорания BN (крист.)	$\Delta Hf_{298,15}$ (B_2O_3)
4 Дворкин, Сасмор, Артсдален [1432]	1954	—90,2±0,5	—302,6

A. Measurement of the heat of combustion of boron in oxygen.
1) Authors;
2) Roth, Borger, Bertram;
3) Todd, Miller;
4) Stegman, Nathan;
5) Eggersgluess, Monroe, Parker;
6) Gal'chenko, Kornilov, Skuratov;
7) Eckstein, Artsdalen;
8) year;

B. Measurement of the heat of hydrolysis of BCl_3 (liqu.)[a]

1) Authors;
2) Troost, Hautefeuille;
3) Berthelot;
4) Laubengayer, Sears [2570);
5) Kapustinskiy, Samoylov;
6) Skinner, Smith;
7) Gunn, Green;
8) year;
9) hydrolysis of BCl_3 (liqu.).

C. Measurement of the heat of hydrolysis of B_2H_6 (gas)[b]
1) Authors;
2) Roth, Berger;
3) Prosen, Johnson, Pergiel;
4) Gunn, Green;
5) year;
6) hydrolysis of B_2H_6 (gas).

D. Measurement of the heat of combustion of BN (cryst.) in oxygen.
1) Authors;
2) year;
3) combustion of BN (cryst.);
4) Dworkin, Sasmor, Artsdalen.

[a] Johnson, Miller and Prosen [2267] recalculated the results of measurements of [4020, 779, 2570, 211] for 298.15°K and the concentration of the products of hydrolysis of $(H_3BO_3 + 3HCl)\cdot 40\,000H_2O$. The ΔH of hydrolysis, given in the table, were recalculated for the concentration of the products of hydrolysis of $(H_3BO_3 + 3HCl)\cdot 2400H_2O$, since in paper [1888] the heat of mixing of HCl and H_3BO_3 solutions was measured, corresponding to this final concentration.

[b] Concentration of the products of hydrolysis of $H_3BO_3\cdot 1000H_2O$.

The value of the heat of formation of diborane from amorphous boron and hydrogen, $\Delta Hf_{298,15} = 6{,}73 \pm 0{,}52$ kcal/mole, obtained by Prosen, Johnson and Pergiel [3335] and the values of the heat of hydrolysis of diborane given in Table 217 permit a calculation of the value of the heat of formation of boron oxide. The measurements of Roth and Borger [3516, 3521, 3523] were insufficiently accurate. More accurate values were obtained by Prosen, Johnson and Pergiel [3338] and Gunn and Green [1888]. Based on these measurements the value of $\Delta H°f_{298,15}(B_2O_3,$ vitr.) = -302.2 ± 0.4 kcal/mole can be calculated.

Gal'chenko, Kornilov, Timofeyev and Skuratov [139b, 36, 140, 248] measured the heat of indirect reaction of boron with nitrogen (see page 1548) and, using the value of the heat of combustion of boron nitride, obtained by Dworkin, Sasmor and Artsdalen [1432],

$$\mathrm{BN}\,(\text{cryst.}) + \tfrac{3}{4}\mathrm{O_2} = \tfrac{1}{2}\mathrm{B_2O_3}\,(\text{vitr.}) + \tfrac{1}{2}\mathrm{N_2} - 90{,}2 \pm 0{,}5\ \text{kcal/mole, XXIII.13)}$$

they calculated a value of $\Delta H^\circ f_{298,15}$ (B_2O_3, vitr.) = -302.6 ± 1.4 kcal/mole. Compared with the method of burning boron in oxygen, this method of determining the heat of formation of boron oxide has the advantage that in this case side reactions are avoided (we only know a single boron nitride BN) and such impurities as oxygen or hydrogen contained in the initial boron sample do not interfere with the determination.

Thus, the values of the heat of formation of boron oxide, obtained by burning elementary boron, by hydrolysis of boron trichloride and diborane and combustion of boron nitride, are in good agreement with one another. It is, obviously, not justified to consider the values obtained by one of the various methods as unrestrictedly superior to the others. The values, obtained from measurements of the heat of hydrolysis of diborane and boron trichloride are, however, more reliable, since in these cases there is no doubt as to the purity of the initial samples and the final state of the reaction products is more definite.

In the following calculations the value of $\Delta H f_{298,15} = -302{,}2 \pm 0{,}5$ kcal/mole is used for the heat of formation of vitreous boron oxide from boron in the amorphous state and oxygen. Since the values of the heats of transition of amorphous boron to crystalline boron and vitreous boron oxide to crystalline boron oxide at 298.15°K amount to -0.4 kcal/g-atom [3814], respectively, a value of

$$\Delta H^\circ f_{298,15}\,(\mathrm{B_2O_3},\ \text{крист.}) = -305{,}76 \pm 0{,}1\ \text{kcal/mole, ь,}$$

corresponds to the chosen value of $\Delta H f_{298,15}$(B_2O_3, vitr.) of amorphous boron and oxygen; this value is accepted in the Handbook.

B_2O_3 (gas). Table 218 gives the values of the sublimation heat of boron oxide calculated on the basis of measurements of the vapor pressure. The last column of the table contains the ΔHs_0 values, calculated from Eq. (IV.15) with the use of the thermodynamic functions of boron oxide in gaseous and liquid states, accepted in the present Handbook and the values of the boron oxide vapor pressure found by experiments. The two columns before the last give the values of ΔHs_T, this is the heat of sublimation at the mean temperature of measurement, calculated from Eq. (IV.14) based on the function $\lg p - 1/T$, and the ΔHs_0 values, obtained by recalculating ΔHs_T for 0°K, using the values of the enthalpy of liquid and gaseous boron oxide, accepted in the Handbook.

Measurements of the boron oxide vapor pressure, made by Cole and Taylor [1151] with the help of the tube method, yielded values that were too high because of insufficient drying of the gas and the apparatus. Similar measurements were made by Soulen, Sthapitanonda and Margrave [3813] but the furnace used in these experiments was lines with platinum which made it possible to avoid humidity and obtain more accurate values.

The results of effusion measurements **[3817, 315a, 3673, 4238]** yielded values which are in good agreement. In Scheer's paper [3611], besides the loss in weight of the effusion vessel, also the torsional moment was measured that arises when the boron oxide vapor leaves the two openings. From these data Scheer determined the molecular weight of the evaporation products of boron oxide as equal to 62 ± 9 (molecular weight of boron oxide equal to 69.64). The boron oxide vapor pressure found by Scheer was considerably lower than those found in other papers. Scheer assumes that this can be explained by the large surface (2.3 mm^2) of the effusor opening or an error in the temperature measurement.

White, Mann, Walsh and Sommer [4238] investigated the temperature dependence of the intensity of the infrared emission spectrum of boron oxide vapor (with the 2040 cm^{-1} band). The value of ΔHs_0 calculated from these data with the help of Eq. (IV.14) is in good agreement with the results of other measurements.

In a paper by Meschi, Chupka and Berkowitz [2853b] the values of the equilibrium constants of the reactions (XXIII.15) and (XXIII.16) were determined. The difference of the thermal effects of these reactions (see page 1538) permitted the calculation of the value of ΔHs_0 (B_2O_3, cryst.) = 99.4 kcal/mole.

Akishin, Nikitin, Khodeyev and Sidorov [5a, 10a] determined the value of the heat of sublimation of boron oxide by means of a mass-spectrometrical method. The boron oxide was evaporated from an effusion chamber with an opening of 0.018 mm^2. Besides the value of the heat of sublimation, calculated from the temperature dependence of the $B_2O_3^+$ ion current, the authors determined also the values of the partial pressures of boron oxide, using a calibration based on the evaporation of silver. The value of ΔHs_0, given in the last column of Table 218 were calculated from these data. In attempts made with common evaporation of silver and boron oxide from a single chamber in papers [5a, 10a] a sharp increase (by about 15%) of the Ag$^+$ ion current intensity was observed near the solidification point of silver. The authors of papers [5a, 10a] therefore used only the data obtained with separate evaporation of boron oxide and silver. In the paper of White, Walsh, Goldstein and Dever [4239b] a value of the heat of evaporation of boron oxide was obtained by means of a mass-spectrometrical method which is in good agreement with the value obtained by Akishin et al in the papers [5a, 10a].

The data given in Table 218 show a considerable deviation of the values of the heat of sublimation of boron oxide, calculated from Eq. (IV.14) with the help of the function $\lg p - 1/T$ obtained, and those calculated from Eq. (IV.15) with the help of the values of the thermodynamic functions of B_2O_3 in liquid and gaseous states and the absolute values of the boron oxide vapor pressure. It must be mentioned that analogous calculations, based on the thermodynamic functions of boron oxide in gaseous state, calculated under the assumption of a bipyramidal structure of the B_2O_3 (gas) molecule (see [2142, 420]) yielded coincident results. However, since the angular structure of the B_2O_3 (gas) molecule is at present an indisputable fact (cf. page 1467), this coincidence must be viewed as accidental. Moreover, as this was shown in a series of examples, the determination of the slope of the straight line $\lg p - 1/T$ is accompanied by considerable errors. The construction of this function with the help of data from many papers enabled Evans, Prosen and Wagman [1515] to find the value of $\Delta Hs_{1500} = 84 \pm 5$ kcal/mole, or $\Delta Hs_0 = 95{,}9 \pm 5$ kcal/mole which agree much better with the value calculated from Eq. (IV.15). Bere and Renich [752] referring to an unpublished paper of the US NBS, recommend an equation for the calculation of the B_2O_3 pressures at various temperatures, to which a value of $\Delta Hs_0 = = 98{,}4$ kcal/mole corresponds, and they give a value of $\Delta Hs_{1500} = 84 \pm 6$ kcal/mole which agrees with that calculated by Evans et al [1515]. The values, calculated from the relation $\lg p - 1/T$ and with the use of all data are more trustworthy than those calculated on the basis of measurements of the individual authors.

Akishin, Nikitin, Khodeyev and Sidorov [5a, 10a] established the fact that the method of degasification and drying of boron oxide usually applied (annealing in vacuo at about 900°C for 1-2 hrs.) is insufficient. A more complete degasification and drying requires heating of the initial samples up to 1200-1300°C. These authors showed also that the results of measurements in [3817, 315a, 428a, 13] at low temperatures are therefore inaccurate and yield a value of $\lg p - 1/T$ calculated from the function ΔHs_0 (Eq. IV.14) which is too low.

For papers [3817, 315a, 428a, 13] Table 218 gives the results of calculations, carried out by Akishin et al [5a, 10a] in which several points, corresponding to the lowest temperatures, have been discarded. The values of ΔH_{s_0} obtained in this way are in much better agreement with those calculated from Eq. (IV.15).

TABLE 218

Results of calculating the heat of sublimation of boron oxide (in kcal/mole)

1 Авторы	2 Год	3 Метод	4 Интервал температуры, °K	5 Число измерений	6 По уравнению (IV.14)		7 По уравнению (IV.15)
					ΔH_{s_T}	ΔH_{s_0}	ΔH_{s_0}
8 Кол, Тейлор [1151]	1935	протока 18	1473—1673	5	65,6	77,91	86,3±2,5
9 Спейсер и др. [3817]	1950	Кнудсена 19	1331—1642	22	77,7	89,5	98,0±0,7
	1950	»	1449—1642	15	80,0	92,1	98,4
10 Ан. Н. Несмеянов, Фирсова [315а,428а,13]	1955	»	1290—1515	12	76,9	88,1	97,9±0,6
	1955	»	1402—1512	7	82,4	94,0	98,5
11 Саулен и др. [3813]	1955	протока	1567—1808	5	77,3[a]	90,3	96,8±2,0
12 Серси, Майерс [3673, 3013а]	1956	Кнудсена	1501—1566	6	76,9	89,0	97,4±0,3
13 Шер [3611]	1957	» 20 (торзионный вариант)	1414—1621	19	83,6	95,6	100,6±0,2
	1957	Кнудсена (дифференци- 21 альный вариант)	1406—1626	13	87,5	99,5	100,8±0,3
14 Уайт, Манн и др. [4238]	1960	Кнудсена	1409—1610	6	—	—	99,1±0,3
	1960	по измерению интенсивности 22 полосы 2040 $см^{-1}$	1400—1800	47	76,0±3,5	89,5	—
15 Меши и др. [2853б]	1960	масс-спектрометрический	1061—1451	10	—	—	99,4
16 Акишин и др. [5а, 10а]	1961	23 »	1315—1529	221	84,3±1	95,7	100±1
17 Уайт, Уолш и др. [4239б]	1961	»	1220—1641	16	82,9±1,5	94,3	98,5

[a] According to log p as a function of 1/T, calculated for the common results of measurements of [3813] and [3817].

1) Authors;
2) year;
3) method;
4) temperature interval;
5) number of measurements;
6) according to Eq. (IV.14);
7) according to Eq. (IV.15);
8) Cole, Taylor,
9) Speiser et al [3817];
10) An. N. Nesmeyanov, Firsova;
11) Soulen et al;
12) Searcy, Myers;
13) Scheer;
14) White, Mann et al;
15) Meschi et al;
16) Akishin et al [5a, 10a];

17) White, Walsh et al;
18) tube;
19) Knudsen;

20) (torsional variant);
21) (differential variant);
22) according to intensity measurements of the 2040-cm^{-1} band;
23) mass-spectrometrical.

Preferring the value calculated according to Eq. (IV.15), the following value is accepted in the Handbook:

$$\Delta Hs_0(B_2O_3, \text{cryst.}) = 98 \pm 5 \text{ kcal/mole}.$$

The divergence between the values of ΔHs_0, calculated from Eqs. (IV.14) and (IV.15) obviously indicates serious errors in the values accepted for the thermodynamic functions of boron oxide in gaseour or liquid states.*

The following values correspond to the accepted value of the heat of sublimation

$$\Delta H^{\circ}f_0(B_2O_3, \text{gas}) = -206{,}282 \pm 5 \text{ kcal/mole},$$
$$D_0(B_2O_3) = 643{,}243 \pm 10 \text{ kcal/mole}.$$

BH (gas). The observation of the predissociation at the levels v' = 0, 1 and 2 of the $A^1\Pi$ state of the BH molecule enabled Almy and Horsfall [523] to estimate the upper limit of the dissociation energy of the BH molecule in the ground state $X^1\Sigma$ as equal to 83 ± 1 kcal/ /mole. But in the paper of Herzberg and Mundi [2037] it was shown that the potential curve of the $A^1\Pi$ state of the BH molecule, just as also the potential curve of AlH, has a maximum and, in connection with this, the actual value of the BH dissociation energy must be considerably lower. Therefore Gaydon [1668] recommends the value

$$D_0(\text{BH}) = 69 \pm 9 \text{ kcal/mole},$$

which has been accepted in the Handbook. A value of

$$\Delta H^{\circ}f_0(\text{BH}, \text{gas}) = 112{,}632 \pm 10 \text{ kcal/mole}.$$

corresponds to it.

HBO (gas). The value of the dissociation energy

$$D_0(\mathrm{HBO}) = 260 \pm 15 \text{ kcal/mole},$$

accepted in the Handbook was estimated on the basis of a comparison of the dissociation energies of BO, BH, CN, CH and HCN (the HCN and HBO molecules are isoelectronic).

$$\Delta H^\circ f_0(\mathrm{HBO, gas}) = -19{,}381 \pm 15 \text{ kcal/mole}.$$

corresponds to the accepted value of $D_0(\mathrm{HBO})$

HBO_2 (gas). The metaboric acid exists in three crystalline modifications: orthorhombic (α), monoclinic (β) and cubic (γ) [3956a, 2470a].

Based on measurements of the water vapor pressure above orthoboric acid, [1643, 3956a, etc] and the heats of dissolution of the various modifications of HBO_2 in water [3833] and in solutions of caustic soda [3523, 3516] (in the calculations some unpublished data of Prosen, Randall and Margrave were used), Evans, Prosen and Wagman [1515] calculated the values of $\Delta H^\circ f_{298.15}$ (HBO_2, orthorhomb.) = -189.13 ± 0.8 kcal/mole and $\Delta H^\circ f_{298.15}$ (HBO_2, monoclin.) = -190.73 ± 0.8 kcal/mole.*

Sokolova, Skuratov, Shemanayeva and Yuldasheva [387] measured the heats of dissolution in water of the orthorhombic (+ 0.47 ± 0.01 kcal//mole) and the monoclinic (+ 1.76 ± 0.01 kcal/mole) modifications of metaboric acid (final state $H_3BO_3 \cdot 500\ H_2O$). From these data the values of $\Delta H^\circ f_{298.15}$ (HBO_2, orthorhomb.) = -189.26 ± 0.3 kcal/mole and $\Delta H^\circ f_{298.15}$ (HBO_2, (HBO_2, monoclin.) = -190.57 ± 0.3 kcal/mole were calculated which, within the limits of error, agree with the values calculated by Evans et al [1515]. The results of paper [387] are preferred.

The heat of formation of the cubic modification of metaboric acid can be calculated on the basis of measurements of Kilday and Prosen [2397a] of the difference (-1.429 ± 0.011 kcal/mole) of the heats of dissolution of this modification and the orthoboric acid in 2N NaOH solution. A value of $\Delta H^\circ f_{298.15}$ (HBO_2, cubic) = -192.69 ± 0.3 kcal/mole were obtained from these data.

In order to calculate the heats of formation of metaboric acid in gaseous state the results of measurements of its vapor pressure and the results of determining the equilibrium constants of reactions involving HBO_2 can be used.

In the paper of Stackelberg, Quatram and Dressel [3833] the volatility of boric acids was investigated in the presence of water vapor. At the highest vapor temperatures (160-180°C), apart from the orthoboric acid, a considerable quantity of metaboric acid was found to exist. From the dependence of the volatility of boric acid on the partial pressure of water vapor, the authors of paper [3833] found that the thermal effect of the reaction

$$H_3BO_3(\text{gas}) = HBO_2(\text{gas}) + H_2O(\text{gas}) \qquad (\text{XXIII.14})$$

at 170°C amounts to 19 kcal/mole or $\Delta H_{298.15} = 19{,}1$ kcal/mole. If we use the value of the heat of sublimation of H_3BO_3 determined in the very same paper (see below), we obtain from this a value of $\Delta H^\circ f_{298.15}$ (HBO_2, gas) = -163 kcal/mole.

A more accurate value of the heat of evaporation of H_3BO_3 as found in paper [2853a] yields a still higher value of $\Delta H^\circ f_{298.15}$ (HBO_2, gas) = -170 kcal/mole. The values of the heat of formation of HBO_2, calculated according to data of [3833], are much too high compared to the results of later and more accurate measurements which might be explained by a mechanical withdrawal of boric acid under the experimental conditions [3833] (cf. [1862]).

Abrikosov, Lyang-Tsun-U and Shashkov [57a] studied the volatility of boron oxide in helium and hydrogen in the presence of water vapor, in a flow system, at a temperature in the range 1133-1637°K, and determined the temperature dependence of the HBO_2 (gas) partial pressure in the equilibrium of

$$^1/_2B_2O_3(\text{liq.}) + ^1/_2H_2O(\text{gas}) = HBO_2(\text{gas}). \qquad (XXIII.15)$$

From the equation, expressing this dependence, the value of the thermal effect of the reaction (XXIII.15) was found to be equal to $\Delta H_{1386} = 43.5$ kcal/mole, and the value of $\Delta H^\circ f_{298.15}$ (HBO_2, gas) = -132.4 kcal/mole. The value of $\Delta H^\circ f_{298.15} = -140.9 \pm 3$ kcal/mole was calculated from the absolute value of the HBO_2 vapor pressure, with the help of Eq. (IV.15).

Randall and Margrave [3369a] investigated the volatility of boron oxide in the presence of water vapor.* The studies were made with the help of the tube method in the interval of 1000-1273°K. An analysis of the dependence of the rate of withdrawal of boron oxide on the water vapor pressure enabled the authors of [3369a] to find out that HBO_2 (gas) was the main product of evaporation at 1273°K and water vapor pressures below $4 \cdot 10^{-2}$ atm. Values of the constant of equilibrium, $K_{p_{1273}} = 3{,}347 \cdot 10^{-3}$, and of the thermal effect, $\Delta H_0 = 46$ kcal/mole, of the reaction (XXIII.15), correspond to the partial pressures of H_2O and HBO_2 obtained by Randall and Margrave (in the calculation the formation of small quantities of $(HBO_2)_3$ and H_3BO_3 was taken into account); a value of $\Delta H^\circ f_0$ (HBO_2, gas) = -134.6 kcal/mole corresponds in its turn to the former values. Using literature data on the thermodynamic functions of the components of reaction (XXIII.15), Randall and Margrave calculated a value of -134.9 ± 1 kcal/mole.

White, Mann, Walsh and Sommer [4239] measured the intensity of the infrared emission spectrum of the gaseous products of the system B_2O_3 (liqu.) – H_2O (gas) in the temperature interval of 1250-1450°K. The thermal effect of the reaction (XXIII.15) was determined from the temperature dependence of the intensity of the band at 2030 cm^{-1} and a value of $\Delta H_{1350} = 39{,}0 \pm 2{,}5$ kcal/mole was found, to which $\Delta H^\circ f_{298.15}$ (HBO_2, gas) = -135.3 ± 3 kcal/mole corresponds.

A mass-spectrometrical investigation of the system B_2O_3 (liqu.) – – H_2O (gas) at 1061-1451°K, carried through by Meschi, Chupka and Berkowitz [2853b], showed that besides B_2O_3 (gas) HBO_2 (gas)* was the main product of this system, containing boron. In this work the boron oxide was heated in a platinum effusion chamber into which water vapor was led simultaneously. Based on measurements of the ion currents, Meschi et al determined the values of the constants of equilibrium and the thermal effects of the reaction (XXIII.15) and the reaction

$$^1/_2H_2O\,(\text{gas}) + {}^1/_2B_2O_3\,(\text{gas}) = HBO_2\,(\text{gas}). \qquad (\text{XXIII.16})$$

Using the values of the equilibrium constants calculated by the authors of paper [2853b] and the values of the thermodynamic properties of the reaction components, accepted in the present Handbook, the following values of the thermal effects of these reactions were calculated: $\Delta H_0 = 47{,}1$ kcal/mole (XXIII.15) and $\Delta H_0 = -2{,}7$ kcal/mole (XXIII.16); the values of $\Delta H^\circ f_{298.15}$ (HBO_2, gas) = -134.5 kcal/mole and -135.2 kcal/mole correspond to them.

For the thermal effect of this reaction a value of $\Delta H_{1258} = 42{,}3 \pm 2$ kcal/mole was found from the temperature dependence of the equilibrium constant of the reaction (XXIII.15); the values of $\Delta H_0 = 48{,}1$ kcal/mole and $\Delta H^\circ f_{298.15}$ (HBO_2, gas) = -133.4 ± 2 kcal/mole correspond to it. As in most other cases, the values of the heat of formation of HBO_2, calculated with the help of the thermodynamic properties, are more accurate.

The values of the heat of formation of metaboric acid in the gaseous state, obtained in the papers of Randall and Margrave [3369a], White et al [4239] and Meschi, Chupka and Berkowitz [2853a], are in good mutual agreement. Based on these data, the following value has been accepted in the Handbook:

$$\Delta H^\circ f_{298.15}\,(HBO_2, \text{gas}) = -135 \pm 1 \text{ kcal/mole}.$$

The heat of sublimation of the thermodynamically most stable modification of metaboric acid,

$$\Delta Hs_{298,15}(\mathrm{HBO_2},\ \text{cub.}) = 57{,}69 \pm 1 \text{ kcal/mole},$$

and the dissociation energy

$$D_0(\mathrm{HBO_2}) = 433{,}781 \pm 5 \text{ kcal/mole}.$$

correspond to the value accepted in the Handbook.

H_3BO_3 (gas). The value of the heat of formation of H_3BO_3 (cryst.) may be calculated from the results of measurements of the heats of dissolution of boron oxide and H_3BO_3 in water. Prosen, Johnson and Pergiel [3335], based on a series of experimental investigations, calculated the thermal effect of the reaction

$$\mathrm{B_2O_3}(\text{vitr.}) + 2003\mathrm{H_2O}(\text{liq.}) = 2\,[\mathrm{H_3BO_3}\cdot 1000\mathrm{H_2O}]\,(\text{soln.}), \quad \text{(XXIII. 17)}$$

as equal to $\Delta H_{298,15} = -7{,}90 \pm 0{,}03$ kcal/mole. The value of the heat of dissolution of orthoboric acid at 298.15°K,

$$\mathrm{H_3BO_3}(\text{cryst.}) + 1000\mathrm{H_2O}(\text{liq.}) = \mathrm{H_3BO_3}\cdot 1000\mathrm{H_2O}\,(\text{soln.}) \quad \text{(XXIII. 18)}$$

is equal to 5.166 ± 0.036 kcal/mole, according to measurements of Artsdalen and Anderson [572] (in the recalculation the heats of dilution of boric acid solutions, given in paper [3769], were used). The above values of the heats of dissolution, together with the accepted value of the heat of formation of vitreous boron oxide (see page 1530), yield the value

$$\Delta H^\circ f_{298,15}(\mathrm{H_3BO_3},\ \text{cryst.}) = -262{,}29 \pm 0{,}3 \text{ kcal/mole}.$$

The value of the heat of evaporation of orthoboric acid was determined by Stackelberg, Quatram and Dressel [3833]. In this paper the water vapor was allowed to pass through a layer of orthoboric acid and the amount of boric acid contained in the condensate was determined analytically. By means of this method the following value of the heat of sublimation was obtained: $\Delta Hs_{413} = 23{,}24$ kcal/mole or $\Delta Hs_{298,15} = 23{,}96$ kcal/mole* and $\Delta H^\circ f_{298,15}(\mathrm{H_3BO_3},$ gas$) = -238.33$ kcal/mole. It must be noted that the value of the heat of evaporation of HBO_2 found by Stackelberg et al. in the same paper [3833] (see above) to be incorrect.

Meschi, Chupka and Berkowitz [2853b] investigated the system $B_2O_3 - H_2O$ at 1061-1451°K by means of a mass-spectrometrical method. Boron oxide was heated in an effuser cell to which water vapor was conveyed simultaneously. H_3BO_3 molecules were only observed at the highest temperature of 1451°K. The authors of paper [2853b] used the observed temperature dependence of the $H_3BO_3^+$ ion current intensity to calculate the thermodynamic functions of $(HBO_2)_3$. The data given in paper [2853b] permit the calculation of the value of

$$\Delta H^\circ f_{298,15}(H_3BO_3,\ \text{gas}) = -247 \pm 5\ \text{kcal/mole}.$$

This value is more accurate than that calculated from the results of paper [3833] and has been accepted in the Handbook; the following values correspond to it:

$$\Delta Hs_{298,15}(H_3BO_3,\ \text{cryst.}) = 15{,}29 \pm 5\ \text{kcal/mole},$$
$$D_0(H_3BO_3) = 706{,}327 \pm 7\ \text{kcal/mole}.$$

BF (gas). The only source of information about the value of the dissociation energy of the BF molecule is an extrapolation of the observed vibrational levels of the ground state and the excited state toward the dissociation limits.

An estimation of the BF dissociation energy on the basis of a linear extrapolation of the vibrational levels of the electron ground state $X^2\Sigma$ yields a very low value of D_0(BF), equal to 123.2 and 116.7 kcal/mole, respectively, according to data of Chretien [1100] and Onaka [3141]. However, by comparing the dissociation energies of the molecules of the halogen elements of group III (AlF, AlCl, etc.)., obtained by different methods, Welti and Barrow [4203] were led to the conclusion that a linear extrapolation of the vibrational levels of the ground state of the group of molecules under consideration yields too low values of the dissociation energies, which amount to about 50-70%

of the real values.

The extrapolation of the levels of the excited electron state $A^1\Pi$. is more reliable. According to the rules of correlation, the BF molecule in the $A^1\Pi$ state may dissociate into atoms that are in the states $B(^2P) + F(^2P_{1/2})$, $B(^2S) + F(^2P_{1/2})$ and $B(^2P) + F(^2P_{3/2})$, respectively. The possibility of formation of fluorine atoms in an excited state can virtually be ignored as the energy of the first excited state is very high (104,730 cm^{-1}). If the excitation energy of the first excited state of the boron atom is taken into account, the value of the dissociation energy of the BF molecule is too low; it is therefore logical to assume that the dissociation limit of the $A^1\Pi$ state correspond to a boron atom and a fluorine atom in the normal states.* A graphical extrapolation of the levels of the $A^1\Pi$ state according to an equation found by Chretien [1100] leads to a dissociation limit of 17,250 ± 4000 cm^{-1}, to which a value of $D_0(BF) = 196 \pm 12$ kcal/mole corresponds. This value is recommended in the second Edition of Gaydon's monograph [1668]. An extrapolation of the vibrational levels of this state with more accurate constants as recommended by Onaka [3141] yields the value $D_0(BF) = 202{,}2$ kcal/mole which, within the limits of error possible in the extrapolation agrees with the value of $D_0(BF)$ calculated from Chretien's equation. A comparison of the dissociation energies of AlF, AlCl and BBr, obtained by thermochemical methods and as the result of predissociation observations, with the extrapolated dissociation limits of the $A^1\Pi$ states of these molecules, carried through by Barrow [646a] showed that the potential curves of the $A^1\Pi$ electron states must possess maxima whose height decreases as the molecular weight increases.** In connection with the fact that the potential curve of the $A^1\Pi$ state of the BF molecule also possesses a maximum, the following value has been chosen in the present Handbook for the BF dissociation energy:

$$D_0(BF) = 185 \pm 15 \text{ kcal/mole.}$$

The following value corresponds to it:

$$\Delta H^\circ f_0(BF, \text{gas}) = -36{,}5 \pm 15 \text{ kcal/mole.}$$

BF$_2$ (gas). The value of the dissociation energy

$$D_0(BF_2) = 320 \pm 20 \text{ kcal/mole}$$

used in the Handbook was estimated from the relation

$$\frac{D_0(BF_2) - D_0(BF)}{D_0(BF_3) - D_0(BF)} = \frac{D_0(AlF_2) - D_0(AlF)}{D_0(AlF_3) - D_0(AlF)}, \qquad \text{(XXIII.19)}$$

i.e., according to the method of Karapetyants. For this purpose the values of the dissociation energies of BF, BF_3, AlF, AlF_2 and AlF$_3$, accepted in the Handbook, were used.

$$\Delta H^\circ f_0(BF_2, \text{газ}) = -153 \pm 20 \text{ kcal/mole.}$$

corresponds to the value accepted for the BF$_2$ dissociation energy.

BF$_3$ (gas). The values of the heat of formation of BF$_3$ given in modern thermochemical Handbooks were calculated from the heat of BF$_3$ dissolution in water, -24.46 kcal/mole, determined by Ammerl [1943] (recalculated with the newest atomic weights) and the heat of reaction of boric and hydrofluoric acids, -27.5 kcal/mole, found by Thomsen [3981]. Laubengayer, Finlay and Sears [2569, 2570] also measured the heat of hydrolysis of BF$_3$ and obtained $\Delta H_{273} = -21{,}9 \pm 0{,}2$ kcal/mole. A sufficiently accurate recalculation of this value for room temperature, however, proved impossible since in literature there are no data on the specific heat of aqueous solutions of BF$_3$.

The values of the heat of formation of BF$_3$, calculated by various authors from these data differ essentially; this is explained by the fact that different values of the heats of formation of HF and H$_3$BO$_3$ have been used in these calculations. The accuracy of the values calculated from these data is considerably reduced by the fact that the final compositions of the products of BF$_3$ hydrolysis in water and the

the products of reaction of boric and hydrofluoric acids were not the same [356, 38, 1657].

Careful measurements of the heats of dissolution of boron trifluoride and boric acid in hydrofluoric acid, permitting the calculation of a more accurate value of $\Delta H^\circ f(\mathrm{BF_3},\ \text{gas})$, were carried out by Skuratove, Kanarskaya and Martynov [38]. The authors of [38] measured the reaction heats of

$$\mathrm{BF_3}(\text{gas}) + \mathrm{HF \cdot 686H_2O}(\text{soln.}) = \mathrm{BF_3 \cdot HF \cdot 686H_2O}(\text{soln.}), \qquad (\mathrm{XXIII.20})$$

$$\mathrm{H_3BO_3}(\text{cryst.}) + 4(\mathrm{HF \cdot 182H_2O})(\text{soln.}) = \mathrm{BF_3 \cdot HF \cdot 728H_2O}(\text{soln.}) + 3\mathrm{H_2O}(\text{liq.}) \qquad (\mathrm{XXIII.21})$$

in an adiabatic calorimeter and established that the final states of the products of these reactions may be considered as identical. The difference of the heats of the reactions (XXIII.20) and (XXIII.21), $\Delta H_{298.15} = -16{,}2 \pm 0{,}1$ kcal/mole, found in paper [38] corresponds to the value of

$$\Delta H^\circ f_{298.15}(\mathrm{BF_3},\ \text{газ}) = -268 \pm 1{,}5 \text{ kcal/mole.}$$

This value has been accepted in the Handbook; the value

$$D_0(\mathrm{BF_3}) = 452{,}826 \pm 5 \text{ kcal/mole.}$$

corresponds to it.

FBO (gas). The FBO dissociation energy was estimated by comparing the dissociation energies of $\mathrm{BF, BO, CF, CN}$ and FCN (the molecules of FBO and FCN are isoelectronic).

The value obtained in this way

$$D_0(\mathrm{FBO}) = \text{gas} \pm 25 \text{ kcal/mole}$$

has been accepted in the Handbook; the following value corresponds to it:

$$\Delta H^\circ f_0(\mathrm{FBO},\ \text{газ}) = -172{,}513 \pm 25 \text{ kcal/mole.}$$

BCl (gas). A linear extrapolation of the vibrational levels of the ground state of the BCl molecule yields the value of $D_0(\mathrm{BCl}) = 97$ kcal/mole which, as in the case of BF, is too low and less reliable than the value obtained by a graphical extrapolation for the $A^1\Pi$ state.

An extrapolation of the vibrational levels of the $A^1\Pi$ excited state according to an equation suggested by Herzberg and Hushley [2034] yields a dissociation limit which is higher by 44,821 cm^{-1} than the zero vibrational level of the ground state. Under the assumption that the BCl molecule in the $A^1\Pi$ state dissociates into atoms in normal states (see page 1542), a value of $D_0(BCl)$ = 127.9 kcal/mole corresponds to the dissociation limit obtained in this way.*

Obviously, as in the case of BF, the potential curve of the $A^1\Pi$ state has a maximum whose height amounts to about 10 kcal/mole. Therefore a value of

$$D_0(BCl) = 118 \pm 10 \text{ kcal/mole},$$

is recommended in the present Handbook for the BCl dissociation energy;

$$\Delta H^\circ f_0(BCl, \text{gas}) = 40{,}55 \pm 11 \text{ kcal/mole}.$$

corresponds to it.

BCl_2 (gas). The heat of formation of BCl_2 was estimated according to Karapet'yants' method. The graph is plotted with the help of data on the heats of formation of $AlCl$, $AlCl_2$, $AlCl_3$, BCl and BCl_2. The value

$$\Delta H^\circ f_0(BCl_2, \text{gas}) = -30 \pm 10 \text{ kcal/mole}$$

found in this way has been accepted in the Handbook. The following value corresponds to it:

$$D_0(BCl_2) = 217{,}1 \pm 11{,}0 \text{ kcal/mole}.$$

BCl_3 (gas). Troost and Hautefeuille [4020] measured the total thermal effect of the reaction of chlorine with amorphous boron and the hydrolysis of the BCl_2 obtained. Moreover, they measured also the heat of hydrolysis of BCl_3 separately. Combining these data permits the calculation of the value of the heat of formation of BCl_3 (liqu.), which is equal to -103.3 kcal/mole (the results of the measurements were reduced to standard conditions by Johnson et al [2267]. This value, however, may only be viewed as approximate since the authors of paper [4020] had no sufficiently pure boron sample at their disposal and, moreover, as shown by Berthelot [779] and Thomsen [3981] (see also [2267]), this paper may contain a systematic error in the determination of the thermal capacity of the calorimeter.

Gal'chenko, Timofeyev and Skuratov [140a, 37, 140] measured the heat of combustion of boron in chlorine. The initial boron was obtained by pyrolysis of diborane and degasified by annealing in vacuo. An X-ray structural analysis showed only traces of the crystalline phase. By means of a spectroscopic analysis it was shown that metallic impurities (mainly calcium) were present in an amount of about 0.01%. It was of great value that in this work the initial boron sample was analyzed by the method of melting in vacuo [422], thus proving the presence of 0.23% oxygen, 0.12% hydrogen and 0.005% nitrogen. The cup containing the boron was heated in a microfurnace in chrlorine atmosphere (6 atm) up to 500-600°C. Under these conditions an almost complete combustion of boron was achieved (99.7-99.8%). According to the weight of the initial portion in the bomb, either BCl_3 in gaseous state or a mixture of gaseous and liquid BCl_3 was obtained as the result of the reaction. From these experiments the authors of paper [140a 47, 140] determined the value of the heat of formation of boron trichloride in liquid state, -103.3 ± 0.6 kcal/mole and in gaseous state -97.4 ± 0.7 kcal/mole.

Johnson, Miller and Prosen [2267] also determined the heat of combustion of amorphous boron in chlorine. Unlike the work of Gal'chenko et al [37, 140], the combustion took place in a flow system: a mixture of chlorine with helium was blown over the boron. A quartz cup with the boron was heated in a resistance furnace up to 400°C. The value of the heat of formation of gaseous boron trichlorid, -97.51 ± 0.32 kcal/ /mole, found in paper [2267], is in good agreement with that obtained by Gal'chenko et al [140a, 37, 140]. The error of the value obtained by Johnson et al [2267] may, however, exceed this value considerably, since the spectroscopic analysis carried through by the authors of paper [2267] could not yield information on the presence of the most important impurities in the sample, namely oxygen, hydrogen and nitrogen.

Based on the heat of formation of BCl_3 (gas) from chlorine and amorphous boron, obtained by Gal'chenko et al [140a, 37, 140], and the value of the heat of transition of crystalline boron to amorphous boron, $\Delta H_{298.15} = 0.4$ kcal/g-atom [3508], in the Handbook we accepted the following value of the heat of formation of BCl_3 (gas) from the elements in the standard state:

$$\Delta H^\circ f_{298.15}(BCl_3,\text{ gas}) = -97{,}0 \pm 0{,}7 \text{ kcal/mole.}$$

$$D_0(BCl_3) = 312{,}426 \pm 5 \text{ kcal/mole.}$$

corresponds to the accepted value of the heat of formation.

Lacher, Scruby and Park [2512] measured the heat of chlorination of diborane

$$B_2H_6(\text{gas}) + 6Cl_2(\text{gas}) = 2BCl_3(\text{gas}) + 6HCl(\text{gas}) \qquad (XXIII.22)$$

and obtained $\Delta H_{298.15} = -343 \pm 3{,}4$ kcal/mole; a value of $\Delta H^\circ f_{298.15}$ (BCl_3, gas) = -101.5 ± 1.8 kcal/mole.* The deviation from the value accepted in the Handbook exceeds considerably the error of the measurements of [2512]. It seems that in paper [2512] a systematic error has been admitted.

The results of measurements of the heat of hydrolysis of BCl_3 were considered on choosing the value of the heat of formation of boron oxide.

BN (cryst.). In the papers of Slade and Higson [3763, 3764] and Lorenz and Woolcock [2656] the dissociation equilibrium of boron nitride was investigated. Processing of the data of these authors yields values of the heat of formation of boron nitride of from -18.1 to -34.5 kcal/mole [3593, 2358, 2355]. The values obtained on the basis of papers [3764, 3763, 2656] may only be considered as the lower limit of the heat of formation of boron nitride since the samples of boron and boron nitride used contained considerable quantities of impurities which might have resulted in an increase of the pressures measured. The value of $\Delta H^{\circ}f_{298.15} = -32{,}1$ recommended in the Handbook [3508] has obviously been obtained by recalculating the data from Kelley's paper [2355].

A more accurate determination of the heat of formation of boron nitride was achieved by Gal'chenko, Kornilov and Skuratov [139b, 36, 140, 248]. These authors measured the heat of direct reaction between nitrogen and amorphous boron, $\Delta H_{298.15} = -61{,}1 \pm 0{,}34$ kcal/mole. By means of an X-ray analysis it was established that boron nitride is obtained in the hexagonal crystalline modification. Since boron and nitrogen react only at high temperatures, the weighed portion of boron was heated in a nitrogen atmosphere up to 1300°C in a small special electrical furnace.

As mentioned in a short communication [3622b], the measurement of nitrogen pressure above BH by means of Langmuir's method yielded a value of $\Delta H^{\circ}f_{298.15}$ (BN, cryst.) ≈ -60 kcal/mole.

The value of the heat of formation of the hexagonal crystalline modification of boron nitride, from boron in crystalline state and gaseous nitrogen,

$$\Delta H^{\circ}f_{298.15}(\text{BN, cryst.}) = -60{,}7 \pm 0{,}4 \text{ kcal/mole.}$$

was obtained by Gal'chenko, Kornilov and Skuratov [139b]. In the calculation the value of $\Delta H_{298.15} = -0{,}4$ kcal/g-atom was used for the heat of transition of amorphous boron to crystalline boron [3508].

BN (gas). The value of the dissociation energy of boron nitride,

$$D_0(BN) = 92 \pm 12 \text{ kcal/mole}$$

accepted in the present Handbook, was obtained by Gaydon [1668] on the basis of a graphical extrapolation of the vibrational levels of the BN molecule in the $X^3\Pi$ ground state and the $A^3\Pi$ excited state, with the help of data from the paper of Douglas and Herzberg [1375].

An estimation of the BN dissociation energy according to the relation suggested by Margrave and Stapitanonda [2777] yields a value of about 70 kcal/mole. A linear extrapolation of the vibrational levels of the ground state is much less accurate than the graphical and yields a value of about 131 kcal/mole.

The following values correspond to the accepted value of the dissociation energy:

$$\Delta H^\circ f_0(\text{BN, gas}) = 150{,}536 \pm 13 \text{ kcal/mole},$$
$$\Delta Hs_0(\text{BN, cryst.}) = 210{,}549 \pm 13 \text{ kcal/mole}.$$

TABLE 219

Accepted Values (in cal/mole) of the Thermodynamic Quantities of Boron and Its Compounds

Вещество 3	Состояние 4	D_0 или 5 $\Delta H s_0$	$\Delta H°f_0$	$\Delta H°f_{293.15}$	$\Delta H°f_{298.15}$	$H°_{293.15}-H°_0$	$H°_{298.15}-H°_0$
B	Крист. 1	130 000[a]	0	0	0	279	292
B	Газ 2	—	130 000	131 207	131 219	1486	1511
B_2	»	62 300	197 700	199 199	199 209	2057	2093
BO	»	183 987	5 000	5 739	5 744	2038	2073
BO_2	»	312 974	—65 000	—64 816	—64 812	2503	2555
B_2O_2	»	486 974	—109 000	—108 617	—108 608	2981	3051
B_2O_3	1 Крист.	98 000[a]	—304 282	—305 756	—305 760	2144	2218
B_2O_3	2 Газ.	643 243	—206 282	—206 994	—207 003	2906	2976
BH	»	69 000	112 632	113 391	113 396	2030	2065
HBO	»	260 000	—19 381	—19 499	—19 504	2173	2216
HBO_2	»	433 781	—134 175	—134 985	—135 000	2501	2551
H_3BO_3	»	706 327	—244 470	—246 973	—247 000	3812	3903
BF	»	185 000	—36 500	—35 774	—35 771	2042	2077
BF_2	»	320 000	—153 000	—152 835	—152 838	2517	2565
BF_3	»	452 826	—267 326	—267 990	—268 000	2724	2784
FBO	»	380 000	—172 513	—172 415	—172 413	2434	2485
BCl	»	118 000	40 550	41 275	41 279	2080	2118
BCl_2	»	217 100	—30 000	—29 691	—29 691	2741	2795
BCl_3	»	312 426	—96 776	—97 000	—97 000	3285	3359
BN	1 Крист.	210 549[a]	—60 013	—60 694	—60 700	617	641
BN	2 Газ	92 000	150 536	151 280	151 284	2041	2076

[a] Value of the sublimation heat given.

1) Crystalline; 2) gas; 3) substance; 4) state; 5) or.

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1438*	In the case of aluminum oxygen compounds under analogous conditions the occurrence of the aluminum monoxide AlO and aluminum (sesquioxide) Al_2O has been established.
1438**	The tetraboric acid $H_2B_4O_7$ in its free state does not exist, only its salts.
1440	The ions BF_2^+ and BCl_2^+ observed in the mass-spectrometric investigations [2782a, 2570, 2483a] were obtained through dissociating ionization of the molecules BF_3 and BCl_3 and therefore, they cannot be considered as a proof for the existence of the BF_2 and BCl_2 molecules.
1442	The use of the method of molecular orbitals for the analysis

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of the electronic states of the B_2 molecule enabled Mulliken to show that the ground electronic state of the B_2 molecule could be one of the following states: ${}^3\Sigma_g^-$, ${}^3\Pi_u$, ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^-$.

1444 The bands of the system $A^2\Pi - X^2\Sigma$ were observed for the first time in the absorption spectrum in 1960 by Thrush [3988] using flash photolysis of BCl_3 in the presence of oxygen and nitrogen. These experiments prove that the ground electron state of the BO molecule is the state $X^2\Sigma$.

1447* Previously also the so-called fluctuation bands of the boric acid have been attributed to the spectrum of the BO molecule [3745, 3746, 3945]. At the present time, however, it has been shown that these bands cannot be assigned to BO, but are associated with multiatomic boron oxygen compounds [288, 2777, 2329a] (see for more details page 1457).

1447** The observation of the band system $A^1\Pi - X^1\Sigma^+$ in the absorption spectrum may be considered an experimental confirmation of the suggestion that the ground electron state of BH should be the state ${}^1\Sigma^+$.

1448 The correct value of a similar estimate of the vibrational constants for BH in the state $X^1\Sigma$. is confirmed by results from corresponding calculations for AlH according to the data of the work [4376], yielding $\omega_e'' = 1710$ and $\omega_e''x_e'' = 20,82\ см^{-1}$, while the values found experimentally are equal to $\omega_e'' = 1682$ $\omega_e''x_e'' = 19,09\ см^{-1}$. The application of the relations (1.36) and (1.38) for estimating the vibrational constants of BH in the $A^1\Pi$ state is unjustified, since for this state of AlH they lead to considerable discrepancies between the experimental data.

1450 The rotational constants have been determined from investigations of the fine structure of the following five bands: 0-1, 2-1, 3-1, 3-2, and 4-2.

1452 The constants of BF in the states $b^3\Sigma$ and $c^3\Sigma$ are not listed in Table 208, since the excitation energy of these states should exceed 50,000 cm^{-1}.

1459 In the article of Kaskan, McKenzey and Millikan [2329a] for BO_2 a linear symmetric structure has been adopted, while the fundamental frequencies ν_1, ν_2 and ν_3 had been estimated of being equal to 1100, 600 and 1400 cm^{-1}.

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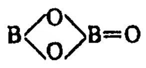
1460 Accepted on the basis of the value $2\nu_3 = 2644\ cm^{-1}$.

1461 In the molecules XCN, where X = F, Cl, Br and H, the value f_a/d_1d_2 practically remains constant and equal to $(0,20 \pm 0,03) \cdot 10^5$ dyne·cm^{-1}.

1462 The calculated value for the frequency ν_3 practically coincided with those observed in the work [4240].

1463 As it is commonly known, the force constant of the $-C \equiv N$ bond in the molecule C_2N_2 is larger than in the radical CN. The constants of the C – C bonds in C_2N_2 cannot be compared with those in the radical C_2 owing to the different multiplicity factor.

1465 In addition to the combination scattering spectra (Raman spectra) in these works also infrared absorption spectra have been obtained and the polarizability of the combination scattering lines (Raman spectral lines) has been investigated.

1467* It should be mentioned that the authors [10, 67b] left the question open whether the diffraction pattern observed should be assigned not only to the B_2O_3 molecule, but also to the radical OBO with unequal boron-oxygen bonds due to the fact that the whole diffraction pattern is sufficiently and satisfactorily interpreted by the group $O \overset{1,30}{—} B \overset{1,20}{=} O$. On the other hand, the presence of a sharp maximum at 2.56 A in the radial distribution curve constructed from the diffraction patterns cancels the possibility to assigning the diffraction pattern to any arbitrary model of the B_2O_3 molecule which does not contain the linear group O – B = O, in particular to the model of the type  and the dipyramidal model.

1467** To prove the data obtained for the B_2O_3 molecule, Akisin and Spiridonov investigated the structure of the molecule B_2S_3 [67a], for which also an angular structure with the parameters $r_{B=S} = 1,65 \pm 0,03$, $r_{B-S} = 1,80 \pm 0,02$ Å and $\angle BSB = 96°$. had been obtained.

1468 Semi-boldface type is used for the frequencies observed in the spectrum.

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1469 According of the data of the work [29a] in the reflection spectrum of liquid boron oxide the bands 1316 and 720 cm^{-1} are present.

1471 In the spectrum of DBO_2, instead of the band 3680 cm^{-1} a band in the region 2750 cm^{-1} has been observed.

1475* This condition may be considered to be an additional confirmation for the truth of the initial suggestion that the vibration frequencies of crystalline boracic acid may be considered to belong to the isolated molecule H_3BO_3.

1475** There exist only discrepancies as to the attribution of some of the frequencies. As opposed to Pistorius, Sidorov and Sobolev attribute the frequency of 886 cm-1 to the valence vibration of the bond B – O, while they associate the frequency of 1169 cm^{-1} to the deformation vibration of BOH. Besides that, in the work [372a] the frequency 3170 cm^{-1} is assigned to the symmetrical valence vibration of the bond O – – H, while the frequency 3240 cm^{-1} is assigned to the antisummetrical vibration. This difference in the interpretation of frequencies does practically not influence the values of thermodynamic functions of H_3BO_3, as the first two frequencies belong to the same type of vibrations (A') and as the values of the valence vibration frequencies of O – H are large and extremely close to each other.

1476 According to the work by Walsh [4139] the molecules under consideration should be non-linear due to the fact that they have 17 valence electrons.

1478 Calculations for the fundamental frequencies of BF_2 according to the force constants of BF_3, as recommended in the work of Gubo, Buse and Campman [1830] lead to the values $\nu_1 = 1250, \nu_2 = 490, \nu_3 = 1380$ см$^{-1}$, which within the limits of the indicated errors coincide with those accepted in this Handbook.

1481 In the calculation of the frequency [illegible] it has been assumed that $x_4' = x_4$.

1486 The components of state $A^2\Pi$ have been calculated according to the constants of sub-state $A^2\Pi_{1/2}$, a procedure through which no errors have been introduced into the results of the calculation.

1492 In this Handbook, the calculation of functions for BF has been carried out with the aid of constants found in the work

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of Kret'yen [1100]. The thermodynamic functions for BF, calculated with the aid of the constants suggested by Onaka [3141] differ from those given in Table 278 (II) by 0.02-0.03 cal/mole•degree.

1503 If it is assumed that the internal rotation around the bonds B – O in the H_3BO_3 molecule is free, the value of $\Phi^{\circ}_{298.15}$ will exceed the value given in Table 277 (II) by 3 cal/mole••degree; if there occurs no internal rotation, and instead, the twisting (torsional) vibration occurs, this value will be smaller than that given in Table 277 (II) by about 5 cal/mole•degree.

1506* In 1961 the work of Jakis and Papousek [2203a] has been published in which the thermodynamic functions for boron trifluoride and boron trichloride have been calculated for $T \leqslant 1500°$ K. The calculation was carried out separately for the isotopic modifications of these gases, containing B^{10} and B^{11} with the aid of constants recommended in the work [4207]. The discrepancies between the data given in the work [2203a] for $B^{11}F_3$ and $B^{11}Cl_3$ on the one hand, and those listed in the Tables 280 (II) and 284 (II) for equilibrium isotopic mixtures of boron trifluoride and boron trichloride on the other hand, do not exceed 0.06-0.08 cal/mole•degree. In the case of BCl_3, these inequalities are practically independent of the temperature, while in the case of BF_3 they increase from 0.01 to 0.07 cal/mole•degree with rising temperatures from 298.15 to 1500°K.

1506** In x-ray diffraction patterns of amorphous ("micro-crystalline") boron spectral lines of a tetragonal modification of boron have been detected (see [356a]). On heating of amorphous boron in the vacuum up to temperatures of the order of 2000°K, amorphous boron changes over into its crystalline form [2279].

1508 The data of Robertson have not been published in the periodical literature and became known to the authors of this Handbook only through the work [1515].

1509 Wise et al [4299a] derived from their own data and those contained in the work [2279] the following equation for the heat capacity of crystalline boron:

$$C_p = R\,[D\,(875/T) + 2E\,(1075/T) + E\,(4050/T)],$$

where D and E are the Debye and Einstein functions (see page 248). They used this equation for calculating the thermodynamic functions for crystalline boron in the temperature range of 100-2400°K. It should be mentioned however, that the heat capacities and enthalpies, calculated according to this equation, are overrated as compared with the experimental data for the samples of boron I and II [4299a].

1510* There are indications [1014] that Westrum and co-workers did measure the heat capacity of crystalline B_2O_3 in the temperature range of 6-350°K, however, these data have not been published as yet.

1510** This value had been subsequently confirmed by Donohue and Hubbard [1361a] who obtained for the melting point of B_2O_3 a value of 724°K.

1512 In 1957 [4207a] a cubic modification of boron nitride was produced which has the structure of diamond and was called borazone. The thermodynamic properties of borazone have as yet not been investigated.

1513* Recently MacDonald and Stull [2700a] measured the enthalpy of BN in the interval of 280-1683°K. The data they obtained agree with those given in Table 285 (II) with an accuracy of $\pm 1\%$.

1513** Wentorf [4208] determined the pressure dependence of the melting point of boron nitride and obtained melting points of 3200, 3400 and 3500°C, with an accuracy of $\pm 100°$, for pressures of 30,000, 65,000 and 80,000 atm, respectively.

1514 In the monographies of Kubaschewski and Evans [2494, 2495], with reference made to a private communication of Prosen, a value of 1.0 kcal/g-atom is recommended for the transition heat. The origin of this value is incomprehensible since Prosen in his papers (cf., e.g., [2267, 3335, 3338]) uses a value of +0.4 kcal/g-atom.

1515 The presence of this coefficient of evaporation, obviously, is the cause of the too high values obtained for the heat of sublimation of boron in the case of evaporation from an open surface (137.5 kcal/g-atom) [3,1,63a] or evaporation from a chamber with a large relative opening (138 kcal/g-atom) [3673].

1516* Paper [1105a] has only become known from brief communications [2170a and 3622b].

1516** The B_2 molecule (see the next paragraph of this section is not very stable and its presence in vapor cannot explain the deviation of the results of measurements made with different

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relative sizes of the effusion openings.

1521 In the paper of Inghram et al [2171] the composition of the condensed phase was not investigated at high temperatures. As indicated by the authors of this paper [2171] (see also [3612]), it is possible that boron oxide reacts with boron in such a way that a new condensed phase is formed. This assumption is based on the fact that the partial pressure of boron oxide over the mixture of boron and boron oxide is lower by a factor of five than the pressure over pure boron oxide.

1522 Soulen and Margrave [3812] recalculated the results of the measurements of [2171] using the values of the thermodynamic functions of boron oxides obtained in own calculations and obtained a similar value of $\Delta H^\circ f_0$ (B_2O_3, gas) = -110.9 kcal/mole.

1525 In the table and in the text values of the heat of formation of vitreous boron oxide from boron in amorphous state and oxygen are given.

1526* In the paper of Eckstein and Artsdalen [1450], making reference to a private communication by Parker, it is indicated that the authors of [1469] revised the results obtained previously and recommend a value of -300 kcal/mole.

1526** In the determination of the quantity of boron oxide by extraction and titration of the solution obtained, the quantity of boron oxide obtained proved smaller than the weighed portion. The authors explain this by an incomplete extraction of boron oxide from the combustion products.

1527 Value given of the heat of formation from boron in amorphous state.

1535 With the help of the heat of sublimation of boron oxide at 1430°K, determined from the relation $\lg p - 1/T$, and the value of the entropy of B_2O_3 (liqu.) at this temperature, White et al [4239b] found a value of S_{1430} (B_2O_3, gas) = 93.9 cal/mole·degree, which is in good agreement with the value calculated in paper [4238]. Using the value of the entropy of B_2O_3 (liqu.) accepted in the present Handbook, a considerably different value of S_{1430} (B_2O_3, gas) = 100.3 cal/mole·degree has been obtained. Obviously, this divergence may only be caused by the difference of the values of the entropy of B_2O_3 (liqu.), used in paper [4239b] and in the present Handbook.

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1536 The values given have been corrected somewhat for the value of the heat of formation of H_3BO_3 (cryst.), accepted in the present Handbook.

1538 This paper has been referred to before, in the articles of a series of authors [2772, 2776, 1851, 752, 1515, 3368b].

1539 In the vapor Meschi, Chupka and Berkowitz also discovered trimeric metaboric acid $(HBO_2)_3$ and calculated its heat of formation: -540 ± 10 kcal/mole. From experiments on the investigation of the equilibrium of (XXIII.15), Margrave et al [3368b, 3369a] obtained the similar value of 537.5 ± 3 kcal/ /mole. In earlier papers Margrave et al (cf. [2773], [752]) suggested the existence of the dimer $(HBO_2)_2$ with a heat of formation of about -357 kcal/mole.

1540 In the recalculation for 298.15°K a value of $(H_{443} - H_{298.15})\ H_3BO_3$, cryst. = 3400 cal/mole was used which was obtained by extrapolating the results of measurements of the specific heat of H_3BO_3 (cryst.) [2280]. In paper [1515], in the recalculation for 298.15°K a similar value was obtained for the heat of sublimation: $\Delta Hs_{298.15} = 23{,}55 \pm 2{,}5$ kcal/mole.

1542* A detailed analysis of the possible errors and a comparison of the dissociation energy values of the halide molecules of Ga and Tl, estimated with the help of an extrapolation of the levels of the $A^1\Pi$ state and those obtained by thermodynamic methods, led Barrow [646a] to the conclusion that atoms in the states $M(^2P_{3/2}) + X(^2P_{1/2})$ correspond to the dissociation limits of the $A^1\Pi$ states of the molecules considered. In the case of boron the energy of the $^2P_{3/2}$ state amounts to only 19 cm^{-1} and has virtually no influence on the quantity $D_0(BF)$.

1542** Maxima of the order of 15 and 9 kcal/mole of the potential curves of the $A^1\Pi$ states correspond to the values of the dissociation energies of AlF and AlCl, obtained as a result of equilibrium investigations and accepted in the present Handbook.

1545 In Gaydon's monograph [1668] it is indicated erroneously that an extrapolation of the vibrational levels of the $A^1\Pi$ state yielded a value of $D_0(BCl) = 118 \pm 9$ kcal/mole.

1547 In the calculation, in accordance with data from [3335] a value of $\Delta Hf_{298.15}(B_2H_6,$ gas) = +6.73 ± 0.52 kcal/mole was used

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(boron in amorphous state).

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[Transliterated Symbols]

1473 пр = pr = proizvedenie = product

1502 вн.вр = vn.vr = vnutrenneye vrashcheniye = internal rotation (occuring with Φ and S).

1502 св.вр = sv.vr = svobodnoye vrashcheniye = free rotation (occurring with Φ, S, and Q).

Chapter 24

ALUMINUM AND ITS COMPOUNDS

(Al, Al^+, Al_2, AlO, Al_2O, Al_2O_3, AlH, AlF, AlF_2, AlF_3, $AlCl$, $AlCl_2$, $AlCl_3$, AlN)

In this chapter aluminum and its compounds with oxygen, hydrogen, fluorine, chlorine and nitrogen are discussed.

In the Handbook the thermodynamic functions of Al (crystalline, liquid, gas), Al_2 (gas) and Al^+ (gas) are given. These data allow us to calculate the thermodynamic properties of aluminum and its vapors within a wide range of temperature and pressure. The literature contains no reference to the existence of a molecule of more complex composition in aluminum vapors.

The aluminum-oxygen system is presented in the Handbook by the compounds Al_2O_3 (crystalline, liquid), AlO (gas) and Al_2O (gas). Apart from the well-known crystalline modification of aluminum oxide, corundum, several other modifications are known (see page 1599) but they are thermodynamically unstable, at least under the usual pressures. The literature contains indications [2089] that under definite conditions in the condensed state, apart from Al_2O_3, the aluminum suboxides AlO and Al_2O occur. However, the absence of the necessary data on these compounds did not admit of calculating tables of their thermodynamic functions. Hence, the estimates of the compositions and thermodynamic properties of substances in the condensed state, forming in the aluminum-oxygen system, under definite conditions (reducing medium, temperatures of 1050-1500°C and above) can be inaccurate.

The gaseous compounds of the aluminum-oxygen system presented in the Handbook are AlO and Al_2O. Apart from these compounds, Al_2O_2 is known to exist in the gaseous state. However, the partial pressures of this compound in saturated vapors of aluminum oxide at 2000-2600°K are two to three orders lower than the pressures of AlO and Al_2O. The problem of the thermodynamic stability of the aluminum oxide Al_2O_3 in the gaseous state remained obscure for a long time. The mass-spectrometric studies [1405a] of evaporation products of aluminum oxide under natural conditions carried out in 1960 have shown that the basic products of evaporation are Al and O, and the partial pressure of Al_2O_3 (gas) is less than 10^{-5} of the partial pressure of monatomic aluminum. In this connection, in the present edition of the Handbook the thermodynamic functions of Al_2O_3 (gas) are not discussed. In order to make it possible to calculate the thermodynamic properties and the composition of evaporation products of aluminum oxide, in Volume II of the Handbook the values of the equilibrium constant are indicated for the reaction

$$Al_2O_3(\text{cryst., liq.}) = 2Al(\text{gas}) + 3O(\text{gas}).$$

Considering the great significance of the problem of the thermodynamic stability of Al_2O_3 (gas) and the close connection of this problem with the selection of the heats of formation of AlO and Al_2O, in the section on the selection of thermochemical values works on the determination of the heat of sublimation of aluminum oxide are discussed.

Out of the compounds of the aluminum-hydrogen system in the Handbook the most simple compound, AlH, is discussed. The compound AlH_3 is equally known but it has a low stability, and carrying out calculations of the compositions of the products formed by the reaction of aluminum with hydrogen it can be neglected.

The aluminum-fluorine system is represented in the Handbook by the following compounds: AlF_3 (crystalline, liquid, gas), AlF_2 (gas) and AlF (gas). Apart from these compounds, a further compound is known, Al_2F_6, but its content in saturated vapors of aluminum trifluoride at elevated temperatures is not high and does not exceed 2% at 1000°K [3307a].

In the Handbook the following compounds of aluminum with chlorine are treated: $AlCl_3$ (crystalline, liquid, gas), $AlCl_2$ (gas) and AlCl (gas). At low temperatures the vapors of aluminum chloride consist practically completely of dimerized Al_2Cl_6 molecules. However, already at 700°K $AlCl_3$ becomes the main component of the vapor. Hence, the calculations of the compositions and thermodynamic properties of the aluminum-chlorine system at higher temperatures can be carried out with satisfactory accuracy on the basis of the data indicated in the Handbook, without consideration of Al_2Cl_6.

It is known that AlOCl occurs in the crystalline state (see, e.g., [3602a]). In some works (e.g., [3612a]) the occurrence of the compounds AlOCl and AlOF is suggested in the gaseous state, too. For the time being, however, no experimental evidence of the existence of these compounds in the gaseous state exists, and they are not discussed in the Handbook.

§95. MOLECULAR CONSTANTS

Al. The Al atom in the ground state has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p$ which corresponds to one term ^2P. The series limit of the states with the electronic configuration $1s^2 2s^2 2p^6 3s^2 (^1S)\, n\ell$ is situated at 48279.16 cm^{-1} above the lower level $^2P_{1/2}$. The states with such a configuration are doublets with $L = \ell$. The states with the configuration corresponding to the excitation of 3s-electrons, and also of electrons with the main quantum number $n = 2$, are not discussed, since the excitation energy of such states is sufficiently high (above 60,000 cm^{-1}).

In Table 220 the energy levels of the Al atom with the configuration $1s^2 2s^2 2p^6 3s^2 (^1S)\ n\ell$ and the values $n \leq 11$ are indicated. The excitation energies of these levels are adopted on the basis of the values proposed by Moore [2941]. As in other cases, in Table 220 the states with similar excitation energies have been incorporated into one level with the total statistical weight and the mean excitation energy.

TABLE 220

Energy Levels of the Aluminum Atom

A Номер уровня	B Состояние		E Статистический вес	F Энергия, см$^{-1}$
	C электронная конфигурация	D терм		
0	$\ldots 3s^2 (^1S)\, 3p$	$^2P_{1/2}$	2	0
1	$\ldots 3s^2 (^1S)\, 3p$	$^2P_{3/2}$	4	112,04
2	$\ldots 3s^2 (^1S)\, 4s$	^2S	2	25347,69
3	$\ldots 3s\, 3p^2$	^4P	12	29097,03
4	$\ldots 3s^2 (^1S)\, 3d$	^2D	10	32436,25
5	$\ldots 3s^2 (^1S)\, 4p$	^2P	6	32960
6	$\ldots 3s^2 (^1S)\, 5s$	^2S	2	37689,32
7	$\ldots 3s^2 (^1S)\, 4d$	^2D	10	38932
8	$\ldots 3s^2 (^1S)\, 5p$	^2P	6	40276
9	$\ldots 3s^2 (^1S)\, 4f$	^2F	14	41318,74
10	$\ldots 3s^2 (^1S)\, 5d$ $\ldots 3s^2 (^1S)\, 6s, 6p$	^2D $^2S, ^2P$	18	42593
11	$\ldots 3s^2 (^1S)\, 5f, 5g$	$^2F, ^2G^{\circ}$	32	43831,08
12	$\ldots 3s^2 (^1S)\, 6d$ $\ldots 3s^2 (^1S)\, 7s$	^2D ^2S	12	44186
13	$\ldots 3s^2 (^1S)\, 6f - 6h$ $\ldots 3s^2 (^1S)\, 7d$ $\ldots 3s^2 (^1S)\, 8s$	$^2F, ^2G^{\circ}, ^2H^{\circ}$ ^2D ^2S	72	45200
14	$\ldots 3s^2 (^1S)\, 7f - 7i$ $\ldots 3s^2 (^1S)\, 8p, 8d$ $\ldots 3s^2 (^1S)\, 9s$	$^2F, ^2G^{\circ}, ^2H^{\circ}, ^2I^{\circ}$ $^2P^{\circ}, ^2D$ ^2S	98	46027
15	$\ldots 3s^2 (^1S)\, 8f - 8k$ $\ldots 3s^2 (^1S)\, 9p, 9d$ $\ldots 3s^2 (^1S)\, 10s$	$^2F^{\circ}, ^2G^{\circ} \ldots ^2K^{\circ}$ $^2P^{\circ}, ^2D$ ^2S	128	46594
16	$\ldots 3s^2 (^1S)\, 9f - 9l$ $\ldots 3s^2 (^1S)\, 10p, 10d$ $\ldots 3s^2 (^1S)\, 11s$	$^2F, ^2G^{\circ} \ldots ^2L^{\circ}$ $^2P^{\circ}, ^2D$ $^2S^{\circ}$	162	46942
17	$\ldots 3s^2 (^1S)\, 10f - 10m$ $\ldots 3s^2 (^1S)\, 11p - 11n$	$^2F^{\circ}, ^2G^{\circ} \ldots ^2M^{\circ}$ $^2P^{\circ}, ^2D^{\circ} \ldots ^2N^{\circ}$	422	47192

In the compendium of Moore [2941] data are given only for a relatively low number of states of Al, mainly for the states S, P, D and F states. The remaining states were not ascertained experimentally and their energies were evaluated based on the regularities formulated in Chapter I. Particularly, to all the states with $L > 3$ (for the given n) the excitation energy of the term with $L = 3$ was attributed. In Table 220 the terms, not indicated in the compendium [2941], are marked with an asterisk.

The maximum error in the evaluation of the energies of the levels must occur for the state $1s^2 2s^2 2p^6 3s^2 (^1S)\ 5g\ ^2G$ and be approximately 1000 cm^{-1}. Considering that the excitation energy of the corresponding term has a value of the order of 45,000 cm^{-1}, a similar inaccuracy in the determination of the energy does not lead to essential errors in the results of the successive calculations.

$\underline{Al^+}$. The positive ion of monatomic aluminum Al^+ in the ground state ^1S has the electronic configuration $1s^2 2s^2 2p^6 3s^2$. The ionization limit of the states with the electronic configuration $1s^2 2s^2 2p^6 3sn\ell$ has the energy 151,860 cm^{-1}. The first two excited states of the Al^+ ion, indicated in Table 211, are connected with the transition of one 3s-electron to the 3p-state. The terms forming on transition of the 3s-electron to higher states have an excitation energy exceeding 90,000 cm^{-1}, and with simultaneous transition of two 3s-electrons to 3p-states, above 85,000 cm^{-1}. Therefore, they are not discussed in the present Handbook.

$\underline{Al_2}$. The existence of the Al_2 molecule has been shown experimentally by mass-spectrometric studies [1107]. To date, however, the spectrum and structure of the Al_2 molecule have not been studied experimentally.* The attempt to obtain the absorption spectrum and the emission spectrum of Al_2, undertaken in the work [30], was not crowned with success. Hence, the molecular constants of Al_2 adopted in the present Handbook are based on the results of approximate evaluations. It should be noted that a sufficiently sound evaluation of the interatomic distance r_{Al-Al} and of the frequency of the vibrations of the Al_2 molecule is impossible, so long as the corresponding constants for Ga_2, In_2 and Tl_2 are unknown. The interatomic distance in the Al_2 molecule was evaluated by comparing the interatomic distances in the molecules B_2, BX and AlX, where X = H, O, N, F, Cl, or Br and taken to be (2.4 ± 0.06) A, which corresponds to $B_e = 0.22 \pm 0.02$ cm^{-1}. On the basis of this interatomic distance the value of the oscillation frequency, Al_2: $\omega_e = 520 \pm 50$ cm^{-1}, was calculated by means of the Guggenheimer equation (see page 88). The reliability of the quantity ω_e so obtained is confirmed by a comparison of the force constants of the X_2 molecules of different groups of the periodic system. By analogy with B_2 it can be suggested that the ground state of Al_2 is the state $^3\Sigma$ and the first excited state has an energy of the order of 30,000 ± 3000 cm^{-1}. The molecular constants of Al_2 adopted in the present Handbook are indicated in Table 222.*

TABLE 221

Energy Levels of the Aluminum Atom

Номер уровня A	B Состояние		E Статистический вес	F Энергия, $см^{-1}$
	C электронная конфигурация	терм D		
0	$1s^2 2s^2 2p^6 2s^2$	^1S	1	0
1	$1s^2 2s^2 2p^6 3s 3p$	$^3P_0$	1	37392,0
2	$1s^2 2s^2 2p^6 3s 3p$	$^3P_1$	3	37453,8
3	$1s^2 2s^2 2p^6 3s 3p$	$^3P_2$	5	37579,3
4	$1s^2 2s^2 2p^6 3s 3p$	^1P	3	59849,7

A) Number of level; B) state; C) electronic configuration; D) term; E) statistical weight; F) energy, cm^{-1}.

AlO. The ground electronic state of the AlO molecule is the state

$X^2\Sigma$. As a result of studying experimentally the AlO spectrum the existence of two further stable states has been ascertained: $B^2\Sigma$ and $C^2\Pi_i$. By analogy with the BO molecule it can be expected that the first excited State of AlO must be a state of the type $A^2\Pi$. For the time being, however, transitions associated with this state were not observed in the AlO spectrum. The evaluation using the Shifrin relation (I.31) and the comparison of the excitation energies of the monotype electronic states of AlO and BO allow the estimate that the energy of the $A^2\Pi$ state of the AlO molecule is approximately 17,000 ± 2000 cm^{-1}.

In the AlO spectrum three systems of bands were identified: the green system $B^2\Sigma - X^2\Sigma$, the ultraviolet system $C^2\Pi - X^2\Sigma$ and the system $C^2\Pi - B^2\Sigma$, situated in the region of 7900-8900 A.

The molecular constants of AlO in the state $X^2\Sigma$ and $B^2\Sigma$ were ascertained by studying the repeatedly investigated green system which has been observed in both the emission spectrum [3681, 3546, 3296, 2828, 2952, 2530, 1290, 3481, 3482, 3484, 1797] and the absorption spectrum [279, 2123, 2400]. The results of papers devoted to the study of this system and published till 1950 are discussed in the Handbook [649] and in the book of Herzberg [2020]. The molecular constants of AlO in the states $X^2\Sigma$ and $B^2\Sigma$ recommended in these publications are based on the data obtained by Sen [3681] (rotation constants) and Roy [3546] (vibration constants). The rotation constants were ascertained by Sen by analyzing the fine structure of the bands 0-0, 1-0, 0-1, 2-1, 1-1 and 1-2 (the bands were recorded in the second order on an apparatus with a dispersion of 0.62 A/mm). The vibration constants of AlO in the states $X^2\Sigma$ and $B^2\Sigma$ were obtained by Roy [3546] using the edges of the bands. Since in the spectrum studied by Roy bands were observed up to v' and $v'' \leq 11$, the constants ascertained by him are much more accurate than the constants obtained earlier by Mecke [2828] using the data of Moerikoefer [2952] and Pomeroy [3296] on the basis of studying a smaller number of bands.

In 1957, Lagerqvist, Nilsson and Barrow [2530] studied again carefully the system $B^2\Sigma - X^2\Sigma$. The spectrum was excited in a direct-current aluminum arc. The 0-0 band was photographed using an apparatus with plane grating (dispersion 0.37-0.43 A/mm), the remaining bands were taken on a Wood concave grating with a dispersion of 1.2 A/mm. The bands with $v' \leq 3$ and $v'' \leq 5$ were studied. The analysis of the rotational structure of the bands led to constants which conform excellently with those found by Sen. The analysis of the vibrational structure was carried out on the beginnings of the bands; the constants ascertained ω''_e, $\omega''_e x''_e$, $\omega'_e x'_e$ differ slightly from the values recommended by Roy [3546].* Subsequently, bands of the green system of AlO were obtained by Goodlett and Innes [1797] on excitation of the spectrum in a coazial cathode. The spectrum was recorded in the third order of the grating on an apparatus with a dispersion of 0.4 A/mm. The results of the analysis of the vibrational and rotational structures of the green bands are in good agreement with the data obtained in the works [3681, 3546, 2530]. The only particularity of the study made in the work [1797] is the determination from the 0-0 band of the constant of spin doubling for the lines with low values of the rotational quantum number K.**

Since in the first edition of the present Handbook the thermodynamic functions of AlO were calculated from the constants $X^2\Sigma$ and $B^2\Sigma$ found by Sen [3681] and Roy [3546] and the difference of the new constants obtained by Lagerqvist, Nilsson and Barrow [2530] has practically no effect on the values of the AlO functions, in the present edition of the Handbook for the molecular constants of AlO in the states

$X^2\Sigma$ and $B^2\Sigma$ the values are used which were ascertained by Sen and Roy and are indicated in Table 222.

The molecular constants of AlO in the state $C^2\Pi$ were detected by studies of the ultraviolet system with complex structure of the bands. The bands of this system in the AlO spectrum were first observed by Coheur and Rosen [1145] who succeeded in achieving only a very approximate analysis of their vibrational structure.* Subsequently, Goodlett and Innes [1797] exciting the AlO spectrum in a coaxial cathode photographed the bands of the ultraviolet system in the second and the third orders of the spectrum. Owing to the use of an apparatus with high dispersion and high resolution the authors of the work succeeded in showing that the bands of this system consist of two subbands each of which in turn is formed by two intense branches. The analysis of the vibrational and rotational structures of the bands led to the conclusion that the lower state of the ultraviolet system is the ground state $X^2\Sigma$, while the upper state is the inverse state $^2\Pi_i$ ($A = -75.78$ cm^{-1}). The molecular constants of AlO detected by Goodlett and Innes [1797] in the state $C^2\Pi$ are indicated in Table 222 and used in the present Handbook.**

AlH. The ground electronic state of the AlH molecule is the state $X^1\Sigma$. The spectrum of the AlH molecule was studied by many authors. The most intense system in the AlH spectrum is the system situated in the range of 4000-5000 A and due to the transition $A^1\Pi \rightleftarrows X^1\Sigma$. Besides, in the AlH spectrum five very weak singlet systems occur and a system of bands, associated with the transition between the triplet states. The results of the works of Holst [2113, 2112], Holst and Hulthen [2115], Howson [2140], Moerikoefer [2952] and Ericksson, Hulthen and Bengtsson [1492] published till 1950 are summarized in the Handbook [649] and in the monography of Herzberg [2020].

In 1954, Zeeman and Ritter [4376] studied again the system of the bands $A^1\Pi - X^1\Sigma$. The spectrum was observed introducing aluminum into the graphite tube of a King oven. The oven was filled with pure hydrogen the pressure of which was varied from 40 to 50 mm Hg. When the temperature of 2100°C was reached the spectrum was taken in both emission and absorption in the second and third orders of a 21-foot concave grating. The rotation constants of AlH in the states $A^1\Pi$ and $X^1\Sigma$ ascertained by analyzing the fine structure of the bands 0-0, 0-1, 0-2, 0-3, 1-0, 1-1, 1-2, 1-3 and 1-4 are indicated in Table 222 and adopted in the present Handbook. The vibration constants of AlH in the ground state and the value $\Delta G_{1/2}$ for the state $A^1\Pi$, ascertained in the work [4376] by means of the wave numbers of the beginning of the bands (the oscillation frequency and constants of the anharmonicity in the state $A^1\Pi$ could not be determined, since only bands with $v' = 0$ and 1 were ascertained) are equally given in Table 222. It should be noted that the constants in the states $X^1\Sigma$ and $A^1\Pi$, ascertained by Zeeman and Ritter [4376] and adopted in the present Handbook, are more accurate than the constants obtained in the old works and recommended in the Handbook [649] and in the monography [2020].

The molecular constants of AlH in the state $a^3\Pi$ given in Table 222 were taken from the data of Holst [2110] who studied the system of bands associated with the transition $^3\Sigma - {}^3\Pi$. The spectrum was ohotographed in the second order of the grating on an apparatus with a dispersion of 0.94 A/mm. Since in the AlH spectrum no intercombination transitions were observed, Table 222 gives the approximate value of the excitation energy of the state $a^3\Pi$, suggested by Holst [2110] on the basis of a rough estimate; it may contain an error of the order of ± 2000 cm^{-1}.

The excitation energies of the remaining known electronic states of the AlH molecule exceed 45,000 cm^{-1}, and, since the molecular constants in these states are very inaccurate, they are not given in Table 222.

TABLE 222

Adopted Values of the Molecular Constants of Al_2, AlO, AlH, AlF, AlCl and AlN

Молекула 1	Состояние 2	T_e	ω_e	$\omega_e x_e$	B_e	$\alpha_1 \cdot 10^3$	$D_0 \cdot 10^6$	r_e
		3 · см$^{-1}$						Å
Al_2	$X^3\Sigma^{а}$	0	$520^{б}$	—	$0,22^{в}$	—	—	$2,40^{в}$
AlO	$X^2\Sigma^{г}$	0	978,1	7,12	0,64148	0,575	1,109	1,6176
	$B^2\Sigma^{д}$	20699,2	870,0	3,80	0,60417	0,453	1,166	1,6668
	$C^2\Pi_i$	33174,6	728,4	7,5	0,6027	0,36	—	—
AlH	$X^1\Sigma$	0	1682,563	$29,090^{е}$	6,39066	$18,581^{ж}$	$357,06^{з}$	1,64822
	$a^3\Pi$	$20000^{в}$	$1688^{к}$	—	$6,704^{к}$	—	400	—
	$A^1\Pi$	$23470,33^{л}$	$1082,76^{м}$	—	6,38688	73,229	$370,1^{н}$	1,64826
AlF	$X^1\Sigma$	0	801,95	4,70	0,55228	0,483	0,97	1,6547
	$a^3\Pi$	$33000^{в}$	827,8	3,93	$0,550^{к}$	—	—	—
	$A^1\Pi$	43947,73	804,69	$6,3525^{о}$	0,55660	0,556	1,10	1,648
AlCl	$X^1\Sigma^+$	0	481,30	1,95	0,242	0,2	$0,25^{п}$	2,13
	$a^3\Pi$	24594	524,35	2,175	0,250	0,2	—	2,10
	$A^1\Pi$	38254,0	449,96	$4,37^{р}$	0,259	0,6	—	2,07
	$b^3\Sigma$	43590	$350^{в}$	—	$0,226^{к}$	—	—	—
AlN	$X^3\Pi^{с}$	0	$1017^{б}$	—	$0,65^{в}$	—	—	$1,68^{в}$

1) Molecule;

2) state;

3) cm^{-1}

a) Adopted in analogy to B_2;

b) evaluated by means of the Guggenheimer Eq. (I.41);

c) evaluation;

d) in the work of Lagerqvist, Nilsson and Barrow [2530] the following molecular constants are proposed for the state $X^2\Sigma$; $\omega_e'' = 979.23$, $\omega_e''x_e'' = 6.97$, $B_v'' = 0.64136-0.00580\ (v + 1/2)$, $D_v'' = (1.08 \pm 0.02)\ (v + 1/2)\cdot 10^{-6}$ cm^{-1}, $r_e'' = 1.6178$ A and for the state $B^2\Sigma$: $T_e = 20688.95$, $\omega_e' = 870.05$, $\omega_e'x_e' = 3.57$, $B_v' = 0.60408-0.00447\ (v + 1/2)$, $D_e' = 1.10\cdot 10^{-6}$ cm^{-1}, $r_e' = 1.6668$ A.

e) in analogy to BO it can be expected that in the system of AlO terms the state $A^2\Pi$ occurs with an excitation energy lower than the energy of the state $B^2\Sigma$ (the evaluation

from the relation of Shifrin (I.31) gives $T_e(A^2\Pi) \sim 17{,}00 \pm$ $\pm$ 2000 cm^{-1});
f) $\omega_0 y_0 = 0.2389\ cm^{-1}$;
g) $\alpha_2 = 0.00161\ cm^{-1}$.
h) the value D_e is given; $\beta_1 = -0.0573 \cdot 10^{-4}$, $\beta_2 = 0.00282 \cdot 10^{-4}$ cm^{-1};
l) the value ω_0 is given, calculated by means of Eq. (I.36);
k) the value B_0 is given;
l) the value ν_{00} is given;
m) the value $\Delta G_{1/2}$ is given;
n) the value D_e is given; $\beta_1 = 4.9957\ 10^{-4}\ cm^{-1}$;
o) $\omega_e y_e = 0.01779$, $\omega_e z_e = 0.004845\ cm^{-1}$;
p) the value D_0 is given, calculated by means of relation (I.36);
q) $\omega_e y_e = -0.216\ cm^{-1}$;
r) taken in analogy to BN.

AlF. The ground electronic state of AlF is the state $^1\Sigma^+$. The AlF spectrum in both emission and absorption was studied repeatedly [3465, 3540, 3028, 3029, 3541, 3030, 3031, 661, 1354, 1455, 657, 3032]. The most intense band system in the AlF spectrum lies in the region of 2360-2200 A and is due to the transition $A^1\Pi - X^1\Sigma$. Apart from this system, a large number of other singlet systems is associated with the AlF molecule and also a series of systems caused by transitions between triplet states. Intercombination transitions were not detected in the AlF spectrum.

First, Rochester [3465] detected AlF bands in the AlF absorption spectrum. By analogy with AlCl and AlBr he identified the system situated in the region of 2360-2200 A, with the transition $A^1\Pi - X^1\Sigma$ and obtained an equation describint the position of the edges of the Q-branches. The vibration constants of AlF in the states $A^1\Pi$ and $X^1\Sigma$ ascertained by Rochester [3465] are recommended in the monography of Herzberg [2020] and in the Handbook [649]. Later, Rawlison and Barrow

[3540] came to the conclusion that the value $\omega_e''x_e''$ found by Rochester is too high and, consequently, the analysis of the vibrational structure of the $A^1\Pi$ -- $X^1\Sigma$ system carried out by him is not correct. This conclusion was drawn based on a comparison of the values of the dissociation energies of AlF ascertained from thermochemical measurements [1863] and calculated by extrapolating the vibrational levels of the state $X^1\Sigma$ of AlF using the constants obtained by Rochester, and as a result of the comparison of the values $x_e\mu^{1/2}$ for the halides of the third group.* The authors [3540] studied again the spectrum of AlF excited in a discharge tube into the coaxial cathode of which a mixture of Al and AlF_3 was introduced. The bands of the system $^1\Pi$ – $^1\Sigma$ were taken on a Hilger quartz spectrograph, with a dispersion of the order of 2 A/mm in the region of 2000 A. Though the frequencies of the edges of the Q branches were consistent with the data of Rochester, the assignment of the bands carried out anew made it possible to obtain the equation

$$\begin{gathered}\nu_Q = 43947{,}6 + [803{,}95\,(v' + {}^1/_2) - 6{,}14\,(v' + {}^1/_2)^2 - 3{,}91 \cdot 10^{-3}\,(v' + {}^1/_2)^4] - \\ - [801{,}52\,(v'' + {}^1/_2) - 4{,}70\,(v'' + {}^1/_2)^2 + 0{,}010\,(v' + {}^1/_2)^3],\end{gathered}$$

which describes the position of the edges of the Q branches much better than the constants ascertained by Rochester.

In 1953-1957, there appeared in the literature a large number of works by Barrow with co-workers [3541, 661, 1354, 1355, 657] and of works by Naude and Hugo [3029, 3028, 3030, 3031, 3032], devoted to the study of the AlF spectrum. The values of the vibration constants of AlF in the states $X^1\Sigma$ and $A^1\Pi$ ascertained by analyzing the systems of bands, associated with transitions including these states, differ very slightly from the values suggested in the work [3540]. The most accurate vibration constants in the states $X^1\Sigma$ and $A^1\Pi$ describing the position of the edges of the Q branches of 40 bands of the $A^1\Pi$ – $X^1\Sigma$

system with v" $\leq$ 6 and v' $\leq$ 16 were obtained by Barrow, Johns and Smith [657] who studied the system $A^1\Pi - X^1\Sigma$ in both emission and absorption spectra. The mean discrepancy between the wave numbers of the edges of the Q branches obtained from the spectrograms and calculated by means of the vibration constants is approximately 0.48 cm^{-1}.

Naude and Hugo [3032] carried out a careful study of the band systems associated with the transitions $B^1\Sigma - X^1\Sigma$ and $C^1\Sigma - X^1\Sigma$ which lie in the vacuum ultraviolet. The spectrum excited in the coaxial cathode of a discharge tube was taken on a three-meter vacuum spectrograph with a dispersion of 0.63 A/mm. In the system $B^1\Sigma - X^1\Sigma$ bands were observed with v' $\leq$ 5 and v" $\leq$ 6, in the system $C^1\Sigma - X^1\Sigma$ bands with v' $\leq$ 3 and v" $\leq$ 5. The vibration constants in the ground state $X^1\Sigma$, ascertained by analyzing both systems are ω''_e = 801.95 and $\omega''_e x''_e$ = 4.70 cm^{-1}, i.e., they are practically consistent with the constants obtained in the work [657]. In the present Handbook vibration constants of AlF in the states $X^1\Sigma$ and $A^1\Pi$ are adopted which are recommended in the work of Barrow, Johns and Smith [657]. These constants are given in Table 222.

For a long time the rotation constants of AlF in the ground electronic state remained unknown, since because of the overlapping by neighboring bands the fine structure of the bands of the system $A^1\Pi - X^1\Sigma$ could be resolved not even in the seventh and ninth orders of the 21-foot concave grating [3028], and other systems associated with the transitions in the state $X^1\Sigma$ are situated in the vacuum ultraviolet. Only in 1956, Barrow, Johns and Smith [657], based on measurements of the distances between the edges of the P and Q branches and the edges of the R and Q branches of 24 bands of the system $A^1\Pi - X^1\Sigma$ as well as on the values of the rotation constants in the state $A^1\Pi$ obtained by Naude and Hugo [3028, 3030] ascertained by means of the equation $\Delta\nu = -\frac{(B' - B'')^2}{4(B' - B'')}$ the values B_v in the state $X^1\Sigma$ for $v'' \leq 6$ and calculated the values B_e, α_1 and r_e equal to 0.5528, 0.00488 cm^{-1} and 1.654 A, respectively.

In 1957, Naude and Hugo [3032] using for recording the AlF spectrum a three-meter vacuum spectrograph obtained in the fourth order of the grating the bands 0-0, 0-1, 0-2, and 1-3 of the system $B^1\Sigma^+ - X^1\Sigma$ and the bands 0-0, 1-3 and 1-4 of the system $C^1\Sigma^+ - X^1\Sigma^+$ with a resolved fine structure. Making use of the values of the rotation constants at different vibrational levels in the states $B^1\Sigma$ and $C^1\Sigma$, obtained by analyzing the systems $C^1\Sigma - A^1\Pi$ and $F^1\Pi - B^1\Sigma$ [3028], the authors of the work [3030] obtained the rotation constants in the state $X^1\Sigma$ of the AlF molecule which are practically consistent with those calculated in the work [657]. These constants are accepted in the present Handbook and given in Table 222. The rotation constants of AlF in the state $A^1\Pi$, indicated in Table 222, were obtained by Naude and Hugo [3028] by analyzing the fine structure of 11 bands of the system $C^1\Sigma - A^1\Pi$, lying in the infrared region of the spectrum.

At present, for the AlF molecule, apart from the low excited state $A^1\Pi$ a large number of other excited singlet states ($B^1\Sigma$, $C^1\Sigma$, $D^1\Delta$, $F^1\Pi$, $G^1\Sigma$) are known with which are associated different systems, ascertained in the emission and absorption spectra of AlF. Since, however, the excitation energies of these states exceed 50,000 cm^{-1} they are not indicated in Table 222.

Apart from singlet systems, in the AlF spectrum band systems are ascertained which are caused by transitions between triplet states. The analysis of the vibrational structure of the triplet system of AlF was first carried out by Barrow and Rowlinson [3540]. Later, Dodsworth and Barrow [1354, 1355] performed an analysis of two more systems associated with transitions from the state $^3\Sigma$ to the general lower state $^3\Pi$.

Since, however, intercombination transitions were not observed in the AlF spectrum, the absolute values of the excitation energies of triplet states are unknown. Dodsworth and Barrow [1355], based on the analogy between the $^3\Pi$ states in the molecules BF, AlF, GaF and InF, came to the conclusion that these states are associated with the same electronic configurations and that the dissociations products in these states must be identical. Comparing the dissociation energies of GaF and InF in the states $a^3\Pi$ with the dissociation energies of these compounds in the ground states $X^1\Sigma$ and suggesting that the corresponding relation is valid in the case of AlF, too, the authors of the work [1355] evaluated the excitation energy of the state $a^3\Pi$ as being approximately 33,000 cm^{-1}. The evaluation using the relation (I.31) gives $T_e(a^3\Pi) = 32{,}500 \pm 3000$ cm^{-1}. In the present Handbook $T_e(a^2\Pi) = 33{,}000 \pm 3000$ cm^{-1} is adopted. Table 222 gives the vibration constants in the state $a^3\Pi$, ascertained in the work [1355]. By analogy with the Ga and In fluorides it is accepted that the state $^3\Pi$ of the AlF molecule is the normal state.

AlCl. The ground electronic state of AlCl is the state $X^1\Sigma^+$. The spectrum of the AlCl molecule was studied in both emission [2247, 805, 2740, 2113, 2111, 2904, 3607, 3408, 2114] and absorption [2905].

The most intense bands of AlCl, situated in the wavelength region 2810-2550 A and caused by the electron transition $A^1\Pi - X^1\Sigma$ were studied by Bhaduri and Fowler [805], Mahanti [2740] and Holst [2113, 2111 2114] in the emission spectrum and by Miescher [2905] in the absorption spectrum. In the work [805] the AlCl spectrum was excited in the discharge in $AlCl_3$ vapors in the presence of helium and taken on a spectrograph with a dispersion of 2.85 A/mm in the region of 2550 and 4.0 A/mm at 2800 A. The analysis of a large number of bands forming the sequence $\Delta v = 0, \pm 1, \pm 2$, 3 and 4 with $v' \leq 9$ and $v'' \leq 13$ enabled

Bhaduri and Fowler [805] to detect the vibration constants of AlCl in the states $A^1\Pi$ and $X^1\Sigma$ which are given in Table 222 and adopted in the present Handbook. The vibration constants in the states $A^1\Pi$ and $X^1\Sigma$ ascertained by Bhaduri and Fowler [805] are recommended in the book of Herzberg [2020] and in the Handbook [649], too. Similar values of the respective constants were obtained by Mahanti [2740] and Holst [2111]. The use of a spectrograph with a dispersion of 0.96 A/mm enabled Holst [2113] to resolve the rotational structure of six bands 9-11, 9-12, 9-13 and 10-14, 10-15, 10-16 and to ascertain the values of the rotation constants for high vibrational levels in the states $A^1\Pi$ and $X^1\Sigma$. The rotation constants indicated in Table 222 for AlCl in these states were detected in the dissertation of Holst [2114] summarizing his previous investigations. Since the authors of the Handbook could not look through this dissertation, in the Handbook the constants from this work, given in reference tables [649, 2020], are adopted.

Studying the spectrum of the noncondensed discharge through $AlCl_3$ vapors in helium atmosphere Sharma [3607] ascertained two new AlCl band systems situated in the wavelength regions of 4154-3970 and 561σ-5265 A. The analysis of the structure of the bands taken in the first order of a 21-foot concave grating has shown that the first group is associated with the intercombination transition $a^3\Pi - X^1\Sigma^+$ and the bands in the green region of the spectrum are caused by the transition between the triplet states $b^3\Sigma - a^3\Pi$. In the system $a^3\Pi - X^1\Sigma$ 12 bands were analyzed forming sequencies $\Delta v = 0, \pm 1$ with $v', v'' \leq 4$. For the analysis use was made of the values of the constants of AlCl in the ground state, ascertained by Bhaduri and Fowler [805] and Holst [2114]. In the triplet system $b^3\Sigma - a^3\Pi$ one succeeded only in obtaining the bands 0-0, 0-1 and 0-2. Transitions from the level $v' = 1$ were not observed. The data obtained in the work [3607] did not allow to carry out a detailed analysis of the fine structure of the bands, since only the branches at the longwave end of each band were resolved. The molecular constants of AlCl in the triplet states $a^3\Pi$ and $b^3\Sigma$ ascertained by Sharma are accepted in the present Handbook and given in Table 222.

Subsequently, Reddy and Rao [3408] investigating the emission spectrum of AlCl ascertained in the wavelength region of 2075-1820 A a large number of bands belonging to six different systems. Five out of them have a general lower state which is the ground state of the AlCl molecule. The approximate analysis allowed the evaluation of the excitation energy and the oscillation frequency of the upper states. Since the excitation energies of these states exceed 50,000 cm^{-1}, they are not given in Table 222.

AlN. The spectrum and structure of the AlN molecule were not studied experimentally. Hence, the molecular constants of AlN, suggested in the present Handbook, are obtained as the result of approximate evaluations. The interatomic distance in the AlN molecule was evaluated based on the comparison of the interatomic distances in the diatomic molecules of the oxides and nitrides of a number of elements. Such a comparison indicated that the interatomic distance in the nitride molecule of the given element (r_{X-N}) is 0.04-0.07 A longer than the interatomic distance r_{X-O} in the molecule of the respective oxide. Since $r_{Al-O} = 1.62$ A, it has been assumed in the present Handbook that $r_{Al-N} = 1.68 \pm 0.08$ A (the corresponding value B_e is 0.65 ± 0.06 cm^{-1}). Based on the value r_{Al-N} so evaluated, by means of Eq. (I.41) the frequency of the normal oscillation $\omega_e = 1070 \pm 100$ cm^{-1} was calculated. By analogy with the molecule BN it was accepted that the ground electronic state of AlN is a state of the type $^3\Pi$. The adopted values of the molecular constants of AlN are given in Table 222.

Al_2O. The existence of the Al_2O molecule has been shown by mass-spectrometric studies [1164a, 1405]. The literature contains, however, no information whatever on studies of the structure and spectra of the Al_2O molecule. Based on general notions on the orientation of chemical bonds it is assumed in the present Handbook that the Al_2O molecule has a nonlinear symmetric structure (point group C_{2v}). A sufficiently well-founded evaluation of the molecular constants of Al_2O is made difficult because of the absence of any data whatever on the nature of the Al-O bond in this molecule. Assuming for Al_2O a nonlinear symmetric structure it can be suggested that the Al-O bonds in such a molecule must be single and the angle between the bonds must have a value of the order of 105°. Based on the comparison of the values of the interatomic distances and the force constants of the bonds in the molecules AlO, BO and in such polyatomic oxygen compounds of boron where the single bond B-O occurs, the length of the Al-O bond and the force of the bond f_{Al-O} were taken to equal 1.78 A and $2.8 \cdot 10^5$ dyne$\cdot$cm^{-1}, respectively.*

TABLE 223

Adopted Values of the Molecular Constants of Al_2O, AlF_2, AlF_3, $AlCl_2$, $AlCl_3$

Молекула 1	ν_1	ν_2	ν_3	ν_4	$I_A I_B I_C$ 3	σ
	2 $см^{-1}$				[illegible] $(г \cdot см^2)^3$	
Al_2O	650	270	700		[illegible]	2
AlF_2	700	240	870	—	375	2
AlF_3	700	300	950 (2)	300 (2)	3974	6
$AlCl_2$	470	130	540	—	7000	2
$AlCl_3$	350	215	610 (2)	130 (2)	$1286 \cdot 10^2$	6

1) Molecule; 2) cm^{-1}; 3) $(g \cdot cm^2)^3$.

Table 223 gives the values of the fundamental frequencies and the products of the main moments of inertia of Al_2O, calculated using

Eqs. (P4.30) and (P3.17) and the above-mentioned constants. The value of the constant f_a/d^2 needed for the calculation of the fundamental frequencies by means of Eqs. (P4.30) was evaluated based on a comparison of the magnitude of this constant with other molecules of the type X_2O and taken to be $0.4 \cdot 10^5$ dyne·cm^{-1}.

It should be noted that the adopted structural parameters of Al_2O are in satisfactory agreement with the results of a preliminary study of the structure of the Ga_2O molecule carried out by the electron diffraction method by Akishin et al [4a]. In accordance with the results of this work, Ga_2O has a nonlinear symmetric structure (point group C_{2v}) with the following structural parameters: $r_{Ga-O} = 1.83 \pm 0.02$ A, ∠GaOGa = 145°. The latter was determined with a low accuracy and in future more precise definitions are required; as to the value r_{Ga-O} it confirms, apparently, the single nature of this bond. At the same time mass-spectrometric studies of the evaporation of aluminum oxides (see page 1612) led to the conclusion that the atomization energy of this molecule is two times higher than the dissociation energy of AlO. The authors of the work [1405a] made the suggestion that this can be caused by the interaction of aluminum atoms; another edplication may be the assumption of a double nature of the Al-O bond in Al_2O which must lead to a simultaneous increase of the angle between the bonds. Both these suggestions are, however, so at variance with the usual notions on the nature of the bonds of the oxygen atom that they are not considered in the evaluation of the Al_2O constants.* The error of the fundamental frequencies of Al_2O, given in Table 223, can be estimated 15-20% of their values, and those of the adopted values r_{Al-O} and ∠AlOAl ± 0.05 A and ±10°, respectively.

An evaluation of the molecular constants of Al_2O has been made in the works of Drowart, De Maria, Burns and Inghram [1405a] and of Cook, Filler et al [1164a]. In both works it has been accepted that the Al_2O molecule has a nonlinear symmetric structure. Drowart et al evaluated the angle AlOAl as being 110° and assuming that the force constant of the Al-O bond and the length of this bond equal to corresponding values in the AlO molecule and the ratio $f_a/d^2/f_d$ in Al_2O is 0.094 (mean for a series of molecules of type X_2O) they ascertained using Eqs. (P4.30); $\nu_1 = 1079$, $\nu_2 = 351$ and $\nu_3 = 921$ cm^{-1}. In the work [1164a] the values of the fundamental frequencies of Al_2O were adopted equal to $\nu_1 = 1580$, $\nu_2 = 500$ and $\nu_3 = 970$ cm^{-1} (the method of evaluating them is not indicated in the work).

$\underline{AlF_2 \text{ and } AlCl_2}$. The literature fails to prode any data on the molecular constants of AlF_2 and $AlCl_2$. An approximate evaluation of the fundamental frequencies and structural parameters of these radicals was carried out by Heimgartner [1983] ($AlCl_2$) and Tatevskiy, Veyts and Gurvich [51] (AlF_2 and $AlCl_2$). Apparently, the values of the fundamental frequencies of $AlCl_2$, ascertained by Heimgartner [1983] $\nu_1 = 900$ $\nu_2 = 550$ and $\nu_3 = 1100$ cm^{-1} are not correct, since they were obtained with the aid of an evaluation based on the comparison of the frequencies of SO_2, NO_2, ClO_2 and Cl_2O. The force constant of the Al-Cl bond in $AlCl_2$ corresponding to the frequencies found by Heimgartner is $8.5 \cdot 10^5$ $dyne \cdot cm^{-1}$, i.e., it is four times higher than the force constant in AlCl, which is unlikely.

Tatevskiy, veyts and Gurvich [51] evaluating the constants of triatomic halides of aluminum proceeded from the assumption that AlF_2 and $AlCl_2$ just as BF_2 and BCl_2 have a nonlinear symmetric structure and belong to the point symmetry group C_{2v}.* Suggesting that the bonds in these molecules are brought about by two p-electrons of the aluminum atom, the authors of the work [51] assumed that the angle XAlX is 110 ± 10° and the interatomic distance r_{Al-F} is 1.65 ± 0.03 A (as in the AlF molecule), and $r_{Al-Cl} = 2.13 \pm 0.03$ A (as in AlCl). Based on the values of the geometric parameters thus obtained the products of the moments of inertia of AlF_2 and $AlCl_2$, given in Table 223, were calculated.

The fundamental frequencies of the AlF_2 and $AlCl_2$ molecules were calculated in the work [51] by means of the equations of the field of valence forces neglecting the constants of the interaction of bonds and the angle and considering the interaction of neighboring bonds [Eqs. (P4.30) and (P4.29)]. The calculations were carried out on the basis of two sets of force constants: 1) force constants of AlX_2 molecules equal to the force constants of AlX_3 molecules (accordingly, for AlF_2 in 10^5 dynes·cm^{-1}: $f_d = 5.0$, $f_{dd} = 0.5$, $f_a/d^2 = 0.2$ and for $AlCl_2$: $f_d = 2.5$, $f_{dd} = 0.25$, $f_a/d^2 = 0.1$) and 2) the force constants of the Al-X bonds equal to the force constants in the corresponding diatomic AlX molecules, and the deformation constants and the constants of the interaction of bonds satisfy the relationships $f/f_d(AlX_2) = f/f_d\ (AlX_3)$ (AlF_2: $f_d = 4.22$, $f_{dd} = 0.4$, $f_a/d^2 = 0.17$ and $AlCl_2$: $f_d = 2.09$, $f_{dd} = 0.21$, $f_a/d^2 = 0.08$. The fundamental frequencies of AlF and $AlCl_2$ so calculated have been adopted in the first edition of the Handbook. The calculation of the frequencies in the work [51], however, has been performed using the incorrect values of the force constants of AlF_3 and $AlCl_3$, obtained in the work of Stepanov [393] (see below).

The fundamental frequencies of AlF_2 and $AlCl_2$ adopted in the present edition of the Handbook and given in Table 223 have been evaluated in the same way as in the work [51], but with force constants of AlF_3 and $AlCl_3$, calculated from the frequencies of these molecules, given in Table 223.

Since the discrepancy between the values of the frequencies calculated applying the different methods amount to 5-10%, it can be suggested that the possible errors in the frequencies recommended have the same magnitude.

Since in the AlF_2 and $AlCl_2$ molecules electrons with unpaired spins occur their ground states must be doublets.

$\underline{AlF_3}$. The electron diffraction study of the structure of the AlF_3 molecule, carried out by Akishin, Rambidi and Zasorin [66] has shown that the AlF_3 molecule has a planar symmetric structure with interatomic distances $r_{Al-F} = 1.63 \pm 0.02$ A and belongs to the symmetry group D_{3h}. The value of the product of the moments of inertia of AlF_3, calculated for this value of the interatomic distance, is given in Table 223.

The spectrum of the AlF_3 molecule has not been studied experimentally. Hence, the vibration frequencies necessary to carry out the calculation of the thermodynamic functions of AlF_3, can be ascertained only as a result of approximate evaluation. The values of the fundamental frequencies of AlF_3 which were adopted in the first edition of the Handbook had been calculated by Stepanov [393] using the force constants of $AlCl_3$, evaluated on the basis of a comparison of the force constants of BF_3, BCl_3, BBr_3 and $AlCl_3$. The results of the works of Heise and Wieland [1984] and Klemperer [2440] show, however, that Stepanov [393] used for the calculation of the force constants of $AlCl_3$ incorrect values of the fundamental frequencies of $AlCl_3$ and, accordingly, miscalculated the force constants and frequencies of AlF_3. In the present edition of the Handbook for the evaluation of the force constants of AlF_3 and the subsequent calculation of the frequencies of AlF_3 the force constants of $AlCl_3$ were recalculated using the frequency values suggested by Heise and Wieland (see below). The calculation was performed by two methods: by means of the equations of the field of valence forces of a more simple type (P4.41) with the constants of interaction being zero, and by means of Eqs. (P4.40) considering the interaction of the bonds. In the assumption that the substitution of fluorine for chlorine in molecules with a central boron atom is equivalent to the analogous substitution in molecules with a central aluminum atom, a comparison of the force constants of $AlCl_3$ with the constants of BF_3 and BCl_3 made it possible to evaluate the constants of AlF_3 * and calculate the fundamental frequencies the values of which are given in Table 223. The values of the AlF_3 frequencies so obtained are very approximate, the possible error in them is 10-20%.

$\underline{AlCl_3}$. For a long time in the literature no experimental data were available on the spectrum and structure of the $AlCl_3$ molecule, since in vapors aluminum chloride occurs mainly in the shape of Al_2Cl_6. The spectrum and structure of Al_2Cl_6 have been studied repeatedly (see [3171, 966, 1686, 1959, 1681]). In the first edition of the Handbook the frequencies and geometric parameters of $AlCl_3$ have been calculated based on approximate evaluations. At the same time it has been suggested that in analogy with the well-known molecules BF_3, BCl_3 and BBr_3 the $AlCl_3$ molecule has a planar symmetric structure and belongs to the point symmetry group D_{3h}. The interatomic distance r_{Al-Cl} was adopted equal to the interatomic distance in the AlCl molecule (r_{Al-Cl} = 2.13 A). For the fundamental frequencies of $AlCl_3$ the values were recommended, evaluated by Heise and Wieland [1984] based on the frequencies of the Al_2Cl_6 molecule: $\nu_1 = 350$, $\nu_2 = 215$, $\nu_3(2) = 615$ and $\nu_4(2) = 130$ cm^{-1}.

In 1956, Klemperer [2440] succeeded first in obtaining the infrared spectrum of $AlCl_3$. The spectrum was studied in the region from 1200 to 325 cm^{-1}. In the emission spectrum,** studied by passing aluminum chloride vapors through the bulb heated by a nichrome furnace to the temperature of 900°C, a single band was ascertained at 610 cm^{-1}.

Since at such a temperature the aluminum chloride vapors consist almost completely of molecules of the monomer $AlCl_3$, Klemperer attributed the band ascertained to the valence vibration of the Al-Cl bond of the $AlCl_3$ molecule. In the opinion of the author of the work [2440] such an interpretation is fully consistent with the suggestion of a planar symmetric structure of the $AlCl_3$ molecule, since a molecule belonging to the symmetry group D_{3h} must have three frequencies active in the infrared spectrum: two of them connected with the change of the angles between the bonds must be situated in a region of longer wavelengths than the region which has been studied in the work [2440], and the third caused by antisymmetric valence vibrations of the Al-Cl bonds must have a frequency of the order of 600 cm^{-1}, i.e., similar to that ascertained in the spectrum. It may be mentioned that the assessed experimental values of the frequencies of the antisymmetric vibrations of the Al-Cl bond in the dimer (Al_2Cl_6) and the monomer ($AlCl_3$), 625 and 610 cm^{-1}, respectively, are similar to the value evaluated for this frequency by Heise and Wieland (615 cm^{-1}); this is a certain confirmation of the correctness of the evaluation of $AlCl_3$ frequencies accomplished by Heise and Wieland [1984]. Besides, it is confirmed by the following considerations. If in analogy with BF_3, BCl_3 and BBr_3 it is suggested that in the $AlCl_3$ molecule the force constant of planar deformation vibrations f_a/d^2 is 1/25 of the value of the force constant of the Al-Cl bond (f_d), then the value found by Klemperer for the frequency of the antisymmetric valence vibration $\nu_3 = 610$ cm^{-1} is in keeping with the value $f_d = 2.5 \cdot 10^5$ $dynes \cdot cm^{-1}$, calculated by means of Eqs. (P4.41). The latter allows to calculate* the frequencies $\nu_1 = 345$ and $\nu_4 = 150$ cm^{-1}. The assumption that the relation of the force constant of some deformation vibrations to the constant f_d in the $AlCl_3$ molecule equals approximately such a relation in the boron halide molecules leads to the values $f_{\Delta}/d^2 = 0.24 \cdot 10^5$ dynes·cm^{-1} and $\nu_2 = 235$ cm^{-1}. The comparison indicates that the frequency values of $AlCl_3$ so ascertained are practically consistent with the frequencies evaluated by Heise and Wieland. Therefore, in the present Handbook the frequency values ν_1, ν_2 and ν_4 suggested in the work [1984] are adopted. The frequency of the antisymmetric doubly degenerate vibration ν_3 is taken to be 610 cm^{-1} in accordance with the results of the study of the infrared spectrum [2440].* Obviously, the errors in the values ν_1, ν_2 and ν_4 do not exceed 15%. The error in the value ν_3 is 10-20 cm^{-1}.

The interatomic distance r_{Al-Cl} in the $AlCl_3$ molecule was considered, just as in the first edition of the Handbook, equal to the interatomic distance in the AlCl molecule: $r_{Al-Cl} = 2.13 \pm 0.03$ A.** The product of the momenta of inertia of the $AlCl_3$ molecule, calculated for this value r_{Al-Cl} and the angle ClAlCl 120° is given in Table 223.

§96. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of aluminum and its compounds, discussed in the present Handbook, in the state of the ideal gas were calculated for temperatures from 293.15 to 6000°K and are indicated in the Tables 288-292, 294-296, 298-300, 302 and 304 of Volume II. The calculations were made using the constants adopted in the preceding section.

Al. The thermodynamic functions of monatomic aluminum, given in Table 288 (II), were calculated by means of Eqs. (II.22) and (II.23). The values of the translatory components of the thermodynamic functions of gaseous monatomic aluminum were calculated by means of Eqs. (II.8) and (II.9) with $A_{\Phi} = 2.5388$ and $A_S = 7.5070$ cal/g-atom·degree, those of the electronic components by means of Eqs. (II.20) and (II.21), based on the energy levels presented in Table 220. To simplify the calculation, all electronic states with $n \leq 11$ were considered in the statistical sum at all temperatures.

At $T \leq 5000$°K the errors of the calculated values of the thermodynamic functions of monatomic aluminum are practically determined solely by the inaccuracy of the adopted values of the physical constants and do not exceed 0.005 cal/g-atom•degree. At higher temperatures the errors due to incorporating the excessive states with $n_{max} \leq n \leq 11$, where n_{max} is calculated by means of Eq. (II.18), into the statistical sum and its derivatives and, besides, errors due to the approximate estimates of the excitation energies of a number of levels become essential. Nevertheless, the total error of the calculated values Φ_T^* of monatomic aluminum in the entire temperature range does not exceed 0.01 cal/g-atom•degree.

The thermodynamic functions of monatomic aluminum have been calculated previously in a number of works (see [2355, 1984, 2142, 2334, 2462]. Among them, the calculations of Kolsky et al [2462] (for $T \leq 8000$°K) and Huff, Gordon and Morrell [2142] (for $T \leq 6000$°K) should be noted. At low temperatures the results of all calculations are in good agreement with each other, with the exception of the data of Heise and Wieland [1984], in whose work, apparently, an error was tolerated. The discrepancy between the data of Table 288 (II) and the work [2462] at $T \geq 6000$°K have magnitudes of the order of 0.01 cal/ /g-atom•degree; they are mainly caused by the fact that in the latter in the calculation of the electronic components a number of levels with $n > 11$ were taken into account. At temperatures above 6000°K the discrepancies must pass through zero and increase again and it is due to this fact that Kolsky et al did not consider the levels with $n \leq 11$ which had not been ascertained experimentally in the spectrum of the

Al atom. In the book of Stull and Sinke [3894] the values of the thermodynamic functions of monatomic aluminum calculated in the work [2142] are indicated.

The discrepancy between the values of the thermodynamic functions of Al given in the first edition of the Handbook and Table 288 (II) reaches 0.006 and 0.047 cal/g-atom•degree in Φ^*_{6000} and S°_{6000}; they are due to the fact that in the present edition a more accurate method of calculating the electronic components was used.

$\underline{Al^+}$. The values of the translatory components of the thermodynamic functions of monatomic ionized aluminum were calculated applying Eqs. (II.8) and (II.9) with the A_Φ and A_S mentioned above for monatomic aluminum; the electronic components the contribution of which to the values Φ^*_T and S°_T at temperatures up to 6000° is negligibly low, are not considered in the calculation. The total error of the calculated values of the functions of Al^+ within the entire temperature range does not exceed 0.01 cal/g-atom•degree in the values Φ^*_T and 0.02 cal/g-atom•degree in the values S°_T.

The thermodynamic functions of onefold ionized aluminum were calculated recently in the work of Green, Poland and Margrave [1851a] ($T \leq 50,000°K$). The evaluation was carried out considering all electronic states of Al^+ indicated in the compendium of Moore [2941]. The discrepancy between the results of this evaluation and the data of the Handbook does not exceed 0.02 cal/g-atom•degree.

$\underline{Al_2, AlN}$. The thermodynamic functions of gaseous diatomic aluminum and aluminum nitride, given in Tables 290 (II) and 304 (II), were evaluated by means of Eqs. (II.161) and (II.162) using the approximate rigid rotator-harmonic oscillator model based on the constants evaluated in the preceding section. Since the constants of the anharmonicity of the vibrations, the centrifugal stretching and the vibrational-

-rotational and spin-orbit interactions are unknown for both molecules, the values ln Σ and ln Δ and their derivatives in Eqs. (II.161) and (II.162) were adopted equal to zero. In Table 224 the values of the constants C_{Φ} and C_S in these equations are given and, besides, the values of the quantity θ for interpolation using the tables of the harmonic oscillator. In connection with the fact that in analogy to B_2 and BN in §95 it has been assumed that the molecules Al_2 and AlN have the ground states $^3\Sigma$ and $^3\Pi$, in the values C_{Φ} and C_S, given in Table 224, the addends R ln 3 (for Al_2) and R ln 6 (for AlN) are included.

TABLE 224

Values of the Constants for the Evaluation of the Thermodynamic Functions of Gaseous Al_2, AlO, AlH, AlF, AlCl and AlN

1 Вещество	θ	$x \cdot 10^3$	β_1	β_2	$\frac{q_0}{T}$	$\frac{d_0 \cdot 10^6}{T}$	C_{Φ}	C_S
	2 град				3 град⁻¹		4 кал/моль·град	
Al_2	820,11	—	—	—	—	—	7,6971	14,6526
AlO	1407,1	7,2787	0,9003	0,83	1,08858	3,78	5,4732	12,4287
AlH	2420,4	17,289	2,9446	9,54	0,110383	$12{,}4^{a}$	−1,7314	5,2231
AlF	1153,8	5,8607	0,8784	0,77	1,26400	4,45	4,5935	11,5490
AlCl	692,35	4,0515	0,8297	0,71	2,88450	5,86	7,1453	14,1008
AlN	1539,5	—	—	—	—	—	7,4852	14,4407

1) Substance; 2) degree; 3) degree^{-1}; 4) cal/mole·degree
a) $f_o \cdot 10^{10}/T^2 = 1.65$

The main errors in the calculated values of the thermodynamic functions of Al_2 and AlN are connected with the lack of experimental data on the constants of the molecules of both gases and the consequent application of an approximate method of calculation. These errors have a magnitude of the order of 0.3, 0.8 and 1.2 cal/mole·degree for Al_2 and 1.5-2 cal/mole·degree for AlN in the quantities $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000}. The gross errors of the thermodynamic functions of aluminum nitride at low temperatures are due to the impossibility of considering the splitting of the rotational levels of the state $X^2\Pi$ of the AlN molecule because of the lack of data on the constant of the spin-orbit coupling.

The thermodynamic functions of Al_2 and AlN, given in the first and present editions of the Handbook, are identical. Other evaluations of tables of the thermodynamic functions of these gases are not known in the literature.

AlO and AlH. The thermodynamic functions of aluminum monoxide and monohydride, given in Tables 291 (II) and 294 (II), were calculated using Eqs. (II.161) and (II.162). The quantities $\ln \Sigma$ and $T\,\partial/\partial T \ln \Sigma$ in these equations were evaluated by the method of Gordon and Barnes [Eqs. (II.137) and (II.138)] neglecting corrections for the limited number of rotational levels of the molecules. The values $\ln \Delta$ and $T\,\partial/\partial T \ln \Delta$ for both gases were adopted equal to zero, though the molecule AlO has a ground electronic state of the type $^2\Sigma$. The evaluations were carried out based on the constants given in Table 222. Table 224 shows the values of the constants C_Φ, C_S, the values θ and x as well as the values of the coefficients in Eqs. (II.137) and (II.138), calculated using the adopted molecular constants of AlO and AlH. Since the molecule AlO has the ground state $^2\Sigma$, the addends R ln 2 are includee in the corresponding values of C_Φ and C_S.

The components of the excited states $a^3\Pi$ and $A^1\Pi$ of the AlH molecule were evaluated using Eqs. (II.126) and (II.127) (i.e., considering the differences of the constants of the ground and excited states; in view of the lack of data on the excitation energy and constants of the state $A^2\Pi$ the components of the constant $B^2\Sigma$ of the AlO molecule were calculated applying a simpler method [relations (II.120), (II.121)], the components of the state $C^2\Sigma$ of the AlO molecule were not taken into account in the calculation.

In spite of the fact that calculating the thermodynamic functions of aluminum monoxide neither the components of the states $A^2\Pi$ and $C^2\Sigma$ were taken into account nor corrections were made for the limited number of rotational levels for the state $X^2\Sigma$, the errors of the calculated values of the thermodynamic functions of this gas, given in Table 291 (II), are small and amount to 0.01, 0.03 and 0.05 cal/mole•degree in $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000}. At the same time, the errors of the values of the thermodynamic functions of AlH are substantially higher, particularly at elevated temperatures where thanks to the low value of the dissociation energy of the molecules of this gas the magnitude of corrections allowing to consider the upper limits in the sums over the rotational states, becomes essential (up to 0.1 cal/mole•degree. in Φ^*_{6000}). The total errors of the calculated values $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} reach values of the order of 0.03, 0.05 and 0.2 cal/mole•degree.

Tables of the thermodynamic functions of AlO were computed in the works of Huff, Gordon and Morrell [2142] ($T \leq 6000$°K), Ward and Hussey [4149] (2000°L $\leq T \leq$ 5000°K) and Gordon [1817] ($T \leq 6000$°K). All evaluations were carried out using the constants suggested in the monography of Herzberg [2020]. The discrepancies between the values of the thermodynamic functions of AlO, given in Table 291 (II) and those calculated in the works [2142, 4149] are due to the fact that in the works mentioned the calculations were performed using the approximate solid rotator-harmonic oscillator model. The discrepancies reach 0.5-0.8 cal/mole•degree in the values S°_T at 5000-6000°K. Apparently, in the work [1817] the evaluation was carried out applying a more accurate method so that the discrepancies with the data of the present Handbook are less important and do not exceed 0.05 and 0.2 cal/mole•

·degree in the values Φ^*_T and S°_T, respectively. These differences are probably due to the fact that Gordon did not allow for the excited electronic state of AlO in his calculation.

Moreover, it should be noted that Inghram and co-workers [1405a] calculated the values Φ^*_T of AlO from 2000 to 2500° for the subsequent handling of the results of mass-spectrometric measurements. This evaluation was carried out using the approximate rigid rotator-harmonic oscillator model and in view of this the discrepancies between the quantities Φ^*_T calculated in this work and those given in Table 291 (II) have values of the order of 0.2 cal/mole·degree.

Previously, the thermodynamic functions of AlH had been evaluated only in the work of Ward and Hussey [4149], the calculation had been carried out using the approximate rigid rotator-harmonic oscillator model for temperatures from 2000 to 5000°K. The discrepancy between the data obtained in this work and those given in Table 294 (II) amount to 0.4 and 1.3 cal/mole·degree, in the quantities Φ^*_{5000} and S°_{5000}.

The tables of the thermodynamic functions of AlO and AlH, given in the first and present editions of the Handbook, are identical.

AlF and AlCl. The thermodynamic functions of aluminum monofluoride and monochloride, presented in Tables 295 (II) and 299 (II), were computed applying Eqs. (II.161) and (II.162). The values $\ln \Sigma$ and $T\, \partial/\partial T \ln \Sigma$ in these equations were calculated applying the method of Gordon and Barnes [Eqs. (II.137) and (II.138)] on the basis of the constants indicated above. The calculations were carried out without introducing corrections for the limited number of rotational levels of the molecules of both gases. In Table 224 the values C_Φ, C_S, θ and x as well as the values of the coefficients in Eqs. (II.137) and (II.138) are given, calculated by means of the adopted molecular constants of AlF and AlCl. The values of the components of the state $a^3\Pi$ of the AlCl molecule in Φ_T^* and S_T°, evaluated using Eqs. (II.126) and (II.127), i.e., taking into account the differences of the constants of the ground and excited states; the values of the components of the state $A^1\Pi$ of the AlCl and AlF molecules were computed using a simpler method [Eqs. (II.120), (II.121)]. The states of the AlF and AlCl molecules with higher excitation energies were not considered in evaluating the thermodynamic functions of the two gases. Nor was the difference of the constants of the $AlCl^{35}$ and $AlCl^{17}$ molecules considered in the calculation in the case of AlCl.

The main errors in the calculated values of the thermodynamic functions of AlF and AlCl are defined by the lack of experimental data on the energy of high vibrational and rotational levels of the ground state and by the fact that into the calculations no corrections were introduced for the limited number of rotational levels of the AlF and AlCl molecules. Nevertheless, owing to the high value of the dissociation energies of both molecules the corresponding errors are small. Thus, in the case of AlCl this correction calculated using Eq. (II.59) does not exceed 0.05 cal/mole•degree in the value Φ_{6000}^*, and the error due to the unsuitability of the adopted vibration constants for the approximation of the levels of the vibrational energy of AlCl near the dissociation limit amounts to about 0.1 cal/mole•degree. In the case of AlF the corresponding errors are still smaller.

Thus, for AlF and AlCl the errors of the calculated quantities $\Phi_{298.15}^*$, Φ_{3000}^* and Φ_{6000}^* do not exceed 0.02, 0.05 and 0.2 cal/mole•degree.

A table of the thermodynamic functions of AlF had been calculated in the work of Altman [526] ($T \leq 6000°K$) on the basis of the same values of the molecular constants that are adopted in the present Handbook.

The discrepancies between the values of the thermodynamic functions, given in Table 296 (II) and in this work, increase as the temperature rises and reach 0.07 and 0.27 cal/mole•degree in the quantities Φ^*_{6000} and S°_{6000}, respectively. Apparently, these discrepancies are due to the difference of the methods of calculation (Altman used the method of Pennington and Kobe) and to the fact that in the work [526] the excited electronic state of AlF was not taken into account.*

The thermodynamic functions of AlCl had been evaluated by Heise and Wieland [1984] (Φ^*_T for $T \leq 1500°$), Foster, Russel and Cochran [1584] (Φ^*_T for $T \leq 2400°K$), Gordon [1817] ($T \leq 6000°K$) and Altman [526] ($T \leq 6000°K$). The results of the evaluations carried out in the works [1984, 1584] are in good agreement (within the limits of 0.1 cal/mole•degree) with the data of Table 299 (II). The values of the thermodynamic functions of AlCl, calculated by Altman and Gordon, are practically identical; at elevated temperatures they differ markedly from those evaluated in the present Handbook. These disrepancies amount to 0.16 and 0.67 cal/mole•degree respectively, in the values Φ^*_{6000} and, apparently, they are due to the fact that in the works [1817, 526] a less accurate method of calculation (method of Pennington and Kobe or Mayer and Geppert-Mayer) had been used and the excited electronic states of AlCl had been neglected.

In the book of Zeise [4384] the thermodynamic functions of AlCl, calculated in the work [1584] are given.

The thermodynamic functions of AlCl, presented in the first and present editions of the Handbook, are identical, the thermodynamic functions of AlF differ by 0.1 cal/mole•degree in the values Φ^*_T and S°_T owing to the fact that becuase of the lack of experimental data the value B_0 for the state $X^1\Sigma$ had been adopted on the basis of an approximate evaluation made by the authors of the Handbook.

Al_2O. The thermodynamic functions of gaseous aluminum semioxide, given in Table 292 (II), were calculated applying Eqs. (II.243) and (II.244) using the approximate rigid rotator-harmonic oscillator model. The evaluation was carried out based on the molecular constants given in table 223. Table 225 presents the values of the quantities θ_n and the constants C'_Φ and C'_S in Eqs. (II.243) and (II.244) calculated using the adopted values of the molecular constants of Al_2O.

The essential errors of the calculated values of the thermodynamic functions of aluminum semioxide are due to the lack of experimental data on the structure of the molecules of this gas and their constants. The above-mentioned errors in the values of the structural parameters and fundamental frequencies (see page 1577) correspond to the errors in $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} of the order of 0.5, 1.2 and 1.5 cal/mole•degree. The errors due to carrying out the evaluation using the approximate rigid rotator-harmonic oscillator model amount to 1 and 1.5 cal/mole•degree in Φ^*_{3000} and Φ^*_{6000}. The total errors of the values Φ^*_T, given in Table 292 (II), at 298.15, 3000 and 6000°K are estimated with ± 1, ± 2.2 and ± 3 cal/mole•degree.

Calculations of the tables of the thermodynamic functions of aluminum semioxide for a wide range of temperatures are not available in the literature. In the works of Cook, Filler, Keyes et al [1164a] and of Inghram and co-workers [1405a] the values Φ^*_T of Al_2O were computed for the subsequent handling of the results of experimental measurements. These evaluations were carried out for several temperatures on the basis of estimated values of the molecular constants. In the work [1164a] no calculated values of Φ^*_T are given; the values Φ^*_T computed in the work [1405a] for T = 2000-2500°K differ from the values given in Table 292 (II) by approximately 2 cal/mole•degree.

The thermodynamic functions of Al_2O, given in the first and present editions of the Handbook, are identical.

TABLE 225

Values of the Constants for the Calculation of the Thermodynamic Functions of Monatomic Aluminum Compounds in the Gaseous State

Вещество 1	θ_1	θ_2	θ_3	θ_4	C'_{Φ}	C'_S
	2 град				3 кал/моль·град	
Al_2O	935,21	388,47	1007,2	—	7,7132	15,6613
AlF_2	1122,3	345,31	1251,8	—	8,0331	15,9822
AlF_3	1007,2	474,80	1366,0(2)	431,64(2)	7,5825	15,5316
$AlCl_2$	676,23	187,04	776,95	—	12,1713	20,1204
$AlCl_3$	503,58	309,34	877,66(2)	187,04(2)	12,4161	20,3642

1) Substance; 2) degree; 3) cal/mole•degree.

AlF_2 and $AlCl_2$. The thermodynamic functions of aluminum difluoride and dichloride, evaluated using Eqs. (II.243) and (II.244) are presented in Tables 296 (II) and 300 (II). The evaluations were carried out using the approximate rigid rotator-harmonic oscillator model based on the molecular constants adopted above (see Table 223). Table 225 gives the values of the quantities θ_n and the constants C'_{Φ} and C'_S in Eqs. (II.243) and (II.244), evaluated on the basis of the molecular constants of AlF_2 and $AlCl_2$ and adopted in the calculations. Since the AlF_2 and $AlCl_2$ molecules have doublet ground electronic states, the addends R ln 2 are included in the values of the constants C'_{Φ} and C'_S.

The essential errors of the calculated values of the thermodynamic functions of aluminum difluoride and dichloride are due to the lack of experimental data on the structure and fundamental frequencies of AlF_2 and $AlCl_2$ (up to 1 cal/mole•degree in the values Φ^*_T) and to the fact that the calculation was carried out using the approximate rigid rotator-harmonic oscillator model (up to 1-1.5 cal/mole•degree in the values Φ^*_T). The total errors of the values Φ^*_T, given in Tables

296 (II) and 300 (II), at 298.15, 3000 and 6000°K have values of the order of 0.5, 2 and 4 cal/mole·degree..

The thermodynamic functions of AlF_2 and $AlCl_2$, given in the first and present editions of the Handbook, differ by a magnitude of the order of 0.1-0.3 cal/mole·degree owing to a more accurate evaluation of the fundamental frequencies of these molecules in the new edition. Other calculations of tables of the thermodynamic functions of these gases are not known in the literature, though in some American publications indications are made concerning calculations of the equilibria of chemical processes in which AlF_2 and $AlCl_2$ are involved.

AlF_3 and $AlCl_3$. The thermodynamic functions of gaseous aluminum trifluoride and trichloride, given in Tables 298 (II) and 302 (II), were calculated using Eqs. (II.243) and (II.244). The evaluation was carried out using the approximate rigid rotator-harmonic oscillator model on the basis of the molecular constants adopted above (see Table 223). Table 225 contains the values of the quantities θ_n and the constants C'_Φ and C'_S in Eqs. (II.243) and (II.244), evaluated on the basis of the molecular constants of AlF_3 and $AlCl_3$ adopted in the calculations.

The main errors of the calculated values of the thermodynamic functions of AlF_3 and $AlCl_3$ are due to the lack of experimental data on the fundamental frequencies of the molecules of these gases (up to 2 and 1.5 cal/mole·degree in the values Φ^*_T for AlF_3 and $AlCl_3$, respectively) and to the fact that the calculations were made using the approximate rigid rotator-harmonic oscillator model (up to 2.5-3 cal/ /mole·degree). The total errors of the values Φ^*_T, presented in Tables 298 (II) and 302 (II), at 298.15, 3000 and 6000°K amount to magnitudes of the order of 0.6, 4 and 6 cal/mole·degree, respectively.

The thermodynamic functions of $AlCl_3$ were calculated in the works of Heise and Wieland [1984] (Φ_T^* for T ≤ 1500°K) and Foster et al [1584] (Φ_T^* for T ≤ 2400°K). The data of Heise and Wieland are consistent with those given in Table 298 (II) within the limits of 0.2 cal/ /mole•degree; this discrepancy cannot be due to the slight difference in the adopted values ν_2 (see page 1582) and is connected, apparently, with some error in the calculation of the above-mentioned authors. The evaluation of Foster, Russel and Cochran was carried out based on constants obtained as the result of rough estimates and their data differ sharply from those presented in Table 302 (II) (up to 5 cal/ /mole•degree in $\Phi_{298.15}^*$). The results of the calculations made in the work [1584] are adopted in the book of Zeise [4384].

Apparently, the thermodynamic functions of $AlCl_3$ have been calculated also in the works of Villa, Blunder, Vries and Newton which remained unknown, however, to the authors of the Handbook.

The thermodynamic functions of $AlCl_3$, presented in the first and present editions of the Handbook, are identical, the functions of AlF_3 differ by at most 1-1.5 cal/mole•degree in the values Φ_T^* and S_T°; these discrepancies are due to a more accurate estimation of the fundamental frequencies of AlF_3 in the preparation of the present edition of the Handbook (see page 760). Other calculations of tables of the thermodynamic functions of AlF_3 are not known in the literature.*

§97. THERMODYNAMIC PROPERTIES OF Al, Al_2O_3, AlF_3, $AlCl_3$ AND AlN IN THE SOLID AND LIQUID STATES

The thermodynamic functions of Al, Al_2O_3, AlF_3, $AlCl_3$ and AlN in the solid and liquid states (Tables 286, 292, 297, 301, 303 of Volume II of the Handbook) were calculated using Eqs. (III.9)-(III.11) based on the thermodynamic values given in Table 226. The errors of the values Φ_T^* evaluated at temperatures of 298, 1000, 1500, 2000 and 3000°K, estimated by analyzing the errors of the initial data, are presented in

Table 227.

Al. Aluminum metal has a cubic face-centered lattice. Polymorphic transitions do not occur in aluminum.

TABLE 226

Adopted Values of the Thermodynamic Functions of Aluminum and its Compounds in the Solid and Liquid States

Вещество 1	Состояние 2	$H^{\circ}_{298,15} - H^{\circ}_{0}$	$S^{\circ}_{298,15}$	$C^{\circ}_{p_{298,15}}$	5 Коэффициенты в уравнении для C_p^a			6 Интервал температуры	Tm или Ttr 7	ΔHm или ΔHtr 7
		3 кал/моль	4 кал/моль·град		a	$b\cdot10^{3}$	$c\cdot10^{-5}$	°K	°K	3 кал/моль
Al 8	Крист.	1094	6,77	5,82	4,94	2,96	—	298,15—932	932	2 610
Al 9	Жидк.	—	—	—	7,4	—	—	932—4300	—	—
Al_2O_3	Крист.	2394	12,175	18,88	Табличные данные 10 [1632]			298,15—1200	—	—
Al_2O_3	»	—	—	—	25,71	3,96	—	1200—2303	2303	28 000
Al_2O_3	Жидк.	—	—	—	34,6	—	—	2303—6000	—	—
AlF_3	Крист.	2777	15,89	17,95	17,27	10,96	2,30	298,15—727	727	150
AlF_3	»	—	—	—	20,93	3,00	—	727—1600	1600	16 000
AlF_3	Жидк.	—	—	—	32,0	—	—	1600—2300	—	—
$AlCl_3$	Крист.	4000	26,0	21,60	13,25	28,0	—	298,15—465,6	465,6	8 500
$AlCl_3$	Жидк.	—	—	—	31,2	—	—	465,6—1400	—	—
AlN	Крист.	924	4,80	7,19	10,98	0,80	3,58	298,15—1800	—	—
AlN	»	—	—	—	8,925	1,88	—	1800—2700	2700	16200
AlN	Жидк.	—	—	—	16,0	—	—	2700—4000	—	—

1) Substance;
2) state;
3) cal/mole;
4) cal/mole•degree;
5) coefficients in the equation for C_p^a;
6) temperature range;
7) or;
8) crystalline;
9) liquid;
10) table data.

a) $C_p^{\circ} = a + bT - CT^{-2}$ (cal/mole•degree)

At low temperatures the specific heat of aluminum was measured in a number of works (references see Kelley [2364]; among them, measurements within a wide range of temperatures were carried out by Maier and Anderson [2744a] (54-297°K) and Giauque and Meads [1717] (15-320°K). The results of these measurements are in satisfactory agreement with each other and lead to $S^{\circ}_{298.15}$ values equal to 6.75 and 6.79 cal/g-atom

•degree, respectively. Based on the data of this works (and additionally several other works in which the measurements of the specific heat of aluminum cover a range down to 1°K) Kelley [2364] suggested the value $S^\circ_{298.15} = 6.77 \pm 0.02$ kcal/g-atom•degree which is adopted in the Handbook. Extrapolation of the specific heat to 0°K gives only 0.0003 cal/g-atom•degree. The value $H^\circ_{298.15} - H^\circ_0 = 1094 \pm 5$ cal/g-atom is adopted based on the data of Giauque and Meads [1717].

Numerous data on the enthalpy and specific heat of solid aluminum in the interval from 298°K to the melting point of 932°K (2493] have been discussed by Kelley [2363, 2364a] who on the basis of these data suggested a linear equation for the specific heat of aluminum (see Table 226); the accuracy of the relative equation for the enthalpy has been estimated by Kelley [2364a] equal to ±0.6%. Based on the measurements of the enthalpy of liquid aluminum, carried out by Wust, Meuthen and Durer [4349] (up to 1273°K) and Awbery and Griffiths [590] (up to 1036°K) Kelley [2363] recommended for the melting heat of aluminum the values $\Delta H_{932} = 2.57$ kcal/g-atom and for the specific heat of liquid aluminum $C_p = 7.0$ cal/g-atom•degree. Based on the results of measurements of the enthalpy of liquid aluminum, carried out by Oelsen and Middel [3109] within a wider temperature range (up to 1425°K) The authors of the present Handbook obtained somewhat higher values equal to $\Delta Hm_{932} = 2.61 \pm 0.03$ kcal/g-atom and $C_p = 7.4 \pm 0.3$ cal/g-atom•degree. The corresponding value of the melting heat of aluminum, 2.61 kcal/g-atom, is higher than the values determined by Wittig [4304] (2.48 kcal/g-atom) and recommended by Kubaschewski [2493] (2.50 kcal/g-atom) but in good agreement with the results of the very accurate measurements made in 1955 by Oelsen et al. [3111] (2.63 ± 0.03 kcal/g-atom).

Since the adopted value of the melting heat must be adjusted to the value of the specific heat of the liquid, in the Handbook the abovementioned values ΔHm and C_p° obtained from the data of Oelsen and Middel [3109] were adopted. Moreover, the value of the specific heat of liquid aluminum, $C_p^\circ = 7.4$ cal/g-atom•degree, was adopted for evaluating the thermodynamic functions of aluminum above 1425°K.

The values of the thermodynamic functions of aluminum in the solid and liquid states, evaluated for temperatures of 293.15-4300°K, are given in Table 286 (II). The errors of the calculated values Φ_T^* are presented in Table 227.

The discrepancies between the values of the thermodynamic functions of aluminum, given in Table 286 (II) and in the Handbooks [3894, 1515 and 2364a] as well as the first edition of the present Handbook, are due to the different values of the melting heat and specific heat of liquid aluminum, adopted in the calculations. These discrepancies do not exceed 0.2-0.3 cal/g-atom•degree in the quantities Φ_T^* and S_T° at temperatures up to 2000-3000°K.

$\underline{Al_2O_3}$. Aluminum oxide has several crystalline modifications, among them the thermodynamically stable α-modification of Al_2O_3, or corundum, having a rhombohedral lattice. The varieties of corumdum, ruby and sapphire, have the same structure and are distinguished from corumdum merely by the color due to the isomorphic admixture of Cr_2O_3 (red ruby) or to colloidal admixtures of oxides of several metals (blue sapphire). Other modifications of aluminum oxide, the hexagonal β-modification, the cubic γ-modification with a spinel-type lattice, and some more are metastable and can occur within a limited temperature range, usually in the presence of impurities. Heated to temperatures of the order of 1500°C these modifications are converted into the α-modification of Al_2O_3. In the Handbook, for the solid aluminum oxide the thermodynamical properties of the α-modification (corundum) are given.

Measurements of the specific heat or enthalpy of corumdum were carried out by many investigators, especially at high temperatures, since corundum has several properties allowing to use it in calorimetric measurements of the specific heat within a wide range of temperatures. These properties are related with the high volume specific heat (at T > 200°K), the heat resistance and the chemical inertia in air up to the melting point, the nonhygroscopicity, the availability of corundum specimens of high purity as well as the absence of polymorphic transitions and anomalies of the specific heat.

Based on three studies on the specific heat of aluminum oxide in the 30-295°K range made until 1935, Kelley [2364] suggested $S^\circ_{298.15} = 12.5 \pm 0.15$ cal/mole·degree. More accurate measurements of the specific heat of Al_2O_3 were performed by Kerr, Johnston and Hallett [2375] (20-295°K) and Ginnings and Furukawa [1753] (14-298°K). The data of these authors are in satisfactory agreement with each other and lead to practically coinciding values of the entropy of Al_2O_3 at 298.15°K equal to 12.165 ± 0.02 and 12.175 ± 0.01 cal/mole·degree, respectively. The extrapolation of the specific heat below 14°K leads to the value $S^\circ_{14} = 0.003$ cal/mole·degree. In the Handbook the quantities $S^\circ_{298.15}$ and $H^\circ_{298.15} - H^\circ_0$ are adopted according to the data of Ginnings and Furukawa [1753] (see Table 226), with an error of ±0.02 cal/mole·degree and ±3 cal/mole, respectively.

As to the enthalpy and specific heat of aluminum oxide within the 273-1173°K range the values are most reliable that have been obtained in several works of the U. S. National Bureau of Standards [1751, 1753, 1632]. On the basis of these studies Furukawa, Duglas, McCoskey and Ginnings [1632] computed a table of the thermodynamic functions of aluminum oxide up to 1200°K and recommended these data as a standard of the specific heat and enthalpy. In a number of later works these values were verified. The measurements of the enthalpy performed by Gomel'skiy [162] (360-1140°K) and Walker, Grand and Miller [4132] (371-975°K) led to values coinciding with the data [1632] with an accuracy of 0.1-0.2%. The results of the measurements of the specific heat of Al_2O_3, made by West and Ginnings [4214, 4215] (300-700°K) and Shmidt and Sokolov [464a] (325-987°K) are consistent up to 650--700°K with the data of the U. S. National Bureau of Standards [1632] with an accuracy of 0.1-0.2%. Above 650°K, the discrepancies between the measured results [464a] and [1632] increase to 0.4%, but remain within the scatter of the values [464a]. The thermodynamic functions of Al_2O_3, calculated by Furukawa et al [1632] up to 1200°K, are adopted in the present Handbook without any changes.

Measurements of the enthalpy of solid Al_2O_3 at temperatures above 1200°K had been carried out in several works, but only in the work of Kantor, Kandyba, Kan, Krasovitskaya and Fomichev [206] data have been obtained on the enthalpy of fused aluminum oxide. The results of measurements of the enthalpy of solid Al_2O_3, carried out by Kantor et al [206] are defined within the 1194-2179°K range with an accuracy of ±0.3% by an equation derived by these authors, and are in good agreement with the data of the U. S. National Bureau of Standards [1632] (at 1200°K), with the results of measurements of the enthalpy, carried out by Rodigina and Gomel'skiy [347] (1373-1673°K) and within the limits of ±0.5% with the values computed using the equation suggested by Kelley [2363] up to 1800°K based on the data of several earlier works [1861, 3713, 76, etc.]. In the present Handbook for the enthalpy of Al_2O_3 at temperatures above 1200°K the data, obtained by Kantor et al [206], are adopted. To make these data agree with the values adopted for the specific heat up to 1200°K an equation was set up by the authors of the Handbook for the specific heat of solid aluminum oxide (see Table 226) in the 1200-2303°K range based on the value C_{p1200} = 30.46 cal/mole•degree [1632] and the value $H_{2300} - H_{1200} =$ = 35,900 cal/mole, obtained from the data of Kantor et al [206].*

The most accurate measurements of the melting point of corundum [206, 1675a, 1675b] lead to values from 2288° to 2312°K. In the Handbook the value 2303°K, obtained in the work of Kantor et al [206] with an accuracy of ±5°, is adopted.

Ten measurements of the enthalpy of liquid aluminum oxide within the 2308-2476°K range, carried out by Kantor et al [206] with an accuracy of ±0.3%, lead to a value of the specific heat of liquid Al_2O_3 equal to 34.6 ± 2 cal/mole•degree and to a value of the melting heat ΔHm_{2303} = 28.0 ± 1.0 kcal/mole which are adopted in the Handbook.

The values of the thermodynamic functions of aluminum oxide in the solid and liquid states, evaluated for temperatures of 293.15--6000°K, are presented in Table 292 (II). The magnitudes of the errors in the calculated values Φ^*_T are given in Table 227.

Up to 1200°K, the values of the thermodynamic functions of solid Al_2O_3, given in the first and present editions of the Handbook, are identical. At higher temperatures the discrepancies between the values Φ^*_T increase to 0.4 cal/moleδdegree at 3000°K, then they decrease, at 4500°K they change the sign and rise to 0.7 cal/mole•degree at 6000°K. The discrepancies between the corresponding values S°_T are at 2000°K 0.6 and at 6000°K 3.4 cal/mole•degree.

The table of the thermodynamic functions of solid and liquid aluminum oxide up to 4000°K have been calculated by Huff, Gordon and Morrell [2142]; the important discrepancies with the values of the thermodynamic functions, adopted in the present edition, which reach up to 9 cal/mole•degree in the value S°_{2500} are caused by the inaccuracy of the thermodynamic values adopted in the work [2142]; in particular, for the melting heat of Al_2O_3 the authors [2142] adopted in the value 6 kcal/mole instead of 28 kcal/mole (the latter has been ascertained experimentally in the work of Kantor et al [206]).

$\underline{AlF_3}$. Aluminum trifluoride has at low temperatures a rhombohedral lamellar structure; at 727°K a polymorphic transition of AlF_3 occurs with a small heat effect (see below).

At low temperatures (54-296°K) the specific heat of AlF_3 of a purity of 99.85% was measured by King [2402] who had calculated the value $S^\circ_{298.15} = 15.89 \pm 0.08$ kcal/mole·degree which includes the value $S^\circ_{51} = 0.56$ cal/mole·degree obtained by extrapolating the specific heat to 0°K. Measurements of the specific heat of AlF_3, made previously by Strelkov and Kostryukov [43] within the 13-30°K range were carried out on an impure AlF_3 specimen and lead to a lower value of $S^\circ_{298.15} = 14.58$ cal/mole·degree. In the Handbook the value $S^\circ_{298.15}$ obtained by King [2402] is adopted; the potential error of this value is ± 0.2 cal/mole·degree. The value $H^\circ_{298.15} - H^\circ_0 = 2777 \pm 10$ cal/mole, adopted in the Handbook, is evaluated using the data of King [2402].

The enthalpy of solid AlF_3 at high temperatures was measured by Lyashenko [284] (440-1060°K), Voskresenskaya and Banashek [12] (709--1430°K), O'Brien and Kelley [3106] (401-1401°K). The data obtained by these authors are consistent within the limits of 1%. Apparently, the most reliable among them are the data of O'Brien and Kelley [3106] the accuracy of which has been estimated $\pm 0.2\%$ by Kelley [2364a]. The equations for the specific heat of the low-temperature and high-temperature modifications of AlF_3 and the value of the heat of transition of AlF_3, $\Delta H_{727} = 0.15$ kcal/mole, obtained in the work [3106] are given in Table 226.

Reliable data on the melting point and heat of AlF_3 are not known in the literature. Brewer et al [1093] show that the melting point of AlF_3 lies above 1545°K. From a comparison of the corresponding values for the halides of several metals (Li, Na, Be, Mg, Al) the values adopted in the Handbook for AlF_3 are for the melting point 1600 ± ± 100°K, the melting entropy $\Delta S_{1600} = 10 \pm 3$ cal/mole•degree and the melting heat $\Delta Hm_{1600} = 16 \pm 5$ kcal/mole. These values may be considered only rough approximations. The specific heat of liquid AlF_3 is estimated equal to 32.0 cal/mole•degree.

The values of the thermodynamic functions of aluminum trifluoride in the solid and liquid states, evaluated for the temperatures of 293.15-2300°K, are given in Table 297 (II). The magnitudes of the errors of the calculated quantities Φ_T^* are presented in Table 227.

The discrepancies between the thermodynamic functions of AlF_3, evaluated in the first and present editions of the Handbook, are in the values Φ_T^* at 298 and 2000°K 0.7 and 1.5 cal/mole•degree, respectively, and due to a much more accurate definition of the specific heat of solid AlF_3 at low and elevated temperatures in the works [2402,2106].

<u>$AlCl_3$</u>. Crystalline aluminum trichloride has a lamella hexagonal structure. Information on a polymorphism of $AlCl_3$ is not known in the literature.

No systematic measurements of the specific heat of $AlCl_3$ have been made at low temperatures. Fischer [1564] carried out three measurements of the mean specific heat within the 90-273°K range. Using these data as well as values of the specific heat of $AlCl_3$, obtained by comparing the specific heats of AlF_3 [2402], MgF_2 [3993] and $MgCl_2$ [2366], the authors of the Handbook estimated the values of the entropy and enthalpy of $AlCl_3$ at 298.15°K equal to $S^\circ_{298.15} = 26.0 \pm$ ± 1.5 cal/mole•degree and $H^\circ_{298.15} - H^\circ_0 = 4000 \pm 100$ cal/mole. The value $S^\circ_{298.15}$ adopted was confirmed by a comparison of the value of the standard entropy of Na, Mg and Al fluorides and chlorides, too. The value $S^\circ_{298.15}$ = 40 cal/mole·degree, accepted in the Handbooks [1093 and 3508] and obtained, apparently, with the aid of less accurate estimates, is much too high just as the corresponding value for AlF_3 ($S^\circ_{298.15}$ = 23 instead of the value $S^\circ_{298.15}$ = 15.89 cal/mole·degree, obtained experimentally). Kubaschewski and Evans [2494] referring to the review of Villa [4109] suggest the value $S^\circ_{298.15} = 26.3 \pm 2.5$ cal/mole·degree which is practically consistent with the value adopted in the Handbook.*

The only work on the measurement of the enthalpy of $AlCl_3$ within the 273-504°K range has been acommplished by Fischer [1564]. Kelley [2363] estimated the accuracy of the measurements made in this work ±2% and suggested an equation for the specific heat of solid $AlCl_3$ within the range from 298°K to the melting point of 465.6°K, the melting heat $\Delta Hm_{465.6} = 8.5 \pm 0.3$ kcal/mole and the specific heat of liquid $AlCl_3$ C°_p = 31.2 cal/mole·degree. These values are adopted in the Handbook (see Table 226).

The values of the thermodynamic functions of aluminum trichloride in the solid and liquid states, evaluated for temperatures of 293.15-1400°K, are given in Table 301 (II). The magnitudes of the errors in the evaluated quantities Φ^*_T are presented in Table 227.

The tables of the thermodynamic functions of $AlCl_3$, given in the first and present editions of the Handbook, are identical.

AlN. Aluminum nitride has a hexagonal structure of the type of wurtzite (ZnS). Information on a polymorphism of AlN is not known in the literature.

Mah, King, Weller and Christensen [2738a] carried out measurements of the specific heat (53-196°K) and enthalpy (399-1799°K) of aluminum nitride. These authors calculated the value $S^\circ_{298.15} = 4.80 \pm 0.02$

cal/mole·degree which includes the value S°_{51} = 0.073 cal/mole·degree, obtained by extrapolating the specific heat to 0°K. The above-mentioned quantity $S^\circ_{298.15}$ and the value $H^\circ_{298.15} - H^\circ_0$ = 925 cal/mole, evaluated using the data [2738a], are adopted in the Handbook. The estimates of $S^\circ_{298.15}$, made previously applying various empirical methods [127, 219, 224, 273, 2385], lead to values from 5 to 6 cal/mole·degree.

Data on the enthalpy of AlN at elevated temperatures (298-1800°K) are described by the authors [2738a] by an equation with an accuracy of ±0.9%. The corresponding constants in the equation for the specific heat of AlN within this temperature range are given in Table 226. The results of measurements of the enthalpy of AlN, carried out previously by Satoh [3594] (273-871°K) with an accuracy of ±3%, are consistent with the data [2738a] within the limits of the error mentioned. Within the 1800-2700°K temperature range the specific heat of AlN was approximated by the equation (see Table 226), derived with the aid of the values C°_{p1800} = 12.31 cal/mole·degree [2738a] and C°_{p2700} = 14.0 cal/mole·degree (see page 258).

Reliable data on the melting point of AlN are not known in the literature. The approximate value of 2700 ± 200°K, adopted in the Handbook, is based on data [1614, 3421a] (according to the former the melting point of AlN is 2500°K, according to the latter it lies above 2670°K).

The melting heat of AlN ΔHm_{2700} = 16.2 ± 6 kcal/mole is evaluated using the melting entropy ΔS = 6 ± 2 cal/mole·degree, estimated by the same method as the melting entropy of boron nitride. The specific heat of liquid aluminum nitride is adopted equal to 16.0 cal/mole·degree (see page 261).

The values of the thermodynamic functions if aluminum nitride in the solid and liquid states, calculated within the 293.15-4000°K range, are given in Table 303 (II). The errors of the calculated values Φ_T^* are presented in Table 227.

The discrepancies between the values Φ_T^* and S_T° for AlN, given in Table 303 (II) and in the first edition of the Handbook, do not exceed 0.1 cal/mole·degree up to 2000°K, but at temperatures of 3000-4000°K they are approximately 0.5 cal/mole·degree.

TABLE 227

Errors (in cal/mole·degree) of the Values Φ_T^* of Aluminum and its Compounds in the Solid and Liquid States

T°, K	298	1000	1500	2000	3000
Al	±0,02	±0,07	±0,2	±0,4	±0,8
Al_2O_3	±0,02	±0,07	±0,12	±0,2	±0,5
AlF_3	±0,2	±0,3	±0,4	±1,2	—
$AlCl_3$	±1,5	±2,5	±3,5	±5,0	—
AlN	±0,02	±0,1	±0,15	±0,25	±0,7

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The standard state of aluminum is Al (cryst.).

Al (gas). Table 228 shows the values of the heat of sublimation of aluminum at 0°K, evaluated by the authors of the Handbook based on data in the literature on the pressure of aluminum vapors. Just like the measurements for a number of other metals with high boiling points the results of the measurements of Baur and Brunner [692] lead to slightly excessive values of the pressure of the saturated vapors and, accordingly, to underestimated values of the heat of sublimation (see review article Eucken [1496]). In the tests of Brewer and Searcy [931], in which effusion chambers of tantalum carbide were used, it was ascertained that the results depend on the size of the effusion aperture (with the reduction of the size of the aperture from 8 to 2

mm^2 the calculated values of the heat of sublimation decreased from 76.7 to 73.6 kcal/g-atom). The best repeatability of results was obtained by Brewer and Searcy in tests with chambers of beryllium oxide. Brewer and Searcy [931] suggest for the heat of sublimation of aluminum the mean value of 76.8 ± 1.4 kcal/g-atom computed from the results of all measurements.

Detailed measurements of the pressure of aluminum vapors have been made by Priselkov, Tseplyayeva and Sapoznikov [21, 338] by an integral variant of the method of Knudsen. The effusion chambers were made of beryllium oxide. The use of a ceramic diaphragm eliminated the "creeping out" of fused aluminum through the effusion apertures. The relation between the internal surface of the chamber and the area of the effusion aperture varied from 1600 to 5000. The value of the heat of sublimation of aluminum, $\Delta Hs_0 = 74.7 \pm 0.3$ kcal/g-atom, calculated using the results of the works [21, 238], remains constant within the temperature range studied. The analysis of potential errors, carried out by the authors of the works [21, 338] has shown that the maximum error in the resultant value of the heat of sublimation does not exceed ±1.0 kcal/g-atom.

Porter, Schissel and Inghram [3306] carried out a mass-spectrometric study of the evaporation of a mixture of aluminum oxide and aluminum (effusion chambers of zirconium oxide) and ascertained ΔHs_{932} (Al, cryst.) = 74 kcal/g-atom, or ΔHs_0 = 77 kcal/g-atom. According to the estimate by the authors of the work [3306] the accuracy of these values is ±3 kcal/g-atom.

Johnson, Hudson, Coldwell, Spedding and Savage [2266] applied for the determination of the heat of sublimation of aluminum a mass-spectrometric method in which the ionization of the aluminum vapors escaping from the effusion chamber took place on an incandescent tungsten tape. Investigating the temperature dependence of the ion current of Al^+, the authors [2266] ascertained for the heat of sublimation of aluminum the value $\Delta Hs_{1327} = 73.5 \pm 0.4$ kcal/g-atom, or $\Delta Hs_0 = 77.5$ kcal/g-atom.

TABLE 228

Results of Evaluation of the Heat of Sublimation of Aluminum

Авторы 1	Год 2	Метод 3	Интервал температур, °K 4	Количество опытов 5	ΔH_{s_0}, ккал/г-атом 6
Фаркас [1529] . 7 . . .	1931	13 Кнудсена	1476	—	77,0
Баур, Бруннер [692] .8.	1934	14 кипения	1734—2237	4	74,1±0,6
Бруэр, Серси [931] . .9.	1951	Кнудсена	1383—1460 1410—1468	4 6	$75,1\pm1,5^{а}$ $77,9\pm0,4^{б}$
Портер, Шиссель, Инграм 10 [3306]	1955	масс-спектрометрический 15	1500—1800	—	77 ± 3^{в}
Джонсон, Хадсон и др. [2266] . . . . 11 . .	1956	»	1150—1500	—	$77,5\pm0,4^{в}$
Приселков, Сапожников, Цепляева [21, 338] .12	1957	Кнудсена	1273—1473	11	74,7±0,3

1) Authors;
2) year;
3) method;
4) temperature range, °K;
5) number of tests;
6) kcal/g-atom;
7) Farkas;
8) Baur, Brunner;
9) Brewer, Searcy;
10) Porter, Schissel, Inghram;
11) Johnson, Hudson, et al.;
12) Priselkov, Sapozhnikov, Tseplyayeva;
13) Knudsen;
14) boiling;
15) mass-spectrometric;
a) Effusion chambers of tantalum carbide;
b) Effusion chambers of beryllium oxide;
c) Computed using the dependence of the logarithm of the ion current of Al^+ on 1/T and converted to 0°K.

Thus, the results of the works discussed are not in satisfactory agreement with each other. Considering the high reliability of the data obtained by Priselkov, Tseplyayeva and Sapoxhnikov [21, 338] in the Handbook the value

$$\Delta Hs_0(\mathrm{Al,\ cryst.}) = \Delta H^\circ f_0(\mathrm{Al,\ ra3}) = 75{,}5 \pm 1{,}5\ \mathrm{kcal/g\text{-}atom},$$

is adopted which is consistent within the limits of the error specified with the values calculated by means of the data of other authors.

Al^+ (gas). The ionization potential of monatomic aluminum is adopted in conformity with the suggestion of Moore [2941] equal to 48,279.16 cm^{-1} or

$$I(\mathrm{Al}) = 138{,}043\ \mathrm{kcal/g\text{-}atom}.$$

The error of this magnitude is about 1 cal/g-atom.

The value I (Al) adopted is in keeping with

$$\Delta H^\circ f_0(\mathrm{Al^+,\ gas}) = 213{,}543 \pm 1{,}5\ \mathrm{kcal/mole}.$$

Al_2(gas). Drowart and Honig [1408] carried out a mass-spectrometric analysis of the composition of the vapors of several elements and, based on the relations of the ion currents of the atoms and diatomic molecules of these elements, they calculated the dissociation energy of the latter. A comparison of the dissociation energies of diatomic molecules of elements of different periods and groups of the periodic system enabled the authors of the work [1408] to ascertain the dependence of the dissociation energies of these molecules on the atomic number of the element in the period and the period number and to evaluate the dissociation energies of some molecules which had not been investigated previously. The dissociation energy of Al_2 is estimated equal to 39 kcal?mole in the work [1408].

Studying the mass spectra of evaporation products of aluminum carbide Chupka, Berkowitz, Giese and Inghram [1107] ascertained that in the vapors apart from aluminum atoms a small quantity of Al_2 molecules occurs. Having evalued the thermodynamic functions of this gas the authors [1107] found $D_0(Al_2)$ = 46 kcal/mole. The recalculation based on the values of the thermodynamic functions of Al_2 adopted in the present Handbook, led to $D_0(Al_2)$ = 45 kcal/mole. The authors of the work [1107] point out that part of the labeled Al_2^+ ions could form owing to the dissociation of the Al_2C_2 molecule on ionization and, consequently, the value obtained may prove to be excessive.

In the Handbook one has adopted the value of the dissociation energy of the Al_2 molecule,

$$D_0(Al_2) = 45 \pm 10 \text{ kcal/mole},$$

computed using the data of the work [1107]. The evaluation of Drowart and Honig [1408] is consistent with this value within the limits of error. The adopted value $D_0(Al_2)$ corresponds to

$$\Delta H^\circ f_0(Al_2, \text{gas}) = 106 \pm 10 \text{ kcal/mole}.$$

AlO (gas). The linear extrapolation of the vibrational levels of the ground electronic state of AlO using the vibration constants adopted in the present Handbook leads to the value $D_0(AlO)$ = 95 kcal/ /mole (4.1 ev). The extrapolation using the vibration constants ascertained by Lagerqvist, Nilsson and Barrow [2530] gives for the dissociation energy of AlO about 97 kcal/mole (4.2 ev). The $D_0(AlO)$ values obtained by linear extrapolation cannot be considered reliable. More accurate values were obtained as a result of effusion, mass-spectrometric and spectrometric measurements. Brewer and Searcy [931] studied the evaporation of aluminum oxide within the 2309-2605°K range from an effusion chamber made of tungsten. Analyzing the potential evaporation products of aluminum oxide the authors of the work [931] came to the conclusion that the main product of evaporation must be the molecule AlO, and ascertained $D_{298}(AlO)$ = 138 kcal/mole. Calculations carried out in the works [420, 296] have shown, however, that the evaporation rate of Al_2O_3 ascertained by the authors of the work [931] cannot be explained satisfactorily, if one reckons that the only product of evaporation under the test conditions is AlO (see page 1617).

Ackermann and Thorn [487] have shown that under the test conditions of the work [931] aluminum oxide has been reduced by tungsten and this has led to excessive values of the pressures evaluated (Sears and Navias [3673b] suggest that the pressures were excessive by 4000 times) and to an excessive value $D_0(AlO)$.*

Drowart, De Maria, Burns and Inghram [1405a] (see also the preliminary communication [1310]) studied the mass spectrum of evaporation products of aluminum oxide from effusion chambers made of tungsten (2188-2594°K) and molybdenum** (2036-2466°K) and computed the values of the partial pressures of the evaporation products of aluminum oxide and of the equilibrium constants of the reaction.

$$AlO_{(gas)} = Al_{(gas)} + O_{(gas)}. \qquad \text{(XXIV.1)}$$

Using the thermodynamic functions of the components of this reaction the authors of the work [1405a] ascertained $D_0(AlO) = 115 \pm 5$ kcal/mole (mean of all tests with different effusion chambers). The recalculation of the measured results of Drowart et al, applying the values of the thermodynamic functions adopted in the present Handbook, led to a consistent value.

Gurvich and Veyts [123, 170] determined by the spectrophotometric method the partial pressures of aluminum in acetylene-oxygen flames and calculated the values of the equilibrium constants of the reaction (XXIV.1) at temperatures of 3150, 3210 and 3250°K. By these calculations it was shown that AlO is the main aluminum compound under these conditions and the other aluminum compounds (Al_2O, AlOH, Al_2O_3, AlH) are present in negligible quantities. Based on these tests the authors of the work [170] calculated $D_0)AlO) = 137 \pm$ kcal/mole. This value was obtained in tests when aluminum was introduced into the flame in the shape of solute aluminum chloride. In the tests where aluminum was introduced into the flame in the shape of solute alum $KAl(SO_4)_2$ the measured partial pressure of aluminum was about two times lower compared to analogous tests with $AlCl_3$. The reasons of this discrepancy remain unclear (the presence of sulfur in the flame cannot explain this phenomenon, since the concentration of AlS molecules under the test conditions must be negligibly low).

The discrepancy between the values $D_0(AlO)$, obtained on the basis of mass-spectrometric [1405a] and spectrophotometric [123, 170] measurements, cannot be explained completely.

In the Handbook the value

$$D_0(AlO) = 115 \pm 5 \text{ kcal/mole},$$

based on mass-spectrometric measurements [1405a] is adopted, since the results of the measurements [123, 170] may result in an excessive value $D_0(AlO)$ owing to the formation of some aluminum compounds, considered not or not accurately enough, in the flames.

To the adopted value corresponds

$$\Delta H^\circ f_0(AlO, \text{gas}) = 19{,}487 \pm 5{,}2 \text{ kcal/mole}.$$

Al_2O (gas). Information on the heat of formation of gaseous aluminum semioxide is based on studies of the evaporation of aluminum oxide under reducing and neutral conditions. Brewer and Searcy [931] studied the pressure of vapors above the system Al (liquid) + Al_2O_3 (cryst.) at 1466-1853°K. The attempt to carry out this investigation by the effusion method failed, since Brewer and Searcy could not find a material for the effusion chamber, chemically resistant against aluminum as well as aluminum oxide. Brewer and Searcy placed a small quantity of aluminum metal on the bottom of a crucible of pure aluminum oxide and filled it up with aluminum oxide powder. On heating the aluminum evaporated and its vapors passed through the aluminum oxide layer. As the tests have shown, the volatility of aluminum increases under these conditions by about 100 times. The authors of the work [931] adduce several arguments in favor of the assumption that the increase of the volatility occurs owing to the formation of gaseous Al_2O. From the quantity of the evaporated aluminum and aluminum oxide it has been ascertained, based on several hypotheses, that the heat effect of the reaction

$$4Al(gas) + Al_2O_3(sol.) = 3Al_2O(gas) \qquad (XXIV.2)$$

equals zero (with an accuracy of about ±20 kcal/mole). To this value corresponds the value $D_0(Al_2O) = 242 \pm 8$ kcal/mole.

The mass-spectrometric study, carried out by Porter, Schissel and Inghram [3306], on the composition of the vapors above the system Al (liquid) + Al_2O_3 (solid) confirmed the suggestion of Brewer and Searcy [931] that Al_2O is the main product of evaporation under the conditions of their tests. By the temperature-dependence of the ion current of Al_2O^+ Porter, Schissel and Inghram ascertained that the heat effect of the reaction

$${}^4/_3Al(liquid) + {}^1/_3Al_2O_3(sol.) = Al_2O(gas) \qquad (XXIV.3)$$

at 932°K is 86 ± 5 kcal/mole,* to which corresponds $D_0(Al_2O) = 251 \pm 5$ kcal/mole.

The most detailed study of the evaporation of aluminum oxide has been carried out by Drowart, De Maria, Burns and Inghram [1405a] (see page 1612). Based on the measured partial pressures of the components of the reaction

$$Al_2O(gas) = 2Al(ra3) + O(gas) \qquad (XXIV.4)$$

and the calculated values of the thermodynamic functions, the authors of the work [1405a] ascertained the value $D_0(Al_2O) = 244.8 \pm 7$ kcal/ /mole (mean of all tests with different chambers). The values Φ_T^* Al_2O) estimated by the authors of the work [1405a] are lower by about 2 cal/mole•degree than the values adopted in the present Handbook (see page 1615). To achieve agreement with the values of the thermodynamic functions adopted in the Handbook the value D_0, ascertained by the authors of the work [1405a], must be reduced to 240.2 kcal/mole. The calculation, based directly on the partial pressures ascertained in the work and the values of the thermodynamic functions of Al_2O adopted in the present Handbook, leads, however, to the value $D_0(Al_2O) = 242$ kcal/mole which is not consistent with the above-mentioned value; the reasons of this discrepancy are not clear.

In the work of Hoch and Johnston [2089] it has been shown that on heating the mixture Al (liquid) + Al_2O_3 (solid) to temperatures of 1050-1600 C and with an Al/O ratio in the mixture equal to two the condensed phase of the composition Al_2O becomes stable. At temperatures above 1500 C and an Al/O ratio equal to 1, still another condensed phase, AlO becomes stable. Hence, the results of the calculations of the tests of Porter et al [3306], based on the suggestion that the composition of the condensed phase Al (liquid) + Al_2O_3 (solid) remains unchanged on heating to 1500-1800°K, may contain a mistake. The same comment may pertain to the tests of Brewer and Searcy [931], too.

Drowart et al [1405a] measured the values of the equilibrium constants of the reaction (XXIV.4) between gaseous substances which made it possible to avoid the error cropping up in connection with the formation of Al_2O and AlO in the condensed state. Hence, one has adopted in the Handbook the value

$$D_0(Al_2O) = 242 \pm 7 \text{ kcal/mole},$$

computed using the partial pressures of the components of the reaction (XXIV.4), found in the work [1405a]. To the adopted value corresponds

$$\Delta H^\circ f_0(Al_2O, \text{gas}) = -32{,}013 \pm 7{,}5 \text{ kcal/mole}.$$

Al_2O_3 (corundum). The heat of combustion of aluminum was determined repeatedly. In the old works of Berthelot [793], Wartenberg and Witzel [4174], Moose and Parr [2945] pure aluminum has been burnt insufficiently. Hence, the heats of combustion of aluminum (related to 2 gram-atom), obtained in these works and equal to -380.2, -396.0 and -375.9 kcal, respectively, are inaccurate.

In the works of Roth and co-workers the following values of the heat of combustion were ascertained: -380.8 kcal [3529], -393.3 kcal [2837] and -402.9 kcal [3535]. In the work of Roth, Wirths and Berendt, [3533] the value of -398 kcal/mole, the mean of the results of the works [2837, 3535], is recommended as most likely.

Snyder and Seltz [3809], Holley and Huber [2108], Schneider and Gattow [3643] and Mah [2738] made very accurate measurements of the heat of combustion of aluminum (purity 99.99% and above) and found values equal to -399.04 ± 0.24, -400.29 ± 0.31, -400.6 ± 1.4 and -400.48 ± 0.25 kcal, respectively. Thus, the heats of combustion of aluminum, ascertained in recent works, are in good agreement. However, in the literature not a single point of view is expressed with regard to the phase composition of the aluminum oxide forming in the combustion.

Wartenberg [4158, 4159] and Schneider and Gattow [3643] reckon that apart from corundum the combustion products of aluminum contain still another modification of aluminum oxide (x-Al_2O_3) which is slowly converted into corundum in the heating process. Schneider and Gattow estimated the quantity of x-Al_2O_3, forming on combustion of aluminum, and the heat of transition of x-Al_2O_3 into corundum. The introduction of a correction calculated on this basis into the results of calorimetric measurements leads to the value of 402 ± 2 kcal/mole for the heat of formation of corundum.

In the works of American scientists [3809, 2108, 2738] it has been suggested that corundum forms in the combustion of aluminum. Mah [2738] carried out an x-ray diffraction analysis of the combustion products and showed that the main product of combustion is corundum and that other modifications form in negligible quantities. This point of view on the composition of the combustion products of aluminum is more reasonable [18].

In the Handbook the value

$$\Delta H^\circ f_{298,15}(\mathrm{Al_2O_3},\ \text{corundum}) = -400{,}4 \pm 3 \text{ kcal/mole},$$

suggested in the work of Mah [2738], is adopted.

Al_2O_3 (gas). The determination of the heat of sublimation of aluminum oxide is made difficult by its extremely low volatility (consequently, the necessity of making the investigations at very high temperatures) and the capacity of being reduced at elevated temperatures.

The results of measurements of the pressure of Al_2O_3 vapors, performed by Ruff and co-workers [3564, 3556], are wrong since under the conditions of their tests aluminum oxide was vigorously reduced by the tantalum of which the crucibles were made.

Brewer and Searcy [931] carried out 11 measurements of the pressure of the vapors above aluminum oxide by an integral variant of the effusion method (2309-3605°K) with tungsten chambers. The authors of the work [931] suggested that AlO is the main product of evaporation of aluminum oxide. The evaluations made [420, 296] showed, however, that the evaporation rates of aluminum oxide ascertained in the work [931] cannot be explained in case AlO is the only product of evaporation. Suggesting that apart from AlO under the test conditions [931] Al_2O_3 evaporates additionally, in the works [420, 296] the value $\Delta Hs_0(Al_2O_3)$ = 172 kcal/mole was computed. But subsequently it was shown in the works [487, 3673b, 1405a, 4158] that under the test conditions [931] tungsten must vigorously reduce the aluminum oxide and, consequently, the measured results [931] cannot lead to a correct value of the heat of sublimation of aluminum oxide.

Wartenberg [4158] studied the volatility of aluminum oxide by the channel method. A tube of pure aluminum oxide was heated to 2223°K in a stream of dry air. From the change of the weight of this tube Wartenberg determined the quantity of aluminum oxide evaporated. It became evident, however, that as a result of heating the weight of the tube increased owing to the condensation of sodium oxide evaporating from other parts of the apparatus, inside of the tube. After the sodium oxide had been washed out a slight reduction of the weight of the tube as compared to the initial weight was observed (the quantity of the sodium oxide precipitated was about 10 times higher than this reduction of weight). The evaluation of the heat of sublimation of aluminum oxide, based on the suggestion that the weight of the tube decreased because of the evaporation of Al_2O_3, leads to the value ΔHs_0 = 176 kcal/mole. The reliability of this value reduces the necessity of introducing into the measured results important corrections for the condensation of sodium oxide and the absence of an analysis of the condensate (possibly, the reduction of weight recorded was du to the evaporation of impurities).

The mass-spectrometric study of the composition of the evaporation products of aluminum oxide under neutral conditions (2036-2594°K) carried out by Drowart, De Maria, Burns and Inghram [1405a], has shown that Al and O are the main products of evaporation. Besides, the vapors contain AlO and Al_2O (partial pressures one to two orders lower than of Al and O) and a small quantity of Al_2O_3 (four orders lower than of Al and O). An ion current of $Al_2O_3^+$ was not recorded in the vapors; this means that the partial pressure of Al_2O_3 must be less than 10^{-10} atm with a total pressure of the evaporation products of about $2 \cdot 10^{-5}$ atm. By means of these data the lower limit of the heat of sublimation of aluminum oxide can be evaluated, $\Delta Hs_0 \geq 200$ kcal/mole. The conclusion on the absence of Al_2O_3 molecules in the vapors of aluminum oxide under conditions of vacuum evaporation cannot be used directly in handling the data of Wartenberg [4158], since the latter were obtained on evaporation of aluminum oxide in air. The limit of potential values $\Delta Hs_0(Al_2O_3$, cryst.), ascertained in the work [1405a], is indisputable, however, and the underestimated value $\Delta Hs_0(Al_2O_3$, cryst.) obtained by Wartenberg is explained, apparently, by the evaporation of impurities.

Thus, data confirming the presence of Al_2O_3 molecules or other heavier molecules in the vapors of aluminum oxide are not known in the literature [1405a]. Accordingly, no experimental values of the molecular constants and the heat of formation of Al_2O_3 (gas) are available. Hence, the thermodynamic properties of Al_2O_3 (gas) are not discussed in the Handbook. In order to make it possible to evaluate the composition of the evaporation products of aluminum oxide, in Volume II of the Handbook [Table 293 (II)] the values are given of the equilibrium constants of the reaction

$$Al_2O_3(\text{cryst., liquid}) = 2Al(\text{gas}) + 3O(\text{gas}), \qquad (XXIV.5)$$

the heat effect of which is

$$\Delta H_0 = 725{,}455 \pm 3 \text{ kcal/mole.}$$

At the same time it should be noted that at temperatures below 2500°K under oxidizing conditions, e.g., on evaporation in air, Al_2O_3 will be the main product of evaporation, if the heat of sublimation of aluminum oxide is 200 kcal/mole. At temperatures above 2500°K, however, AlO will become the main product of evaporation under oxidizing conditions.

Studies of the evaporation of aluminum oxide under oxidizing conditions and the experimental determination of its heat of sublimation are extremely desirable.

AlH (gas). The study of the predissociation in the AlH spectrum, carried out by Herzberg and Mundie [2307] leads to a value of the dissociation energy equal to 71.5 kcal/mole. Since the curve of the potential energy of the state $A^1\Pi$ shows a small maximum, the actual value of the dissociation energy of AlH must be slightly lower. Hence, Gaydon [1668] suggests the value

$$D_0(\mathrm{AlH}) = 67 \pm 5 \text{ kcal/mole},$$

which is adopted in the present Handbook. This value is practically consistent with the value of the dissociation energy, evaluated by linear extrapolation of the vibrational levels of the ground state of AlH using the constants ascertained by Zeeman and Ritter [4376]. To the adopted value of the dissociation energy corresponds

$$\Delta H°f_0(\mathrm{AlH}, \text{gas}) = 60{,}132 \pm 5{,}2 \text{ kcal/mole}.$$

AlF (gas). The linear extrapolation of the vibrational energy levels of the ground state of the AlF molecule using the constants adopted in the present Handbook leads to the value $D_0(\mathrm{AlF}) = 101.48$ kcal/mole. Welti and Barrow [4203] have shown, however, that the linear extrapolation of the vibrational levels of the ground state of the molecules of monofluorides of Group-III elements leads to values which amount to about 65% of the value of the dissociation energy of these molecules. For AlF this gives $D_0(\mathrm{AlF}) \approx 152$ kcal/mole. A brief diagrammatic extrapolation of the vibrational levels of the excited state $A^1\Pi$ of the AlF molecule, carried out by Barrow, Johnson and Smith [657], leads to the dissociation limit, situated 58,544 cm^{-1} above the level $v = 0$ of the state $X^1\Sigma$. Assuming that in analogy to GaF and InF the dissociation limit of the state $A^1\Pi$ of the AlF molecule corresponds to the dissociation to $\mathrm{Al}(^2P_{3/2}) + \mathrm{F}(^2P_{3/2})$, the authors of the work [657] obtained $D_0(\mathrm{AlF}) = 167$ kcal/mole, which exceeds by about 12 kcal/mole the D_0(AlF) value obtained by investigating the equilibria (see below).* As pointed out in the works [3540, 643], this discrepancy can be explained on the basis of the assumption of the presence of a maximum on the potential curve of the state $A^1\Pi$ of the AlF molecule. A similar phenomenon is no rare exception, analogous maxima are observed likewise on the curve of the state $A^1\Pi$ of the AlCl molecule and on the curves of the states $B^3\Pi$ of the AgCl, AgBr and AgI molecules [2996].

A more accurate value of the heat of formation and, accordingly, the dissociation energy of AlF has been ascertained studying the equilibrium of the reaction

$$AlF_3(\text{cryst.}) + 2Al(\text{liquid.}) = 3AlF(\text{gas}). \qquad (XXIV.6)$$

Porter [3303a] carried out a mass-spectrometric analysis of the compositions of the products of his reaction at about 950°K and ascertained that AlF is the main gaseous component.

Gross, Campbell, Kent and Levi [1863] ascertained the equilibrium constant of the reaction (XXIV.6) at 1193°K. The reaction was carried out in a graphite vessel having an outlet in the shape of a fine capillary. At the same time lead evaporated from this vessel. The analysis of the condensate rendered it possible to ascertain the relation of the aluminum and lead quantities precipitated on the collector, and to calculate the partial pressure of AlF. The evaluation using the values of the thermodynamic functions adopted in the Handbook leads to the value $\Delta H_0 = 177.91 \pm 1.0$ kcal/mole for the heat effect of this reaction, to which corresponds $\Delta H^\circ f_0(AlF) = -59.2 \pm 1.0$ kcal/mole.

In the work of Baymakov [81], based on an analysis of the curves of the rate of the weight loss of the crucible in which the reaction (XXIV.6) took place, the temperatures were ascertained at which the pressure of the AlF vapors became equal to a definite value. From the five experimental points so obtained (1287-1349°K) the value of the heat effect of this reaction, $\Delta H_0 = 179.1 \pm 5.0$ kcal/mole, and $\Delta H°f_0$ (AlF) = -58.8 ± 2.0 kcal/mole, were estimated with the aid of the values of the thermodynamic functions adopted in the present Handbook.

The partial pressure of AlF, forming as a result of the reaction (XXIV.6), were measured by Witte and Barrow [4302] by a torsional variant of the effusion method (830-932°K). The reaction was performed in an effusion chamber of carbon. Based on the temperature dependence of the pressure, obtained in two most reliable test series, Witte and Barrow [4302] ascertained the value of the heat effect of the reaction (XXIV.6), $\Delta H_0 = 173.7 \pm 2$ kcal/mole, or $\Delta H°f_0$(AlF), gas) = -60.61 ± 1.2 kcal/mole. The calculation based on the values of the thermodynamic functions of AlF computed by the authors [4302] led to $\Delta H_0 =$ $= 171.8 \pm 1.3$ kcal/mole. The recalculation of the results of these tests using the thermodynamic functions adopted in the present Handbook leads to the similar value of 171.2 kcal/mole to which corresponds $\Delta H°f_0$(AlF), gas) = -61.4 ± 1 kcal/mole.

Semenkovich [368a] measured the equilibrium constants of the reaction (XXIV.6) using the transfer method (LL33-1473°K). To the resulting partial pressures of AlF corresponds the heat effect of the reaction $\Delta H_0 = 169.6$ kcal/mole and $\Delta H°f_0$(AlF) = -62 kcal/mole.

The most accurate measurements of the equilibrium constant (XXIV.6) were made by Witte and Barrow [4302]. Giving preference to this work

$$\Delta H°f_0(\text{AlF, gas}) = -61 \pm 1{,}5 \text{ kcal/mole.}$$

is adopted in the Handbook. The error of the adopted value is determined in the first place by the error of the value $\Delta H°f_{298.15}$(AlF_3, cryst.) used in the calculations.

To the adopted value of the heat of formation corresponds

$$D_0(\text{AlF}) = 155 \pm 2{,}2 \text{ kcal/mole,}$$

that is 12 kcal/mole less than the value ascertained by diagrammatic extrapolation of the vibrational levels of the state $A^1\Pi$.

AlF_2 (gas). Experimental data confirming the presence of AlF_2 molecules in aluminum fluoride vapors are not known in the literature. Mass-spectrometric studies of the composition of the evaporation products of aluminum fluoride [3307a] and a mixture of aluminum with aluminum fluoride [3303a] have shown the presence of a large quantity of AlF_2^+ ions. These ions formed, however, in the dissociation ionization of AlF_3 molecules. If, thus, in the vapors a small quantity of AlF_2 molecules was present additionally, it could not be detected by this method.

In analogy with aluminum chloride (see page 1629) it has been suggested that AlF_2 becomes a component of the composition of the evaporation products of aluminum fluoride. The value of the heat of formation adopted in the Handbook

$$\Delta H^\circ f_0(AlF_2, \text{gas}) = -173 \pm 10 \text{ kcal/mole}$$

was evaluated by the method proposed by Karapet'yants. For the evaluation data on the heat of formation of AlF, AlF_3, AlCl, $AlCl_2$ and $AlCl_3$ were used. To the adopted value corresponds

$$D_0(AlF_2) = 285{,}5 \pm 10 \text{ kcal/mole}.$$

AlF_3 (cryst.). The calculation of the heat of formation of aluminum trifluoride on the basis of data on the heats of solution is made difficult because of the formation of crystalline hydrates and the insolubility of anhydrous AlF_3. The values obtained in the works [813, 3508, 4153] for the heat of formation of aluminum trifluoride, based on thermochemical cycles including the heat of solution, differ significantly from each other and are very inaccurate, since the results of rough estimates were used in computing them. The most accurate estimate of this type was made by Brewer [1093] who evaluated the heat of hydration and the entropy of AlF_3 (cryst.) and, using the data on the solubility of AlF_3 [1470] and the entropy of the ions [2564], he ascertained the value of the heat of formation of crystalline aluminum trifluoride, $\Delta H°f_{298.15} = -323 \pm 15$ kcal/mole.

In the work of Gross, Hayman and Levi [1864] the heat effect of the reaction

$$\frac{3}{2}PbF_2(\text{cryst.}) + Al(\text{cryst.}) = AlF_3(\text{cryst.}) + \frac{3}{2}Pb(\text{cryst.}), \qquad (XXIV.7)$$

has been measured, equal to $\Delta H_{298.15} = -117.9$ kcal/mole. In total, six tests were made. The initial mixtures contained aluminum in excess. No analysis of the lead fluoride and reaction products was carried out (these authors detected no satisfactory method of analysis), and the calculations of the tests were made in the assumption that the reaction is fully accomplished. It has been observed that the heat of reaction depends were markedly on the method of drying the initial lead fluoride.

The heat effect of the reaction (XXIV.7) was measured repeatedly by Skuratov, Kolesov and Martynov [41]. The investigation was made within a wider range of compositions of the initial mixtures and under more different conditions of carrying out the tests (different stages of grinding the starting materials; different materials of the crucibles containing the reaction mixture; different stage of compressing the mixture, etc.). In this work 24 measurements were made and the heat of reaxtion $\Delta H_{298.15} = -117.7$ kcal/mole was ascertained. Thus, the results of the measurements of the heat effect of the reaction (XXIV.7), obtained by Gross, Hayman and Levi [1864] and Skuratov, Kolesov and Martynov [41], were in very good agreement in spite of the test conditions.

In the Handbook one has adopted the value

$$\Delta H^{\circ}f_{298.15}(AlF_3,\ \text{cryst.}) = -357 \pm 3\ \text{kcal/mole},$$

computed using the results of measurements of the heat effect of the reaction (XXIV.7).

AlF$_3$ (gas). The composition of AlF$_3$ vapors was studied by the mass-spectrometric method by Porter and Zeller [3307a]. In this work it has been ascertained that AlF$_3$ is the main component of the vapor. The quantity of the dimer $(AlF_3)_2$ amounts to about 2% and, consequently, the formation of the dimer can be neglected in calculating the heat of sublimation of aluminum fluoride. Porter and Zeller found the value of the heat effect of the reaction

$$(AlF_3)_2\ (\text{gas}) = 2AlF_3\ (\text{gas}), \qquad \text{(XXIV.8)}$$

equal to $\Delta H_{1000} = 48.0 \pm 4$ kcal/mole.

The pressure of saturated vapors of aluminum trifluoride was measured by Albrich [3125] (spring balance method, 1371-1567°K), Ruff and Le Boucher [3559] (spring balance method, 1367-1524°K), Naryshkin [305] (channel method, 1108-1273°K), Yevseyev, Pozharskaya, Nesmeyanov and Gerasimov [13, 183] (Knudsen method, 980-1123°K), Gross, Campbell, Kent and Levy [1863] (simultaneous evaporation with lead, 1193°K) and Witte and Barrow [4302] (torsional variant of the effusion method, 955-1063°K). From these data with the aid of the values adopted in the present Handbook for the thermodynamic properties of AlF$_3$ in the condensed and gaseous states the values ΔHs_0(AlF$_3$ cryst.) were calculated equal to 71.5 ± 0.6, 70.3 ± 0.5, 71.3 ± 0.3, 69 and 71.0 ± 0.2 kcal/mole. With the exception of the measurement of Gross et al [1863], the results of the remaining measurements are in good agreement. The most accurate measurements were carried out by Yevseyev et al [13, 183] and Witte and Barrow [4302]. From the temperature-dependence of the AlF$_3$ pressure [Eq. (IV.14)] using the data [13, 183] the value $\Delta Hs_0 = 81$ kcal/mole and using the data [4302] $\Delta Hs_0 = 71.54 \pm 0.6$ kcal/mole were computed. The discrepancy of the value ΔHs_0, calculated by two methods using the data [13, 183], is indicative of errors in the determination of the temperature-dependence of the pressure of AlF_3 vapors in these works.

In the Handbook one has adopted the value

$$\Delta Hs_0(AlF_3,\ \text{cryst.}) = 71 \pm 1{,}5 \text{ kcal/mole},$$

calculated using the results of the measurements [13, 183, 4302]. The error of this value is due to the important errors of the thermodynamic functions, particularly, of AlF_3 (gas), used in these calculations. To the adopted value of the heat of sublimation correspond

$$\Delta H^\circ f_0(AlF_3,\ \text{gas}) = -284{,}517 \pm 3{,}3 \text{ kcal/mole},$$
$$D_0(AlF_3) = 415{,}517 \pm 4 \text{ kcal/mole}.$$

AlCl (gas). The study of the predissociation in the spectrum of the AlCl molecule leads to a dissociation limit of the state $A^1\Pi$ corresponding to $D_0(AlCl) = 119.7$ kcal/mole [2113]. The close value of 123.4 kcal/mole gives the limit of the coincidence of the vibrational levels of the state $A^1\Pi$. However, these values of the dissociation energy can exceed the true value, since on the potential curve of the state $A^1\Pi$ of the AlCl molecule a maximum may occur [643]. The linear extrapolation of the vibrational levels of the ground state of AlCl as well as for other diatomic halides of Group-III elements lead to an underestimated value, $D_0(AlCl) = 84.2$ kcal/mole.

The most reliable value of the dissociation energy of AlCl can be computed on the basis of equilibrium studies. Heise and Wieland [1984] investigated the absorption spectra of AlCl forming in the reactions

$$AlCl_3(\text{gas}) = AlCl(\text{gas}) + Cl_2(\text{gas}),$$
$$AlCl_3(\text{gas}) + 2Al(\text{liq.}) = 3AlCl(\text{gas}).$$

From the temperature-dependence of the intensity of the absorption bands of AlCl Heise and Wieland calculated the value $\Delta H^\circ f_{298.15}$(AlCl, gas) = 10.5 ± 2 kcal/mole. In the work of Foster, Russel and Cochran [1584] the equilibria of the reactions (XXIV.9) and (XXIV.10) were evaluated, too. From data in the literature Foster et al adopted $\Delta H°f_0$(AlCl, gas) = -13.85 kcal/mole, computed the partial pressure of AlCl, obtained as a result of the reaction (XXIV.9), and comparing them with the measured intensities of the absorption spectrum they ascertained the dependence of the intensity of the absorption spectrum of AlCl on the partial pressure. Using this dependence and the intensities of the AlCl absorption spectrum, measured experimentally in the products of the reaction (XXIV.10), Foster et al ascertained the partial pressures of AlCl forming in the reaction (XXIV.10). The authors [1584] ascertained that the data obtained by them are consistent with the value $\Delta H°f_0$(AlCl, gas) = -13.85 kcal/mole, adopted in the calculation. These data cannot be used, however, to obtain the independent value $\Delta H°f_0$(AlCl).

By means of the quantity of aluminum carried off by passing over it a definite volume of $AlCl_3$ vapors, Russel, Martin and Cochran [3568] ascertained the value of the equilibrium constant of the reaction (XXIV.10) equal to 0.539 at 1388°K and of the $AlCl_3$ pressure equal to 740 mm Hg. From these data using the values adopted in the Handbook for the thermodynamic properties of the components of the reaction (XXIV.10) the value $\Delta H°f_0$(AlCl, gas) = -13.3 kcal/mole was evaluated.

A detailed study of some equilibria in which AlCl takes part was carried out by Gross, Campbell, Kent and Levi [1863]. Passing argon, saturated at a definite temperature with $AlCl_3$ vapors, through fused aluminum and analyzing the reaction products forming, these authors ascertained the values of the equilibrium constants of the reaction (XXIV.10) within the 1225-1278°K temperature range. Based on these data and the values adopted in the Handbook for the thermodynamic properties of the components of the reaction (XXIV.10) $\Delta H^\circ f_0(\mathrm{AlCl})$ = = -11.8 kcal/mole was evaluated. Besides, Gross et al [1863] measured the partial pressures of AlCl obtained on heating in a special vessel a mixture of aluminum metal with NaCl or KCl. In these systems, apart from NaCl or KCl vapors the products of the reactions

$$\mathrm{NaCl}(\text{cryst.}) + \mathrm{Al}(\text{liquid.}) = \mathrm{AlCl}(\text{ra3}) + \mathrm{Na}(\text{gas}),$$
$$\mathrm{KCl}(\text{cryst.}) + \mathrm{Al}(\text{liquid.}) = \mathrm{AlCl}(\text{ra3}) + \mathrm{K}(\text{gas}).$$

became part of the gaseous phase.

The equilibrium vapor was removed from the vessel and in it the relation was determined between Al and NaCl or Al and KCl, respectively. Using the well-known vapor pressures of NaCl and KCl the values of the partial pressures of AlCl were ascertained. The recalculation of the results of the measurements of Gross et al with the aid of the values adopted in the Handbook for the thermodynamic properties of the components of these reactions led to the values $\Delta H^\circ f_0$(AlCl, gas) equal to -11.5 kcal/mole (equilibrium with NaCl (cryst.), 1053°K), -10.0 kcal/mole (equilibrium with NaCl (liquid), 1243°K), and -11.9 kcal/mole (equilibrium with KCl (cryst.), 1023°K)_

In the work of Heimgartner [1983] a study of the equilibrium (XXIV.10) was carried out within a much wider range of temperatures (878-1383°K). Based on this study Heimgartner ascertained the value $\Delta H^\circ f_{298.15}$(AlCl, gas) = -10.28 kcal/mole.

With the exception of the value $\Delta H^\circ f_0$(AlCl, gas), obtained in the work [3568], all remaining values agree satisfactorily. In the Handbook the mean value

$$\Delta H^\circ f_0(\mathrm{AlCl},\ \text{gas}) = -11 \pm 0{,}8 \text{ kcal/mole},$$

is adopted to which corresponds

$$D_0(\mathrm{AlCl}) = 115{,}05 \pm 1{,}7 \text{ kcal/mole},$$

that is 5-8 kcal/mole less than the values derived from the dissociation limit in the spectrum of AlCl.

$AlCl_2$ (gas). Direct experimental data allowing to ascertain the presence of $AlCl_2$ molecules in vapors of aluminum trichloride are not known in the literature. The mass-spectrometric study made by Porter and Zeller [3307a] has revealed the presence of a large quantity of $AlCl_2^+$ ions, obtained by electron bombardment of aluminum trichloride vapors. Porter and Zeller have shown, however, that these ions form on dissociation ionization of $AlCl_3$ molecules. If, thus, even a small amount of $AlCl_2$ is contained in the composition of the evaporation products, it cannot be detected by this method.

Heimgartner [1983] studied the reaction (XXIV.10) within the 878-1383°K range. In the works [1863, 4198, 3568] discussed above the same reaction was investigated within much more restricted temperature ranges. The wide temperature range enabled Heimbartner to ascertain that the results of his study cannot be explained, if it is assumed that in the vapors above the mixture of Al and $AlCl_3$, AlCl (gas) and $AlCl_3$ (gas) are contained exclusively. Hence, Heimgartner proposed that under the conditions of his tests $AlCl_2$ (gas), forms, too, and evaluated the heat of formation of this gas equal to -76 kcal/mole.

Previously, Miescher [2904, 2905] found by means of the situation of the longwave limit of the spectrum of $AlCl_3$ vapors that the energy of the bond $D(AlCl_2 - Cl)$ must be less than 106 kcal/mole. This is consistent with the value $\Delta H^\circ f_0(AlCl_2, \text{gas})$ the absolute value of which exceed 62 kcal/mole.

In the Handbook one has adopted

$$\Delta H^\circ f_{298.15}(AlCl_2, \text{gas}) = -76 \pm 5 \text{ kcal/mole},$$

ascertained by Heimgartner [1983]. To this value corresponds

$$D_0(AlCl_3) = 208{,}386 \pm 5{,}2 \text{ kcal/mole.}$$

AlCl$_3$ (cryst). In the Handbook [3508] on the basis of data on the heat of solution of aluminum in hydrochloric acid [1056, 3534, 4367, 815, 3433] and the heats of solution of aluminum trichloride [3526]* and sulfate [4368] the value $\Delta H°f_{298.16}$(AlCl$_3$, cryst.) = -166.2 kcal/mole is proposed. The error of this value is 1-1.5 kcal//mole [1093, 267].

Siemonsen [3720] determined the value of the heat of formation of AlCl$_3$, burning aluminum metal in chlorine. The reaction was carried out in a calorimetric bomb at a chlorine pressure of 7-8 atm. By this method it was ascertained that $\Delta H°f_{293.15}$(AlCl$_3$, cryst.) = -167.5 ± 0.4 kcal/mole.

The most accurate measurement of the heat of formation of aluminum chloride was carried out by Coughlin [1196]. In this work the heat of solution of aluminum chloride was measured in a solution of hydrochloric acid. Making use of the value of the heat of solution of aluminum metal in hydrochloric acid, measured in his previous study [1194], Coughlin ascertained for the heat of formation of aluminum chloride the value

$$\Delta H°f_{298.15}(AlCl_3, \text{ cryst.}) = -168{,}57 \pm 0{,}2 \text{ kcal/mole.}$$

AlCl$_3$ (gas). Under the conditions of tests in which the pressure of saturated vapors is measured the vapors of aluminum trichloride are composed almost completely of dimerized molecules. Hence, in order to compute the value of the heat of sublimation of aluminum trichloride

$$AlCl_3(\text{cryst.}) = AlCl_3(\text{gas}), \qquad (XXIV.13)$$

the values of the equilibrium constants of the reaction

$$Al_2Cl_6(\text{gas}) = 2AlCl_3(\text{gas}). \qquad (XXIV.14)$$

must be known. These values were evaluated by Fischer, Rahlfs and Benze

[1567] (605-869°K) and by Smits and Meyering [3803] (669-816°K) based on measurements of the density of saturated vapors of aluminum trichloride.

The most accurate measurements of the pressures of saturated vapors of aluminum trichloride were obtained by various methods by Fischer, Rahlfs and Benze [1567] (393-450°K) Treadwell and Terebesi [4015] (365-519°K), Smits and Meyering [3803] (420-482°K), Takahashi [3917] (390-424°K) and Dunne and Gregory [1421] (295-323°K).

Extrapolating the values of the equilibrium constants of the reaction (XXIV.14), ascertained in the works [1567], [3803], to the range of lower temperatures, the authors of the Handbook computed the values P_{AlCl} and the heats of sublimation of $AlCl_3$ at 0°K, equal to 26.05 [1567], 25.93 [4015], 25.83 [3803], 26.17 [3917] and 26.6 kcal/mole [1421]. These values are in good agreement with each other, with the exception of the results obtained by Dunne and Gregory [1421]. The measurements in the work [1421] had been carried out, however, at very low temperatures, which required a much more extensive extrapolation of the values of the equilibrium constants of the reaction (XXIV.14), by which, apparently, the discrepancy obtained is explained.

In the Handbook the value of the heat of sublimation of aluminum chloride is adopted in conformity with the equation of the reaction (XXIV.13) equal to

$$\Delta Hs_0(AlCl_3,\ \text{cryst.}) = 26{,}0 \pm 1{,}5\ \text{kcal/mole}.$$

The error of this value is defined by the inaccuracy of the thermodynamic functions of aluminum chloride in the condensed state and the necessity of extrapolating the values of the equilibrium constants (XXIV.14) to lower temperatures.

To the adopted value correspond

$$\Delta H^\circ f_0'(\mathrm{AlCl_3},\ \text{gas}) = -142{,}185 \pm 1{,}5\ \text{kcal/mole},$$
$$D_0(\mathrm{AlCl_3}) = 303{,}335 \pm 2{,}1\ \text{kcal/mole}.$$

AlN (cryst.). Neumann, Kroger and Haebler [3053] measured the heat of interaction of aluminum metal with nitrogen. The value ascertained in this work for the heat of formation of aluminum nitride $\Delta H^\circ f_{298.15}$ = -57.4 kcal/mole, got into several Handbooks [2358, 3508]. Brewer [1093] proposed in a survey on the thermodynamic properties of nitrides a slightly higher value of -64 kcal/mole, evaluated using data from the review of Kelley [2358].

The value of the heat of formation of AlN can be computed by determining the equilibrium constants of reactions in which it takes part. Thus, Satoh [3592], based on his own measurements of the specific heat of aluminum nitride and the data of Frankel [1597] on the equilibrium of the reaction

$$\mathrm{Al_2O_3}(\text{крист.}) + 3\mathrm{C}(\text{graphite}) + \mathrm{N_2}(\text{gas}) = 2\mathrm{AlN}(\text{cryst.}) + 3\mathrm{CO}(\text{gas}), \quad (\text{XXIV.15})$$

ascertained that the heat effect of this reaction at 298.15°K amounts to 150.2 kcal. The possibility of side reactions with formation of the highly volatile lower aluminum oxides reduces the accuracy of this value. To the heat effect ascertained corresponds the heat of formation of aluminum nitride, $\Delta H^\circ f_{298.15}$ = - 85 kcal/mole. In the work of Satoh [3592] the value of -74.7 kcal/mole was ascertained which differs markedly from the above-mentioned value. The discrepancy is explained by the obsolete value of the heat of formation of aluminum oxide, used by Satoh in the calculation.

The equilibrium of the reaction

$$4\mathrm{AlN}(\text{cryst.}) + 3\mathrm{C}(\text{graphite}) = \mathrm{Al_4C_3}(\text{cryst.}) + 2\mathrm{N_2}(\text{gas}) \qquad (\text{XXIV.16})$$

has been studied by Prescott and Hincke [3315] at temperatures of 1700-1900°K. Kelly [2358] converted the heat effect of this reaction to standard conditions. The evaluation of the heat of formation of aluminum nitride using the data of Prescott and Hincke [3315] leads to

$\Delta H°f_{298.15}$ = -72 kcal/mole [3211]. This value is more reliable than the value computed according to the data of Frankel [1597], since Prescott and Hincke [3315] selected for the study of the equilibrium (XXIV.16) in which many secondary processes have been ruled out.

Neugebauer and Margrave [3049, 3051] determined the heat of formation of aluminum nitride by the method of direct nitration. Aluminum powder was burnt in a calorimetric bomb at a nitrogen pressure of 30 atm. In this work the value $\Delta H°f_{298.15}$(AlN cryst.) = -76.47 ± ± 0.2 kcal/mole was ascertained.

Mah et al [2738a] measured the heat of combustion of aluminum nitride in oxygen and calculated the value $\Delta H°f_{298.15}$(Aln, cryst.) = = -75.6 ± 0.4 kcal/mole. The values obtained in the works [3049, 3051] and (2738a] are in good agreement with each other. In the Handbook one has adopted

$$\Delta H°f_{298.15}(\text{AlN, cryst.}) = -76 \pm 0.5 \text{ kcal/mole}.$$

The value computed using the measurements of Prescott and Hincke [3315], coincides within the limits of potential errors with the adopted value.

AlN (gas). In the literature no experimental data are available on the basis of which it would be possible to evaluate directly the dissociation energy of the AlN molecule. Since also the spectrum and the structure of AlN have not been studied experimentally, the use of different polyempirical and theoretical relationships linking the interatomic distance and the force constant with the dissociation energy can lead only to a very approximate value.

Margrave and Stapitanonda [2777] using the approximate relation

$$D_0(MN) = U_g^\circ - I - A,$$

where $U_g^\circ = e^2/r$ is the energy of the ionic bond, I the ionization potential of the metal M, and A the affinity of the electron of the nitrogen atom N,* obtained for $D_0(AlN)$ two values: 82 and 137 kcal/mole corresponding to two values of the interatomic distance r_{Al-N}, evaluated on the basis of the ionic radii r_{N-} adopted equal to 1.08 and 0.70 A.

The evaluation based on the values $r_{Al-N} = 1.68$ A and I(Al) = 138 kcal/mole, adopted in the Handbook, leads to values $D_0(AlN)$ of 86 and 60 kcal/mole, in dependence on the adopted value A(N) which is -26 kcal/mole according to the data [2769], but zero according to the recommendation of Skinner and Pritchard [3760].

In the Handbook one has adopted the value

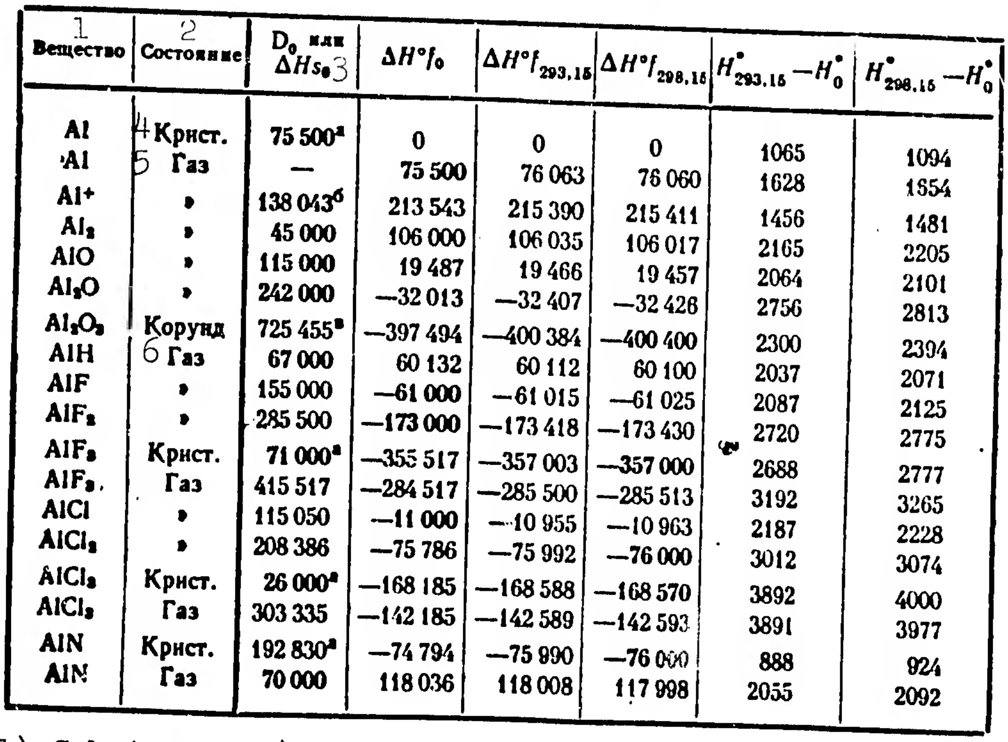
$$D_0(AlN) = 70 \pm 20 \text{ kcal/mole.}$$

To this value correspond

$$\Delta H^{\circ}f_0(AlN, \text{gas}) = 118{,}036 \pm 20 \text{ kcal/mole,}$$
$$\Delta Hs_0(AlN, \text{cryst.}) = 192{,}830 \pm 20 \text{ kcal/mole.}$$

TABLE 229

Adopted Values (in Kcal/mole) of the Thermochemical Parameters of Aluminum and its Compounds



1 Вещество	2 Состояние	D_0 или ΔHs_0 3	$\Delta H°f_0$	$\Delta H°f_{293,15}$	$\Delta H°f_{298,15}$	$H^{\circ}_{293,15} - H^{\circ}_0$	$H^{\circ}_{298,15} - H^{\circ}_0$
Al	4 Крист.	75 500^а	0	0	0	1065	1094
Al	5 Газ	—	75 500	76 063	76 060	1628	1654
Al^+	»	138 043^б	213 543	215 390	215 411	1456	1481
Al_2	»	45 000	106 000	106 035	106 017	2165	2205
AlO	»	115 000	19 487	19 466	19 457	2064	2101
Al_2O	»	242 000	−32 013	−32 407	−32 426	2756	2813
Al_2O_3	Корунд	725 455^в	−397 494	−400 384	−400 400	2300	2394
AlH	6 Газ	67 000	60 132	60 112	60 100	2037	2071
AlF	»	155 000	−61 000	−61 015	−61 025	2087	2125
AlF_2	»	285 500	−173 000	−173 418	−173 430	2720	2775
AlF_3	Крист.	71 000^а	−355 517	−357 003	−357 000	2688	2777
AlF_3	Газ	415 517	−284 517	−285 500	−285 513	3192	3265
AlCl	»	115 050	−11 000	−10 955	−10 963	2187	2228
$AlCl_2$	»	208 386	−75 786	−75 992	−76 000	3012	3074
$AlCl_3$	Крист.	26 000^а	−168 185	−168 588	−168 570	3892	4000
$AlCl_3$	Газ	303 335	−142 185	−142 589	−142 593	3891	3977
AlN	Крист.	192 830^а	−74 794	−75 990	−76 000	888	924
AlN	Газ	70 000	118 036	118 008	117 998	2055	2092

1) Substance; 2) state; 3) or; 4) cryst; 5) gas Value of the heat of sublimation; b) value of the ionization potential of the aluminum atom; c) value of the heat effect of the reaction Al_2O_3 (cryst.) = 2Al (gas) + 3O (gas) at 0°K.

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[Footnotes]

1563 Sharma [3607] ascertained in the spectrum of discharge through $AlCl_3$ vapors in helium atmosphere bands in the wavelength region of 3310-2950 A, the wave numbers of the edges of these bands are defined by the equation $\nu = 31450.8 + (391.4\ (v' + 1/2) - 0.9\ (v' + 1/2)^2) - (592.0\ (v'' + 1/2) - 3.0\ (v'' + 1/2)^2)$. Sharma made the suggestion that these bands can be associated with the Al_2 molecule, since, as to the order of magnitude, the value ω''_e is similar to the value expected of this molecule. In later works, no indications were found on the nature of the emitter of the bands observed by Sharma.

1564 Chupka, Berkowitz, Giese and Inghram [1107] evaluated a vibration frequency of Al_2 of 400 cm^{-1} and an interatomic distance of 2.5 A.

1566 The molecular constants of AlO in the states $X^2\Sigma$ and $B^2\Sigma$ ascertained in the work of Lagerqvist, Nilsson and Barrow [2530] are indicated in the notes of Table 222.

1566 In the works [3681 and 2530] these constants were obtained for lines with high values of the quantum number K. Below, results of measurements of the values γ (in cm^{-1}) are given, based on the data of various authors:

	[3681]	[2530]	[1797]
γ'	0,030	0,021±0,005	0,019±0,005
γ''	0,021	0,010±0,005	0,008±0,006

1567 The authors of the work [1145] found the following constants of AlO in the state $C^2\Pi$: $\nu_{00} = 33{,}085$, $\omega_0 = 845$ and $\omega_0 x_0 = 4$ cm^{-1}.

1567 The rotation constants were calculated from the results of measurements of the fine structure of the bands 4-2, 1-0, 0-0 and 0-1.

1571 Vago and Barrow [4046] detected that the values $x_e\mu^{1/2}$ must be approximately constant for analogous molecules. Actually, for BF, GaF, InF and TlF the values $x_e\mu^{1/2}$ are 0.021, 0.020, 0.019 and 0.020, respectively. With the constants obtained by Rochester, $x_e\mu^{1/2}$ for AlF is 0.033. According to the data of Rowlinson and Barrow [3540], $x_e\mu^{1/2} = 0.020$.

1577 Since in the AlO molecule the bond is double, it is accepted that in Al_2O the length of the bond is 0.16 A longer than in AlO, and the force constant of the bond is 0.5 k_e (AlO).

1578 The high atomization energy of Al_2O can be explained within the frame of the conventional notions on the orientation of the valences of the Al and O atoms, if one suggests that this molecule has, like N_2O, a linear symmetric structure Al = Al = O. Apparently, such an accumption would find its configuration in the fact that in mass spectra of the Al-O system Al_2^+ ions are detected the formation of which is explained by the authors [1405a] with the dissociation of Al_2O.

1579 According to the rule of Walsh [4139], the molecules under discussion must be nonlinear, since they have 17 valence electrons.

1582 $f_d = 5\cdot 10^5$, $f_{dd} = 0.5\cdot 10^5$, $f_a/d^2 = 0.2\cdot 10^5$ and $f_\Delta/d^2 = 0.43$.

$\cdot 10^5$ dynes2cm^{-1}.

1582 The intensity of the corresponding band in the absorption spectrum is markedly lower than in the emission spectrum.

1583 The values f_d and accordingly ν_1 and ν_4 depend slightly on the adopted value of the deformation constant f_a/d^2.

1584 It should be noted that the frequencies of the planar vibrations pf $AlCl_3$, adopted in the works of Stepanov [393] and Venkateswarlu and Sundaram [4086] based on the studies of the spectrum of Raman scattering of liquid aluminum trichloride (541, 348 and 808 cm^{-1}) are apparently wrong. They are not consistent with the value of the frequency of the antisymmetric vibration, ascertained by Klemperer, and the force constants of $AlCl_3$ calculated by Venkateswarlu and Sundaram by means of these frequencies, have unreasonable values; thus, the force constant of the Al-Cl bond is $5.1 \cdot 10^5$ dynes$\cdot$cm^{-1} which is more than two times higher than the value of the force constant of the bond of the AlCl $k_e = 2.09 \cdot 10^5$ dynes$\cdot$cm^{-1}).

1584 No definite regularity was ascertained in the change of the interatomic distance on transition from diatomic boron and aluminum halides (XY) to tetratomic molecules (XY_3). A comparison of the respective values of the interatomic distances r_{X-Y} in the molecules BF-BF_3, BCl-BCl_3 and AlF-AlF_3 shows that the discrepancy between them does not exceed ± 0.03 A.

1592 Witte and Barrow [4302] indicate the equation $S^\circ_T = S_{kol} + 11.5453 + 16.0154 \ln T$ for the calculation of the values S°_T; in this equation the value of the constant term is in good agreement with the value C_S, given in Table 224.

1596 In the work of Witte and Barrow [4302] the thermodynamic functions of AlF_3 were calculated, apparently, for handling experimental data, but in the paper only the equation S°_T is given.

1602 In 1960-1961, Kirillin, Sheyndlin and Chekhovskoy [227a, 227b) published results of measurements of the enthalpy of corundum within the 771-2266°K range with an accuracy of up to ±0.9%. Within the limits of the error specified these data are consistent with the values given in the present Handbook.

1605 There are indications (see [1014] that Degazarion et al measured the specific heat of $AlCl_3$ within the 15-320°K range, however, to date these data have not been published.

1612 In the work [1310] it is pointed out that Brewer recalculated again the results obtained in the work [931] and found

$D_0(AlO) = 119 \pm 8$ kcal/mole.

1612 In the work [1309a] the same authors studied the evaporation of a mixture of aluminum oxide and uranium from molybdenum effusion chambers (1876-2322°K).

1614 In the work of Porter, Schissel and Inghram [3306] the value of the heat of this reaction, $\Delta H_{932} = 85 \pm 5$ kcal/mole, has been ascertained. The value specified in the text has been obtained by recalculating the data of the work [3306] taking into account the enthalpy values of the components of this reaction, specified in the Handbook.

1621 In the work [657] vibrational levels of the state $A^1\Pi$ were observed to v = 16, the height of which above the level v = 0 of the ground state 156.4 kcal/mole. With the normal shape of the potential curve of the state $A^1\Pi$ this value must give the lower limit $D_0(AlF)$. It exceeds, however, by approximately, 1.5 kcal/mole the value of the dissociation energy, obtained as a result of studying the equilibrium of chemical reactions in which AlF is involved.

1630 As regards the heat of solution of $AlCl_3$ see also the work of Eley and Watts [1473].

1634 Evaluating $D_0(AlN)$ Margrave and Stapitanonda considered using the data of the work [2769] that A = -26 kcal/mole.

Chapter 25

BERYLLIUM AND ITS COMPOUNDS

(Be, BeO, BeH, BeF, BeF_2, $BeCl$, $BeCl_2$, BeN)

In the present chapter the thermodynamic properties of beryllium and of some of its simple compounds with oxygen, hydrogen, chlorine, fluorine and nitrogen are considered. The more complex compounds of beryllium with these elements (BeH_2, BeOh, $Be(OH)_2$, Be_3N_2 etc.) are not considered primarily because of lack of data in the literature on their structure and molecular constants. It can be assumed that most of these complex molecules will be unstable at high temperatures, and that thermodynamic calculations performed without taking into account their formation will lead to results which are close to the true ones. Predictions of this kind, however, should be made with great precaution because the results of recent mass-spectroscopic work show that in many cases the contrary picture is observed – at high temperatures in saturated vapours the complex molecules become relatively more stable. Thus, in the evaporation of beryllium oxyde it was discovered [1106] that at higher temperatures the polymeric molecules $(BeO)_n$ gain more and more importance. Moreover, under reduction conditions the Be_2O molecule may become important [72]. From the evaporation products of beryllium oxyde only Be and BeO are considered in the Handbook. Therefore these data are not sufficient for a full description of the system beryllium-oxygen, they can only give information on the amounts of atomic beryllium and beryllium oxyde in the vapours.

Also not included in the Handbook is the Be_2 molecule, because the dissociation energy of this molecule apparently does not exceed 16 kcal/mole* [1408] and it should desintegrate into atoms already at comparatively low temperatures. It should be noted that in paper [72] data were obtained according to which Be_2 is the main evaporation product of beryllium in the region 1400-1550°K, whereas monoatomic beryllium becomes the main component of the vapour only above the melting temperature (1556°K). However, these data are apparently wrong because they can only be explained in the case of $D_0(Be_2) > 50$ kcal/mole which is in disagreement with the results of all other investigations.

From the possible components of the system beryllium-oxygen-hydrogen, Be, BeO and BeH are considered in the Handbook. There are data in the literature indicating that under certain circumstances such molecules as $Be(OH)_2$ and perhaps BeOH can exist in the system Be – O – H besides the three component considered [1865]. Because of lack of data on the molecular constants and the heats of formation of these compounds they are not considered in the present Handbook.

In the Handbook four compound of beryllium with halides are considered: BeF, BeF_2, BeCl and $BeCl_2$. In addition to these compounds, dimeric molecules $(BeX_2)_2$ may be present in the beryllium-halide systems: they are not considered in the present Handbook. Apparently these compounds can exist only at moderate temperatures.

In the Handbook the thermodynamic properties of BeN(gas) are quoted. Beryllium nitride in its solid state – Be_3N_2 has considerable thermal stability: according to the data of [1093] the dissociation temperature is 2510°K. Therefore, the data quoted in the Handbook do not allow the calculation of the composition and the thermodynamic properties of the system beryllium-nitrogen below this temperature.

§99. MOLECULAR CONSTANTS

Be. In its ground state the beryllium atom has the electronic configuration $1s^22s^2$, with the corresponding term ^1S. Through the excitation of one 2s-electron of the beryllium atom a group of singlet and triplet terms is formed which correspond to the configuration $1s^22s(^2S)nl$ with the values $L = \ell$. The ionization limit of this group is at 75,192.29 cm^{-1}, whereas the first excited state $2p\,^3P^{\circ}$ is 21,980cm^{-1} higher than the ground state ^1S. Quoted in table 230 are five energy levels of the Be atom which were taken into account in the calculations of thermodynamic functions and which correspond to the transition of the 2s-electron to 2p- and 3s-states. Higher levels with excitation energies of more than 56,000 cm^{-1} can be disregarded in the following calculations.

TABLE 230

Energy Levels of the Beryllium Atom

A Номер уровня	B Состояние		E Статистический вес	F Энергия, $см^{-1}$
	C электронная конфигурация	D терм		
0	$1s^22s^2$	^1S	1	0
1	$1s^22s2p$	^3P	9	21980
2	$1s^22s2p$	^1P	3	42565,3
3	$1s^22s3s$	^3S	3	52082
4	$1s^22s3s$	^1S	1	54677

A) Number of level; B) state; C) electronic configuration; D) term; E) statistical weight; F) energy, cm-1.

The excitation energies of the singlet levels were taken from Moore [2941], of the triplet levels from Moore [2941] and the paper of Botsmann, Corliss, Meggers and Trice [882].

<u>BeO</u>. The electronic ground state of the BeO molecule is the state $X^1\Sigma$.* The bands of BeO occupy a broad region of the spectrum – from the far ultraviolet to the infrared region. The most thoroughly inves-

tigated in the emission spectrum are three systems of bands: the systems $A^1\Pi \rightarrow X^1\Sigma$ [2051, 2538, 2520, 3946, 2521] and $B^1\Sigma \rightarrow A^1\Pi$ [2521], lying in the infrared region, and the system of bands $B^1\Sigma \rightarrow X^1\Sigma$, lying in the region 4200-5700 A [742, 3487, 1963, 1964, 1309, 3945a, 2832, 2539, 2521, 2250]. Besides the systems quoted above a large number of bands has been observed in the BeO spectrum in the region 3600-2600 A. However, because of the complexity of the structure and the appreciable overlap of different systems formed by these bands, the analysis is difficult and their assignment remains to a large extent uncertain [742, 1114, 1115, 1969, 2521].

The results of work concerned with the investigation of the spectrum of BeO are collected and critically analyzed in the thesis of Lagerkvist [2521]. Lagerkvist again recorded the spectrum of BeO in the region from 2000 to 13,600 A, measured the position of 20,000 lines and performed a thorough analysis of the various systems of bands of BeO. The excitation source was an arc burning in air between electrodes of metallic beryllium. At a spectrometer with a dispersion of 1.2 and 0.5 A/mm the ultraviolet bands and the bands of the systems $B^1\Sigma - X^1\Sigma$, $A^1\Pi - X^1\Sigma$ and $B^1\Sigma - A^1\Pi$ were investigated.

In the system $B^1\Sigma - X^1\Sigma$ the fine structure of 25 bands with $v' \leqslant 11$, $v'' \leqslant 9$, and in the system $A^1\Pi - X^1\Sigma$ 26 bands with $v' \leqslant 11$, $v'' \leqslant 3$, were investigated, and in the system $B^1\Sigma - A^1\Pi$ 27 bands were identified. The results of the analysis of the vibrational and rotational structure of these systems of bands allowed Lagerkvist to calculate with great accuracy the values of the molecular constants of BeO in the states $X^1\Sigma$, $A^1\Pi$ and $B^1\Sigma$, which are quoted in Table 231 and are accepted in the present Handbook. The same constants of BeO are recommended in the book [2020] and in the Handbook [649].

As mentioned above, a large number of bands of BeO lie in the ultraviolet region of the spectrum. An analysis of these bands, performed by Bengtson-Knave [742], Harvey and Bell [1969], Ciccone [1114, 1115] and Lagerkvist showed that some ultraviolet bands are connected with the transition between the state $A^1\Pi$ and a singlet state lying approximately 40,000 cm^{-1} higher than the state $X^1\Sigma$. The vibrational and rotational constants of BeO in this state, as found by Lagerkvist, are quoted in Table 231. Moreover, it is shown in the papers of Ciccone [1114, 1115] and Lagerkvist [2521] that a number of ultraviolet bands of very complicated structure are connected with the transition between the state $A^1\Pi$ and the triplet state of BeO. Since up to now an analysis of these bands has not been performed the excitation energy and the type of the triplet state is unknown.

TABLE 231

Accepted Values of the Molecular Constants of BeO, BeH, BeF, BeCl and BeN

1 Молекула	2 Состояние	T_e	ω_e	$\omega_e x_e$	B_e	α_1	$D_e \cdot 10^6$	r_e
		3 см⁻¹						Å
BeO	$X^1\Sigma$ $A^1\Pi$ $B^1\Sigma$ $D^{з}$ h	0 9 405,61 21 253,95 39 120,1	1487,323 1144,238 1370,817 1081,8	$11,8297^{а}$ a $8,4145^{в}$ c $7,7455^{е}$ f 9,1	1,6510 1,3661 1,5758 1,31	0,0190 $0,01628^{г}$ d 0,0154 0,01	$8,198^{б}$ b $7,79^{д}$ e $8,41^{ж}$ g —	1,3310 1,4632 1,3623 1,49
BeH	$X^2\Sigma$ $A^2\Pi$	0 $20 027,9^{к}$ k	2058,5 2087,7	$35,5^{и}$ i $39,9^{и}$ j	10,308 10,470	0,300 0,329	980 1020	1,297 1,287
BeF	$X^2\Sigma$ $A^2\Pi$	0 $33 234,16^{н}$	1265,61 1171,36	$9,234^{л}$ l $8,523^{о}$ o	1,4977 1,41865	0,01685 0,01610	$8,225^{м}$ m 8,301	1,357 1,390
BeCl	$X^2\Sigma$ $A^2\Pi$	0 $27 972,76^{т}$ s	846,43 821,03	$5,15^{п}$ p $5,01^{у}$ t	$0,8^{р}$ q $0,8^{р}$ q	— —	— —	$1,71^{с}$ r $1,71^{с}$ r
BeN	$X^4\Sigma^{ф}$ u	0	$1500^{х}$ v	—	$1,57^{х}$ v	—	—	$1,40^{х}$ v

[а] $\omega_e y_e = 0{,}02235\ \text{см}^{-1}$.

[б] $\beta_1 = +0{,}0096 \cdot 10^{-6}\ \text{см}^{-1}$, $F_v = [12{,}5 - 1{,}1\,(v + 1/2)] \cdot 10^{-12}$.

[в] $\omega_e y_e = 0{,}03389\ \text{см}^{-1}$.

[г] $\alpha_2 = 0{,}000055\ \text{см}^{-1}$.

[д] $\beta_1 = 0{,}044 \cdot 10^{-6}\ \text{см}^{-1}$.

[е] $\omega_e y_e = -0{,}00027\ \text{см}^{-1}$.

[ж] $\beta_1 = 0{,}07 \cdot 10^{-6}\ \text{см}^{-1}$, $F_v = [27 - 2\,(v + 1/2)] \cdot 10^{-12}$.

h) The type of this state is not accurately known. Bengtson-Knave [742] and Harvey and Bell [1969] assume that the D-state is the state $^1\Pi$; Lagerkvist [2521] conjectures that this state may also be the state $^1\Sigma$ or $^1\Delta$.

[и] $\omega_e y_e = -0{,}5\ \text{см}^{-1}$.

[к] $A = 2{,}14\ \text{см}^{-1}$.

[л] $\omega_e y_e = 0{,}02259\ \text{см}^{-1}$.

[м] $\beta_1 = 0{,}0290 \cdot 10^{-6}\ \text{см}^{-1}$.

[н] $A = -16{,}46\ \text{см}^{-1}$.

[о] $\omega_e y_e = -0{,}00497\ \text{см}^{-1}$.

[п] $\omega_e y_e = 0{,}0205$, $\omega_e z_e = -0{,}0000582\ \text{см}^{-1}$.

q) Quoted is the value of B_0.

r) Quoted is the v value of r_0.

[т] $A = 25\ \text{см}^{-1}$.

[у] $\omega_e y_e = -0{,}0368\ \text{см}^{-1}$.

u) Accepted on the basis of the rules of correlation.

v) Estimate.

1) Molecule; 2) state; 3) cm^{-1}.

It should be noted that on the basis of the results of a perturbational analysis in the systems $A^1\Pi - X^1\Sigma$ and $B^1\Sigma - X^1\Sigma$ Lagerkvist [2521] considers as possible the existence of another two electronic states of BeO with energies of the order of 11,000 and 26,000 cm^{-1}, which were not seen in the spectrum of BeO.

BeH. The electronic ground state of the BeH molecule is the state $X^2\Sigma$.* In the emission spectrum of the BeH molecule only two systems of bands are identified: the system $A^2\Pi \rightarrow X^2\Sigma$, lying in the region from 4800 to 5600 A [4181, 3229, 741, 3135], and the system $^2\Pi^* \rightarrow X^2\Sigma$, lying in the region 1880-1960 A [4181, 4182]. The absorption spectrum of BeH has not been observed. The most complete analysis of the vibrational and rotational structure of the system $A^2\Pi - X^2\Sigma$ was done by Olsson [3135]. The bands of BeH in paper [3135] were obtained in the spectrum of an arc with beryllium electrodes burning in a hydrogen atmosphere. The spectrum was recorded in first and second order of the grating (the dispersion being 1.8 and 0.9 A/mm, respectively). The analysis of nine bands forming the sequences $\Delta v = 0, -1$ $(v'' \leqslant 4,\ v' \leqslant 4)$, enabled Olsson [3135] to determine the values of the rotational and vibrational constants in the states $X^2\Sigma$ and $A^2\Pi$. The constants found by Olsson are accepted in the present Handbook and are quoted in Table 231. The same values of the molecular constants of BeH in the states $X^2\Sigma$ and $A^2\Pi$ are recommended in the Handbook [649] and in the monograph of Hertzberg [2020].

The ultraviolet system of bands of BeH $(^2\Pi^* - X^2\Sigma)$ is investigated much worse than the system $A^2\Pi - X^2\Sigma$. In the paper of Watson and Humphries [4182] approximate values of the molecular constants of BeH in the state $^2\Pi^*$ are found as a result of an analysis of three bands of this system. Since the excitation energy of the state $^2\Pi^*$ exceeds 50,000 cm^{-1} ($T_e \sim 50\,934$ cm^{-1}), this state is not included in Table 231.

It can be expected by analogy with other molecules of the hydrides of alcaline earth metals that between the two states $^2\Pi$ ($A^2\Pi$ and $^2\Pi^*$) there is the state $B^2\Sigma$ with an excitation energy which is smaller than that of the state $^2\Pi^*$. An estimate by the method of Shifrin (see page 53) leads to a value of T_e for the state $B^2\Sigma$ equal to 26,000 ± 4000 cm^{-1}.

<u>BeF</u>. The electronic ground state of the BeF molecule is the state $X^2\Sigma$. In the spectrum of BeF only one system of bands lying in the

region 3400-2800 A has been observed. Fowler [1587] observed the absorption spectrum of BeF vapour when heating BeF_2 in a King oven up to a temperature of 2000°C.

For the first time the bands of this system were obtained by Dutt [1266] in the spectrum of a carbon arc containing BeF_2. The spectrum was recorded in first order in a spectrograph with a concave grating (dispersion 5.5 A/mm). Basing on the analysis of the results of the measurements of spectrograms obtained by Dutt [1266], Millican [2974] showed that the bands are connected with the transition $A^2\Pi - X^2\Sigma$, and found an equation describing the position of the heads of five groups of bands forming the sequences $\Delta v = 0, \pm 1$ and ± 2. A sixth group of bands lying in the region 3347-3392 A did not fit into the scheme of Mullican. Therefore Jevons [2251] anew obtained and analyzed the system of bands of BeF. In the spectrum which was excited in an arc and recorded in a quarz spectrograph (dispersion 6-4 A/mm in the region 3500-3000 A) the wavenumbers of the heads of the Q_1-branches of bands with v' and $v'' \leqslant 8$ and the wavenumbers of the heads of the R_1- and the R_2-branches of bands with $v', v'' \leqslant 13$ were measured. As a result of the processing of the obtained data Jevons found the vibration frequencies and the anharmonicity constants of BeF in the states $X^2\Sigma$ and $A^2\Pi$ ($\omega''_e = 1265{,}62$, $\omega''_e x''_e = 9{,}12$, $\omega'_e = 1172{,}58$, $\omega'_e x'_e = 8{,}78$ and $T_e(A^2\Pi) =$ $= 33\,233{,}6$ см$^{-1}$). These values of the constants are recommended in the monograph of Hertzberg [2020] and in the Handbook [649]. To determine the dissociation energy of BeF Tatevskiy, Tunitskiy and Novikov [414] investigated anew the vibrational structure of the bands of BeF. The spectrum was photographed in the spectrograph DFS-3 (dispersion 2 A/mm). Since gas-discharge tubes working in the stationary and impulse mode were used as excitation source, the bands of BeF had a weakly developed fine structure which made it possible to identify much more bands than in the paper of Jevons [2251]. An analysis performed on the heads of the Q_1-branches of bands with $v' \leqslant 15$ and $v'' \leqslant 17$, allowed to obtain the vibrational constants (ω_e, $\omega_e x_e$ and $\omega_e y_e$), which describe the positions of the experimentally observed bands much better than the constants found by Jevons [2251]. These constants are accepted in the present Handbook and are quoted in Table 231.

The fine structure of the three most intense bands of the system $A^2\Pi - X^2\Sigma$ was investigated by Jenkins [2229]. The bands 0 – 0, 1 – 0 and 0 – 1 were obtained in the spectrum of a carbon arc containing BeF_2 and were photographed in second order in a spectrograph with a concave grating (dispersion 0.97 A/mm). As a result of the analysis of the band structure Jenkins obtained two values for the constant A of the spin-orbit coupling in the state $A^2\Pi$: +22.10 and -16.46 cm^{-1}. Due to the insufficient resolution of the lines with small J it was impossible to make an unequivocal choice between these values. Considering the relative values of the Λ-splittings in the F_1 and F_2 series of terms of the state $^2\Pi$, Jenkins [2229] suggested that the state $A^2\Pi$ is the normal state $^2\Pi_r$ with the constant bond A = +22.10 cm^{-1}. Later, Malliken [2980] on the basis of a more detailed examination of the Λ-splitting as a function of J came to the conclusion that the $A^2\Pi$ state is an inverted one with the constant A = -16.46 cm^{-1}. The rotational constants of BeF in the states $X^2\Sigma$ and $A^2\Pi$ found in the paper of Jenkins [2229] are accepted in the present Handbook and are quoted in Table 231. The same values of the rotational constants are recommended in the book of Hertzberg [2020] and the Handbook [649].

BeCl. Only one system of bands $A^2\Pi - X^2\Sigma$, lying in the region 3686-3468 A was observed in the spectrum of BeCl. The emission spectrum of BeCl was investigated in the papers of Fredrikson and Hogan [160] and Novikov and Tunitskiy [321]: the absorption spectrum of BeCl was not investigated. Comparison of the spectrum and the observed electronic states of the BeCl molecule with the spectra and the electronic states of the molecules of BeF, MgF, MgCl and CaCl, for which the absorption spectrum was observed and the type of the electronic ground state is known, allows to assume that the electronic ground state of the BeCl molecule is the state $X^2\Sigma^+$.

The spectrum of the BeCl molecule was obtained for the first time by Fredrikson and Hogan [1603]. The excitation source was a beryllium arc burning in a fluorine atmosphere. The spectrum was recorded in third and fourth order of a 21-foot grating. An analysis of the band structure showed that the bands are connected with the electronic transition $A^2\Pi - X^2\Sigma$, and the type of bonding in the state $^2\Pi$ is intermediate between the cases a and b of Hund. As a result of an analysis of the rotational structure, performed on the heads of the Q_1-branches of bands with v' and $v'' \leqslant 3$, Fredrikson and Hogan found the vibrational constants of BeCl in the states $A^2\Pi$ and $X^2\Sigma$ (in cm^{-1}): $\omega_e''=846{,}58$, $\omega_e''x_e''=5{,}11$, $\omega_e'=824{,}19$, $\omega_e'x_e'=6{,}03$. These constants are recommended in the Handbook [649] and in the book of Hertzberg [2020]. Later on Novikov and Tunitskiy [321] anew investigated the emission spectrum of BeCl excited in a gas-discharge impulse tube. The spectrum was recorded in the spectrograph DFS-3 (dispersion 2 A/mm, revolving power 144,000). The analysis of 40 bands of the molecule BeCl^{35} and 26 bands of the molecule BeCl^{37} forming the sequences $\Delta v = 0, \pm 1, \pm 2$ c v' and $v'' \leqslant 10$, enabled the authors [321] to find the values of the vibrational constants of BeCl in the states $X^2\Sigma$ and $A^2\Pi$ which, although only slightly different from the constants found by Fredrikson and Hogan [1603], better describe the position of the investigated bands. The values of the vibrational constants found in paper [321] are accepted in the present Handbook and are quoted in Table 231.*

Up to now no complete analysis of the vibrational structure of the bands of BeCl could be successfully performed, since, because of the overlap of bands, lines in different branches of the bands could not be identified even in the fourth order of the 21-foot grating. As a result of measurement of the position of several lines near the heads of the $^{S}R_{21}$- and the R_1-branches of the 0 – 0 band, and the observation of a weak head belonging to the $BeCl^{37}$ molecule and lying at a distance of 0.98 cm^{-1} from the head of the $^{S}R_{21}$-branch of the 0 – 0 band of $BeCl^{35}$, Fredrikson and Hogan [1603] calculated the values of the vibrational constants for the zero vibrational levels of the states $X^2\Sigma$ and $A^2\Pi$: $B''_0 \sim 0{,}8$ and $B'_0 \sim 0{,}8$. These values of the vibrational constants which should be considered only as approximate are accepted in the Handbook and are quoted in Table 231.

An estimate of the interatomic distance in BeCl, on the basis of the combination of the values of r_{Be-F} in BeF and BeF_2 and of r_{Be-Cl} in $BeCl_2$, leads to a value $r_{Be-Cl} = 1{,}71 \pm 0{,}05\,Å$. This makes it possible to estimate the possible error in the value of B_0 found by Fredrikson and Hogan [1603] to be ±0.05 cm^{-1}.

It should be noted that in the paper of Parker [3187] the appearance was reported in the spectrum of an arc containing beryllium salts, of a system of bands $^2\Pi - {}^2\Sigma$, lying in the yellow-green region of the spectrum and assigned by the author to the BeCl molecule. A comparison of the vibrational constants found by Parker [318] ($\omega''_e = 551{,}5,\ \omega''_e x''_e = 6{,}2,\ \omega'_e = 540{,}0,\ \omega'_e x'_e = 7{,}1\ \text{см}^{-1}$), with the constants of BeCl calculated in the papers of Fredrikson and Hogan [1603] and Novikov and Tunitskiy [321] shows that both electronic states of Parker's systems are not identical with the states $X^2\Sigma$ and $A^2\Pi$, investigated in the papers [1603, 321]. To clarify the nature of this system, the spectrum of BeCl in the region from 3000 to 6000 A excited in a gas-discharge tube was investigated in paper [321]; since the bands of Parker's system were not seen therein, the conclusion can be made that this system does not belong to the BeCl molecule.*

BeN. The spectrum of the BeN molecule has not been observed experimentally. Therefore in the Handbook an approximate estimation of the molecular constants of BeN was performed.

The interatomic distance in the BeN molecule was estimated as a result of combination of interatomic distances in diatomic molecules of the oxydes and nitrides of several elements. This comparison shows that the interatomic distances in the molecule of the nitride of a given element is larger by 0.04-0.07 A than in the molecule of the corresponding oxyde. On the basis of the value $r_{Be-O} = 1{,}33\,\text{Å}$ [2521], $r_{Be-N} = 1{,}40 \pm 0{,}08\,\text{Å}$ is accepted in the Handbook. To the accepted value of the interatomic distance corresponds a rotational constant B_e equal to 1.57 ± 0.18 cm^{-1} and a frequency of normal vibration $\omega_e = 1500\,cm^{-1}$, calculated according to the Guggenheim relation (see page 88). The possible error of the value of frequency estimated in this way is 20%. The molecular constants of BeN accepted in the present Handbook are quoted in Table 231. According to the rules of correlation it is accepted that the ground state of the BeN molecule is a state of the type $^2\Sigma$.

BeF_2. The electronographic investigation of molecules of the vapors of beryllium fluoride oerformed by Akishin, Spiridonov and Sobolev [68] showed that the BeF_2 molecule has a linear symmetrical structure with an interatomic distance $r_{Be-F} = 1{,}40 \pm 0{,}03\,\text{Å}$ and belongs to the point symmetry group $D_{\infty h}$. Therefore the BeF_2 molecule must have three main vibrations – the symmetrical and antisymmetrical valence vibrations of the bonds Be – F and the doubly degenerate deformation vibration connected with a change of the angle FBeF.

Attempts to obtain and to identify the spectrum of the BeF_2 molecule were done for the first time in the papers of Prokof'ev, Neporent, Yaroslavskiy et al [28, 19, 29]. To obtain the BeF_2 spectrum a special device was designed consisting of a high-temperature cuvette with a heater of large length and a infrared spectrometer allowing the recording of the spectrum in the region from 5000 to 250 cm^{-1}. In the absorption spectrum of BeF_2 vapours at $T \sim 900-950°$ two bands with maxima at 9.8 mk (1020 cm^{-1}) and 29 mk (345 cm^{-1}) were obtained which were assigned to the frequencies ν_3 and ν_2 respectively. However, the authors [29] remark that the investigated sample of beryllium fluoride contained only 60% BeF_2 and 40% different admixtures which were not analyzed. Moreover the authors of the paper [29] emphasize that generally the absorption bands at 9.8 and 29 mk can be assigned to the absorption of gaseous beryllium fluoride only with precaution since in the cuvette a condensed state in form of smoke was always present which could substantially distort the results of measurements.

Much more reliable data about the spectrum of BeF_2 were obtained by Buechler and Klemperer [1002] who investigated in detail the spectrum of gaseous beryllium fluoride. The pressure of BeF_2 vapour necessary to obtain the absorption spectrum (about 100 mm Hg) was attained by heating BeF_2 in a King oven to a temperature of about 1000°C. The spectrum in the region from 2300 to 700 cm^{-1} was recorded in a Perkin-Elmer spectrometer with a KBr prisma. The authors of paper [1002] obtained two intense absorption bands with frequencies 1520 and 825 cm^{-1} which were interpreted as bands connected with the antisymmetrical (ν_3) and deformation (ν_2) vibrations respectively. The values of the frequencies ν_2 and ν_3 found in the paper [1002] make it possible to calculate, assuming $f_{dd} = 0,1 f_d$, the force constants of the BeF_2 molecule: $f_d = 5,51 \cdot 10^5$, $f_{dd} = 0,55 \cdot 10^5$ and $f_\alpha / d^2 = 0,73 \cdot 10^5$ dyne/cm^{-1} If it is assumed, following Buechler and Klemperer, that $f_{dd} = 0$, then $f_d = 4{,}96 \cdot 10^5$ dyne//cm^{-1} and $\nu_1 = 666$ cm^{-1}. In the Handbook a rounded average of these values ($\nu_1 = 700$ cm^{-1}) is accepted and assumed that the possible error therein does not exceed 10%. This value is given together with the experimentally determined ν_2 and ν_3 frequencies in Table 232.* The same table contains also the value for the moment of inertia of BeF_2 calculated from structural parameters found by Akishin, Spiridonov, and Sobolev [68].

$BeCl_2$. It was found, as a result of electronographic investigations of the beryllium chloride structure, by Akishin, Spiridonov, and Sobolev [68], that the $BeCl_2$ molecule has a linear symmetrical structure with an interatomic distance $r_{Be-Cl} = 1.75 \pm 0.03$ A and belongs to the punctate group $D_{\infty h}$. Such a molecule must have three normal vibrations – a symmetric and antisymmetric valent vibration of the Be-Cl bonds, and a twice degenerated deformational vibration due to the change of the ClBeCl angle.

Buechler, and Klemperer [1001, 1002] were the first who investigated the infrared spectrum of $BeCl_2$ vapors in the range 200 to 2000 cm^{-1}. In the absorption spectrum of beryllium chloride vapors at a temperature of 500°C were found four absorption bands with frequencies 484, 608, 857 and 1113 cm^{-1}. At an increase of temperature to 1000°C remained in the spectrum only two frequencies: 1113, and 484 cm^{-1}. The authors explained this by the presence of beryllium chloride at $T = 500°C$ principally in the form of a dimer [1093] (hence are the frequencies 857 and 608 cm^{-1} related to Be_2Cl_4 vibrations), while at an increase of temperature in the spectrum can be seen bands only related to vibrations of $BeCl_2$ monomer molecules.

Besides the absorption spectrum in paper [1002] was also studied the $BeCl_2$ emission spectrum at a high temperature. In the emission spectrum of $BeCl_2$ was observed only two bands with maxima at 1113 and 484 cm^{-1}, which were obtained by absorption at $T \sim 1000°C$. The high frequency band at 1113 cm^{-1} related the authors of the paper [1002] to the antisymmetric vibration ν_3, and the 484 cm^{-1} frequency to the deformation vibration ν_2.

Corresponding to the values ν_2 and ν_3 found in the work [1002], assuming that $f_{dd} = 0,1 f_d$, are the force constants of $BeCl_2$ [Eqs. (P4.29)] $f_d = 3,24 \cdot 10^5$, $f_{dd} = 0,32 \cdot 10^5$, and $f_a/d^2 = 0,28 \cdot 10^5$ dyn·cm^{-1}, and the frequency of symmetric vibration $\nu_1 = 412$ cm^{-1}. The force constant of the Be – Cl bond, calculated by equations of the valency field forces, not considering the constant of bond interaction [Eqs. (P4.30)], and based upon experimentally determined ν_3 frequency, $f_d = 2,92 \cdot 10^5$ dyn·cm^{-1}. To this f_d value corresponds $\nu_1 = 375$ cm^{-1}. It must be said that Klemperer [2441] determined the values of ν_3 frequencies and calculated the force constants of $M - X$ (f_d) bonds of zinc, cadmium, and mercury halogenides investigating the infrared absorption spectrum of their molecules in the frequency range of asymmetric vibrations, supposing on the basis of results of investigations of mercury halogenide spectra [2442], that the force constants of bond interaction are equal to zero. Comparison with force constants of corresponding biatomic molecules led to the proportion $f_d(MX_2)/k_e(MX) = 1,3 - 1,4$ (for Zn, and Cd), and equal about 2 (for Hg), while for $BeCl_2$ we obtain $f_d(BeCl_2)/k_e(BeCl) = 0.96$ based upon data of Buechler, and Klemperere [1002], and supposing that $f_{dd} = 0$. Therefore it is more expedient to use the proportion between force constants similar to the proportion for other linear triatomic molecules $(f_{dd} \sim 0,1 f_d)$ in estimations of vibration frequencies of triatomic molecules of halogenides of the beryllium subgroup.

Thus, it can be suggested with an accuracy up to 10% for ν_1 the approximate value 400 cm^{-1}. This value is quoted together with experimentally determined ground frequencies ν_2 and ν_3 in Table 232.*

It should be noted, that in the paper of Neporent, Girin et al [59] was reported the observation of a band with a maximum at 12 μ (833 cm^{-1}) in the absorption spectrum of $BeCl_2$ vapors at $T \sim 350-400°C$ Comparison with results of the paper [1002] shows, that this frequency might be related to vibrations of the Be_2Cl_4 dimer.

The value of the $BeCl_2$ moment of inertia quoted in Table 232 was calculated on the basis of structural parameters found in the paper [68].

TABLE 232

Accepted Values of BeF_2, and $BeCl_2$ molecular constants

1 Молекула	2 ν_1	ν_2 (2) 3	4 ν_3	5 I	8 σ
	6 $см^{-1}$			10^{-40} г·см² 7	
BeF_2	700	825	1520	12,4	2
$BeCl_2$	400	484	1113	36,1	2

1) Molecule, 2) ν_1, 3) ν_2 (2), 4) ν_3,
5) I, 6) cm^{-1}, 7) $g \cdot cm^2$, 8) σ.

§100. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of beryllium and its compounds with oxygen, hydrogen, fluorine, chlorine, and nitrogen in the ideal gas state were calculated for temperatures from 293.15 to 6000°K by the constants given in §99, and presented in Tables 306, 308, 310, 312, 313, 315 and 316 of the II. volume of the Handbook. The difference of constants of isotopic modifications of molecules of the investigated compounds was not considered in the calculations. The constants of intermolecular interaction of substances discussed in the present chapter are unknown.

Be. The translational components in the values of thermodynamic functions of monoatomic beryllium were calculated by Eqs. (II.8) and (II.9) with $A_{\Phi} = -0,7296$ and $A_S = +4,2386$, the electronic components – by Eqs. (II.20) and (II.21) based upon the energy levels of the Be atom and are quoted in Table 230. At temperatures below 4500-5000°K is the accuracy of the calculated values of functions determined only by the accuracy of the applied physical constants, and the errors of the values Φ^*_T and S°_T do not exceed 0.003-0.005 cal/g-atom•degree. The error increases with higher temperatures because of the disregard of electronic states with excitation energies above 55,000 cm^{-1} and the main quantum number $n \leqslant 11$, but, since the contribution of such levels is small, the error of the value S°_{6000} does not exceed 0.02 cal/g-atom• •degree.

Tables of thermodynamic functions of atomic beryllium were calculated by Katz, and Margrave [2334] ($T \leqslant 2000°$ K), Kol'skiy et al [2462] ($T \leqslant 8000°$ K) and Stall, and Zinke [3894] ($T \leqslant 3000°$ K). Divergencies between the values presented in Table 306 (II), and data from these authors and the values presented in the first edition of the Handbook too are determined only by the difference of the physical constants applied in the calculations.

BeO. The thermodynamic functions of gaseous beryllium oxide quoted in Table 308 (II) were calculated by the method of Gordon and Barnes upon the basis of molecular constants presented in Table 231. Due to the fact that the BeO molecule has two electronic states with low excitation energies (see Table 231) the calculation of the values Φ^*_T and S°_T was carried out by Eqs. (II.131) and (II.132). The translational components in the values of these functions were calculated by the proportions (II.8) and (II.9), the components of electronic states $X^1\Sigma$, $A^1\Pi$ and $B^1\Sigma$ through the values M_i, N_i, found by Eqs. (II.115) and (II.116). In Table 233 are quoted the values θ and κ, and also the values of coefficients in Eqs. (II.137) and (II.138) applied for calculations of the values M_i and N_i. There are also presented the values for the constants A_Φ and A_S in Eqs. (II.8) and (II.9). Calculating the values M_i and N_i no corrections were made related to the limitation of the number of rotational levels.

TABLE 233

Values of Constants for the Calculation of Thermodynamic Functions of Gaseous BeO, BeH, BeF, BeCl, and BeN

1 Вещество	2 0	$x \cdot 10^3$	$\beta_1 \cdot 10^2$	$\beta_2 \cdot 10^4$	$\frac{q_0}{T}$	$\frac{d_0}{T} \cdot 10^6$	C_Φ	C_S
	град				град⁻¹		3 кал/моль·град	
BeO $X^1\Sigma$	2139,5	7,9539	1,1508	1,32	0,423496	4,23	2,3140[a]	7,2819[a]
$A^1\Pi$	1646,0	7,3542	1,200	1,49	0,511907	5,87	—	—
$B^1\Sigma$	1974,9	5,6506	0,98185	0,995	0,433319	4,76	—	—
BeH	2961,3	17,245	2,9477	9,55	0,068436	13,20	—4,3643	4,5902
BeF	1820,9	7,296	1,14	1,3	0,46993	5,22	2,5285	9,4830
BeCl	1217,8	6,072	—	—	—	—	5,1263	12,0818
BeN	2158,2	—	—	—	—	—	1,8250	8,7805

[a] Brought values A_Φ and A_S

1) Substance; 2) degrees; 3) cal/mole·degree.

Principal errors in calculations of values of thermodynamic functions of beryllium oxide were stipulated by the fact, that the applied values of BeO vibrations constants are not very suitable for the determination of energies of high vibration levels of the ground state, as well as by the fact that in the BeO molecule exist presently unknown electronic states with low excitation levels (see page 1643). At temperatures up to 3000-3500°K this does not result in considerable errors of the calculated values of functions (the error of Φ_T^* values does not exceed 0.02-0.03 cal/mole·degree). At higher temperatures they have to increase quickly and might attain 0.1-0.3 cal/mole·degree at 6000°K.

The values of thermodynamic functions for BeO, presented in the first and the present edition of the Handbook are identical; other tabulated calculations of thermodynamic functions of gaseous beryllium oxide are not published in the literature.

BeH. Thermodynamic functions of the beryllium monohydride, quoted in Table 309 (II) were calculated by Eqs. (II.161) and (II.162). The values $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ were calculated by the method of Gordon and Barnes [proportions (II.137) and (II.138)] from constants presented in Table 231. The calculations were carried out without introducing corrections for the limitation of the number of rotational levels of the electronic ground state of BeH. In Table 233 are quoted values C_Φ and C_S for the calculation of the components of the transversal movement and rigid rotator, and also the values θ, x, and the coefficients in Eqs. (II.137) and (II.138) used in calculations. Since the BeH molecules has the electronic ground state $X^2\Sigma$, in the values C_Φ and C_S were included the components R ln 2. The components of the $A^2\Pi$ excited state of the BeH molecule were calculated from Eqs. (II.126)-(II.127), i.e., considering the difference of the vibration frequencies and the $X^2\Sigma$ and $A^2\Pi$ rotational constants of BeH in the ground state.

The errors in the calculated values of thermodynamic functions of beryllium monohydride are mainly due to the inaccuracy of the applied calculation method, particularly by neglecting the second constant of anharmony and the neglect of the necessity of the limitation of the number of rotational levels of the BeH molecule. The corresponding errors in values of Φ^*_T at 3000°K are 0.003 and 0.008 cal/mole·degree, and at 6000°K = -0.05 and 0.4 cal/mole·degree. The total errors of the values $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} are of the order 0.02; 0.1 and 1 cal//mole·degree. The values of thermodynamic functions of BeH cited in the first and the present Handbook are identical. Other calculations of thermodynamic functions of BeH were not published in the literature.

BeF. The thermodynamic functions of BeF quoted in Table 310 (II) were calculated by Eqs. (II.161) and (II.162). The values $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ in these equations were calculated by the method of Gordon and Barnes [proportions (II.137) and (II.138)] from the constants presented in Table 231. Calculating these values corrections for the limitation of the number of rotational levels of the energy of the ground state $X^2\Sigma$ were not considered. In Table 233 are quoted the values for the constants C_Φ and C_S in Eqs. (II.161) and (II.162), θ and $\underline{x}$ – for interpolations by means of tables of auxiliary functions, and also the coefficients in Eqs. (II.137) and (II.138). To consider the multiplicity of the $X^2\Sigma$ ground state of the BeF molecule in the values C_Φ and C_S were included the components R ln 2. The components of the $A^2\Pi$ state were calculated by Eqs. (II.120) and (II.121), i.e., without considering the difference of the BeF constants in the ground and the excitated states. Owing to the high excitation energy of the $A^2\Pi$ state this simplification does not cause errors at $T \leqslant 6000°K$.

At $T \leqslant 3000°K$ the errors of the calculated values of BeF functions do not exceed 0.01-0.02 cal/mole·degree for Φ^*_T. At higher temperatures increase the errors because the calculations, according to the presented method, do not consider the second constant of anharmony, and the BeF vibrational levels calculated without this constant converge considerably lower than the dissociation limit (see below, page 1677).The corresponding error for the value Φ^*_{6000} is of the order 0.05 cal/mole·degree. Errors due to the disregarding of corrections which consider the necessity of limiting the number of rotational energy levels, are, thanks to the great dissociation energy of BeF at $T \leqslant 6000°K$, negligibly small.

The values of thermodynamic functions of BeF presented in the first and the present edition are practically identical; other calculations of thermodynamic BeF functions are unknown.

BeCl. Thermodynamic functions of BeCl given in Table 313 (II) were calculated by Eqs. (II.161) and (II.162). The values $\ln \Sigma$ and $T \frac{\partial}{\partial T} \ln \Sigma$ were calculated in approximation of the model rigid rotator-anharmonic oscillator by the method of Gordon, and Barnes [proportions (II.137) and (II.138)], and by constants quoted in the preceeding chapter. The constants β_1, β_2, q_0, and d_0 in Eqs. (II.137) and (II.138) were in calculations assumed to be equal to zero, since the values of constants of the oscillation-rotational interaction, and centrifugal stress of BeCl are unknown. In Table 233 are given the values C_Φ and C_S for the calculation of translational motion components and the rigid rotator, and also values for θ and $\underline{x}$ for the calculation of the components of the anharmonic oscillator. In relation to the fact that the BeCl molecule has the $X^2\Sigma$ ground state, the components R ln 2 were included into the values C_Φ and C_S; the components of the $A^2\Pi$ state of the BeCl molecule were calculated from Eqs. (II.120) and (II.121), i.e. not considering differencies of the BeCl constants in the $X^2\Sigma$ and $A^2\Pi$ states.

The total error of the calculated values of thermodynamic functions of BeCl at low temperatures is due to the inaccuracy of the applied value for the rotational constant of this molecule. The corresponding errors for the values Φ^*_T and S°_T are for instance ±0.1 cal//mole·degree. At temperatures above 1000°K are getting the essential errors connected to the inaccuracy of the applied calculation method, in particular to the fact, that the centrifugal stress and also the interaction of rotation and vibration of the BeCl molecule were not considered. At 6000°K these errors have values of the order 0.1 cal//mole·degree for Φ^*_T values. The total error of the calculated values $\Phi^*_{298.15}$, Φ^*_{3000} and Φ^*_{6000} are estimated with ±0.1, ±0.2 and ±0.3 cal//mole·degree respectively.

Divergencies in the values of BeCl thermodynamic functions quoted in the first and the present edition are generally due to the different applied vibrational constants of the BeCl molecule; they do not exceed 0.06 cal/mole·degree for the values Φ_T^* and S_T°. In the literature do not exist informations upon other calculations of thermodynamic functions for this gas.

BeN. The thermodynamic functions of beryllium nitride quoted in Table 316 (II) were calculated by Eqs. (II.161) and (II.162), and the constants accepted in the preceeding chapter. So far as the constants characterising deviations of the BeN molecule from the model rigid rotator-harmonic oscillator are not known the calculation was carried out in approximation of the model rigid rotator-harmonic oscillator i. e., the values $\ln \Sigma$ and $T\frac{\partial}{\partial T}\ln \Sigma$ in Eqs. (II.161) and (II.162) were taken equal to zero. In Table 233 are presented the values for C_Φ and C_S in these equations and the θ values for the calculation of the components of the harmonic oscillator. Since in §99 was assumed that the ground state of BeN is the $^2\Sigma$, state the components R ln 2 were included in the C_Φ and C_S values.

The fundamental error of the calculated values of thermodynamic functions of beryllium nitride is determined by the absence of authentic data upon molecular constants of BeN, and at high temperatures – by the approximative method of calculation. The error due to the inaccurate estimation of the value B_0 is for example ± 0.9 cal/mole·degree for the values Φ_T^* and S_T°, and due to the inaccuracy of ω_2 – about ±0. .03, ±0.3 and ±0.4 cal/mole·degree for the values $\Phi_{298.15}^*$, Φ_{3000}^*, Φ_{6000}^* respectively. Errors in these values caused by the neglect of the anharmony of vibrations, the centrifugal stress, and the interaction of rotation and vibration of the BeN molecule are of the order 0.01, 0.2 and 0.5 cal/mole·degree, and those caused by the disregard of corrections for the limitation of the number of rotational BeN levels – about 0.4 cal/mole·degree for Φ_T^*. The total error of the calculated Φ_T^* values is ±0.3, ±1 and ±2 cal/mole·degree at T = 298.15, 3000 and 6000°K respectively. The values of thermodynamic functions of beryllium nitride given in the first and the present edition of the Handbook are identical. Other calculations of thermodynamic functions of BeN in the literature are unknown.

BeF_2 and $BeCl_2$. Thermodynamic functions of gaseous beryllium fluoride and chloride, quoted in Table 312 (II) and 315 (II), were calculated by Eqs. (II.241) and (II.242) in approximation of the model rigid rotator-harmonical oscillator. The calculation was carried out on the basis of molecular constants presented in Table 232. In Table 234 are quoted values of the constants C_Φ and C_S in Eqs. (II.241) and (II.242), and also values of θ by means of which were calculated components of harmonic oscillators.

TABLE 234

Values of Constants for the Calculation of Thermodynamic Functions of Gaseous BeF_2 and $BeCl_2$

Вещество 1	θ_1	θ_2	θ_3	C_Φ	C_S
	2 град			3 кал/моль·град	
BeF_2 $BeCl_2$	1007,1 575,52	1187,0 696,37	2187 1601,4	5,0516 8,7572	12,0071 15,7127

1) Substance; 2) degree; 3) cal/mole·degree.

The errors of the calculated values of thermodynamic functions of beryllium fluoride and chloride are stipulated by the approximative character of the calculation (the neglect of the anharmony of vibration and other effects), the absence of experimental data upon the dimension of frequencies of symmetrical valency vibrations of both molecules and the unsufficient accuracy of the accepted values of other frequencies and moments of inertia.

The errors at T = 298.15°K are of the order of 0.1 cal/mole·degree for the values Φ_T^* and S_T° and are stipulated by the inaccuracy of determining the bond length in BeF_2 and $BeCl_2$ molecules. Errors of the values of Φ_{3000}^* for both gases are about 1 and 1.5 cal/mole·degree respectively (errors caused by the unreliability of the accepted v_1 values do not exceed 0.2 cal/mole·degree).

Deviations between the values of thermodynamic functions of beryllium fluoride and chloride given in the first and the present edition of the Handbook are stipulated by differences in fundamental frequencies used in the calculations and attain 0.6-0.9 cal/mole·degree for the values Φ_T^* and S_T°. In the literature do not exist indications upon other calculations of thermodynamic functions for BeF_2 and $BeCl_2$.

§101. THE THERMODYNAMIC PROPERTIES OF Be, BeO, BeF_2 AND $BeCl_2$ IN SOLID AND LIQUID STATES

The thermodynamic functions of Be, BeO, BeF_2 and $BeCl_2$ in solid and liquid states (Tables 305, 307, 311 and 314 of Vol. II) were calculated from Eqs. (III.9)-(III.11) with the help of the thermodynamic quantities given in Table 235. The choice of these values from the results of experimental investigations or approximate estimates is considered in what follows. The errors of the calculated values of Φ_T^* at the temperatures of **298, 1000, 1500, 2000** and 3000°K, estimated on the basis of an analysis of the possible errors of the initial data, are given in Table 236.

Be. We know the following polymorphous modifications of beryllium: the hexagonal close-packed modification (structural type of Mg), which is stable in the wide temperature interval of from 4 to 1523°K and the cubic space-centered modification (structural type of α-Fe) which, according to data of Martin and Moore [2784a], forms near the melting point of 1523°K. When measuring the enthalpy of beryllium [208] the polymorphous transformation was not observed so that it was not taken into account in the calculation of the thermodynamic functions of beryllium in the present Handbook. (An indication as to the polymorphism of Be near 4°K may be found in the paper of Gindin et al [152a]).

TABLE 235

Accepted Values of the Thermodynamic Quantities of Beryllium And Its Compounds in Solid and Liquid States

1 Вещество	2 Состояние	$H^{\circ}_{298,15} - H^{\circ}_0$	$S^{\circ}_{298,15}$	$C^{\circ}_{p_{298,15}}$	3 Коэффициенты в уравнении для $C_p^{\circ a}$			4 Интервал температуры	Tm	ΔHm
		5 кал / моль	6 кал / моль·град		a	$b \cdot 10^3$	$c \cdot 10^{-5}$	°K	°K	кал / моль
Be	Крист. 7	468	2,28	3,93	—[б]	—	—	298—1200	—	—
Be	»	—	—	—	5,374	1,38	—	1200—1556	1556	3500
Be	Жидк. 8	—	—	—	7,1	—	—	1556—4400	—	—
BeO	Крист. 7	686	3,37	6,11	8,69	3,62	3,25	298—1000	—	—
BeO	»	—	—	—	10,70	1,29	—	1000—2821	2821	17000
BeO	Жидк. 8	—	—	—	16,00	—	—	2821—6000	—	—
BeF_2	Крист. 7	1900	10,80	12,0	11,98	8,12	2,13	298—1076	1076	4000
BeF_2	Жидк. 8	—	—	—	23,0	—	—	1076—2300	—	—
$BeCl_2$	Крист. 7	2900	15,0	17,0	13,86	10,53	—	298—678	678	3000
$BeCl_2$	Жидк. 8	—	—	—	24,0	—	—	678—1200	—	—

[a] $C_p^{\circ} = a + bT - cT^{-2}$ (cal/mole·degree); [b] Tabulated data from [1752].

1) Substance
2) state
3) coefficients in the equation for C_p°
4) temperature interval
5) cal/mole
6) cal/mole·degree
7) cryst.
8) liqu.

Kelley [2364] used the data on the specific heat of beryllium, obtained by Cristescu and Simon [1221] (10-300°K) and recommended a value of $S^{\circ}_{298,15} = 2,28 \pm 0,02$ cal/g-atom·degree. More accurate measurements of the specific heat of beryllium were carried out later on by Hill and Smith [2074] (4-300°K, 150 measurements). The data they obtained in the interval of 100-200°K lie higher than the specific-heat curve obtained by Cristescu and Simon, at other temperatures they are lower than this curve. The values of $S^{\circ}_{298.15} = 2{,}28 \pm 0.02$ cal/g-atom·degree and $H^{\circ}_{298.15} - H^{\circ}_{0} = = 468 \pm 4$ cal/g-atom, calculated by Hill and Smith, are accepted in the present Handbook.

Based on five papers on the measurement of the enthalpy of beryllium at high temperatures Kelley [2363] recommended a linear equation to describe the specific heat of beryllium with an accuracy of ±2% in the interval of 298-1300°K. Later on more reliable data on the enthalpy of beryllium were obtained by Ginnings, Douglas and Ball [1752] (273-1170°K) and Kantor, Krasovitskaya and Kisel' [208] (619°K – Tm).

At temperatures near 1000°K these data are in good agreement with one another (deviations less than 0.5%); at low temperatures more accurate data were obtained by Ginnings, Douglas and Ball [1752] with the help of an ice calorimeter, whereas the massive calorimeter, used in paper [208] was not suited for measurements in this temperature interval.

The thermodynamic functions of beryllium, given in Table 305 (II) in the interval 298-1200°K were calculated from data of [1752] with the help of graphical and numerical integrations. In the interval of from 1200°K to the melting point of beryllium, equal to 1556°K [3508], a linear equation (see Table 235) was derived for the specific heat of beryllium, based on the values of $C^{\circ}_{p_{1200}} = 7{,}03$ cal/g-atom·degree [1752] and $H^{\circ}_{1556} - H^{\circ}_{1200} = 2590$ cal/g-atom [208]. *

Kantor, Krasovitskaya and Kisel' [208] measured the enthalpy of liquid beryllium in the interval of 1566-2166°K and derived an equation for the specific heat,

$$C^{\circ}_{p} = 5{,}926 + 0{,}568 \cdot 10^{-3} T + 4{,}314 \cdot 10^{5} T^{-2},$$

according to which the specific heat of liquid beryllium rises from 6.99 to 7.27 cal/g-atom·degree, as the temperature increases. However, since the values of the enthalpy of beryllium found in paper [208] display a considerable scatter (on the average about 1%), a constant value of C_p° = 7.1 cal/g-atom·degree with a possible error of ±0.2 cal/g-atom·degree, has been chosen in the present Handbook for the specific heat of liquid beryllium. This very value is used in the calculations of the thermodynamic functions of beryllium at temperatures above 2200°K.

According to data from [208] the melting point of beryllium is equal to 3.57 ± 0.1 kcal/g-atom. In the Handbook we accept the value of $\Delta H_{1556} = 3,50 \pm 0,1$ kcal/g-atom, calculated from the equation for the enthalpy of solid and liquid beryllium which have been used in the calculations of the thermodynamic functions of beryllium.

The values of the thermodynamic functions of beryllium in solid and liquid states, calculated for temperatures in the range 293.15-4400°K, are given in Table 305 (II). The values of the errors of the values calculated for Φ_T^* are given in Table 236.

The values of the thermodynamic functions of solid and liquid beryllium, given in Table 305 (II), differ greatly from the values calculated in the first edition of the present Handbook and in the Handbook by Stull and Sinke [3894]. At 3000°K the deviations reach 0.25 and 0.6 cal/g-atom·degree for the values of Φ_T^* and S_T° respectively, and are due to the essential improvements achieved with the values of the melting point of beryllium and the specific heat of liquid beryllium as the result of measurements, made by Kantor and co-workers [208].

<u>BeO</u>. Beryllium oxide is known in the form of a hexagonal modification (structural type of Wurtzite ZnS). Kelley [2359] measured the specific heat of beryllium oxide from 55 to 293°K and calculated the value of $H^\circ_{298,15} - H^\circ_0 = 686 \pm 5$ cal/mole·degree; the value found by an extrapolation below 53°K amounts to 0.037 cal/mole·degree. The value calculated from data of [2359] amounts to $S^\circ_{298,15} = 3,37 \pm 0,02$ cal/mole.

The enthalpy of BeO at temperatures up to 1200°K was measured by Magnus and Danz [2734] (293-1175°K) and Rodigina and Gomel'skiy [31] (364-1128°K). The data of these authors agree with one another within the limits of 1%. Similar are also the equations for the specific heat of beryllium oxide, derived by Kelley [2363] according to data of Magnus and Danz [2734] and Rodigina and Gomel'skiy [31], respectively:

$$C_p^{\bullet} = 8{,}45 + 4{,}00 \cdot 10^{-3} T - 3{,}17 \cdot 10^{5} T^{-2},$$

$$C_p^{\bullet} = 8{,}69 + 3{,}62 \cdot 10^{-3} T - 3{,}25 \cdot 10^{5} T^{-2}.$$

In the Handbook the thermodynamic functions of BeO up to 1000°K were calculated with the help of the second equation since this equation is based on the more accurate experimental data.

The enthalpy of beryllium oxide was measured at temperatures above 1200°K by Kandybaya, Kantor, Krasovitskaya and Fomichev [17] (1169-2142°K, 22 measurements) and [15] (1208-2645°K, 25 measurements). The data obtained in paper [15], up to 2300° display a slight spread (about 0.6%), at higher temperatures (2377-2645°K) a certain increase in spread of the measuring results can be observed (up to 2-3%). Based on the value of $H^{\bullet}_{2300} - H^{\bullet}_{298.15} = 23660$ cal/mole, according to data from [15], and also the value of $C^{\bullet}_{p1000} = 11{,}99$ cal/mole·degree and $H^{\circ}_{1000} - H^{\circ}_{298.15} = 6983$ cal/mole [31], the authors of the Handbook derived a linear equation for the specific heat of BeO for the range of from 1000 to 2300°K (cf. Table 235). This equation is also used to calculate the thermodynamic functions of beryllium oxide up to the melting point which, according to data of [208], is equal to 2821°K. The melting heat of beryllium oxide, equal to 17 ± 3 kcal/mole, was calculated from an approximate value of the melting entropy of $\Delta S_{2821} = 6 \pm 1$ cal/mole·degree, obtained by comparing the melting entropies of oxides of the alkaline-earth metals. The specific heat of liquid BeO was estimated as amounting to 16 cal/mole·degree.*

The values of the thermodynamic functions of beryllium oxide in solid and liquid states, calculated for the temperatures in the range 293.15-6000°K, are given in Table 307 (II). The magnitudes of the errors of the calculated values of Φ_T^* are given in Table 236.

The differences between the thermodynamic functions of beryllium oxide, given in Table 307 (II) and in the first edition of the present Handbook, do not exceed 0.2 and 0.3 cal/mole·degree in the values of Φ_T^* and S_T° and are due to an improvement of the data on the specific heat of BeO in the result of paper [17].

BeF$_2$. With beryllium fluoride two crystalline forms have become known, a hexagonal modification of quartz-like structure and a tetragonal one of cristobalite structure.* At not too high temperatures the quartz-like form (Q-BeF$_2$) is thermodynamically stable; it suffers a polymorphous transformation at 220°C and melts at about 580°C [321a]. The crystobalite-like form (C-BeF$_2$) is in equilibrium at temperatures near its melting point (about 800°C). At lower temperatures, however, the cristobalite-like form of BeF$_2$ is fully stable, suffers an enantiotropic transformation near 120°C with a low heat of transition (about 200 cal/mole according to data of [273a]) and goes over to the quartz-like form of BeF$_2$ only in the case of a long annealing in the temperature interval of 300-400°C (cf. [321a]). According to an idea suggested by Novoselova [321a], there exists a third crystalline form of BeF$_2$ which is in thermodynamic equilibrium at temperatures of from 420 to 680°C; its structure is unknown (maybe it is analogous to tridymite, denoted as T-BeF$_2$). The true scheme of polymorphal transformations of BeF$_2$ is thus the following [321a]:

$$\begin{tikzcd}
\beta Q\text{-BeF}_2 \arrow[r, shift left] & \alpha Q\text{-BeF}_2 \arrow[l, shift left, "220^\circ\text{C}"] \arrow[r, shift left] & T(?)\text{-BeF}_2 \arrow[l, shift left, "430\text{—}480^\circ\text{C}"] \arrow[r, shift left] & \alpha C\text{-BeF}_2 \arrow[l, shift left, "\sim 680^\circ\text{C}"] \arrow[r, shift left] \arrow[d, shift right] & \text{fused} \arrow[l, shift left, "\sim 800^\circ\text{C}"] \\
 & & & \beta C\text{-BeF}_2 \arrow[u, shift right, "120^\circ\text{C}"'] &
\end{tikzcd}$$

Owing to the fact that the heat of formation of beryllium fluoride has only been determined for the crystobalite-like modification, the thermodynamic functions were calculated for this very modification of BeF_2. Since in literature there are no experimental data on the specific heat and the enthalpy of crystobalite-like BeF_2, its polymorphism has not been taken into account in the calculation of the thermodynamic functions.

The entropy of BeF_2 at 298.15°K ($S^\circ_{298.15} = 10,8 \pm 0,5$ cal/mole·degree) was chosen for the Handbook according to an estimate by Karapet'yants [219], on the basis of a method elaborated by him and the wellknown values of $S^\circ_{298.15}$ for BeO, MgO, MgF_2, CaO, CaF_2, BaO, BaF_2. This value was verified by an estimate obtained by another empirical method, proposed by Kireyev [224] (10.4), Drozin [180] (10.9), Venner [127] (11.5), and also according to Latimer's method [2565] where an empirical correction (10.4 cal/mole·degree) was introduced. The value of $H^\circ_{298.15} - H^\circ_0 = 1900 \pm 100$ cal/mole was estimated on the basis of a comparison of the corresponding experimental data for MgF_2 and CaF_2.

The enthalpy of vitreous beryllium fluoride at high temperatures was measured by Rodigina and Gomel'skiy [31] (373-971°K) and Kutsyna, Kantor, Kandyba, Krasovitskaya and Fomichev [17] (477-1375°K). A systematic divergence is observed between the data of these authors which amounts to about 5% and is obviously due to a difference in the phase state of the BeF_2 samples investigated. In the Handbook the data obtained by Rodingina and Gomel'skiy [31] for solid BeF_2 are accepted.

Based on the values of $C^\circ_{p298.15} = 12,0$ cal/mole·degree, $H^\circ_{570} - H^\circ_{298} = 3873$ cal/mole $H^\circ_{971} - H^\circ_{298} = 11\,030$ cal/mole, obtained from data of [31], the specific heat equation given in Table 235 was derived, which was used in calculating the thermodynamic functions of solid BeF_2 up to the melting point at 1076°K [3686]. The accuracy of this equation amounts to about 5%, since in paper [31] the phase state of the BeF_2 sample was not investigated and the heat of the polymorphous transformations were not taken into account.*

Direct determinations of the melting heat of beryllium fluoride was not determined. An approximate value of the melting heat of BeF_2 may be found from the values of the heat of sublimation and evaporation, calculated from the temperature dependence of the saturated vapor pressure of solid and liquid BeF_2. According to Sense, Snyder and Clegg [3686], applying to a comparatively narrow temperature interval (1019-1055°K and 1094-1241°K), the values of $\Delta Hs = 56{,}6$, $\Delta Hv = 50{,}91$ and $\Delta Hm = 5{,}7$ kcal/mole were calculated. The data of other authors concerning the vapor pressure of solid [434] and liquid BeF_2 [323] in a wider temperature interval (846-1376°K) yielded essentially different values: $\Delta Hs = 52{,}0$, $\Delta Hv = 48{,}0$ and $\Delta Hm = 4{,}0$ kcal/mole. The value of the melting heat of BeF_2, $\Delta Hm =$ 4.0 kcal/mole, accepted in the Handbook, may possess an error of about 1-1.5 cal/mole. The melting entropy of BeF_2, equal to 3.7 cal/mole·degree, corresponding to this value, is lower than the melting entropy of $BeCl_2$ (4.4 cal/mole·degree); the same is true for the fluorides and chlorides of the other elements of group II. In connection with this, we see that the estimate of the melting heat of BeF_2, obtained by Brewer [1093] must be too high as the corresponding value of the melting entropy amounts to 6 cal/mole··degree.

The value of the specific heat of molten beryllium fluoride above 1076°K (C_p° = 23.0 cal/mole·degree) was calculated from the results of measuring the enthalpies of vitreous and liquid BeF_2 up to 1375°K [17] (accuracy 5-10%). The same value has been used in the Handbook to calculate the thermodynamic functions of BeF_2 at higher temperatures.

The values of the thermodynamic functions of beryllium fluoride in solid and liquid states, calculated for the temperatures of 293.15-2300°K, are given in Table 311 (II). The values of the errors in the calculated values of Φ_T^* are given in Table 236.

The differences between the thermodynamic functions of BeF_2 given in Table 311 (II) and in the first edition of the present Handbook, at 2000°K, reach 1.7 and 3.2 cal/mole·degree with the values of Φ_T^* and S°. The deviations are due to the fact that in the new edition the newest experimental data on the enthalpy of BeF_2 [17, 31] have been taken into account.

$\underline{BeCl_2}$. Just as BeF_2, beryllium chloride may occur in several polymorphous transformations (see paper [267a]). Since in literature there are no data on the specific heat, the enthalpy and heat of transformation of $BeCl_2$, the polymorphism of beryllium chloride has not been taken into account in the calculation of its thermodynamic properties.

The estimation of the values of $S^\circ_{298.15} = 15{,}0 \pm 1$ cal/mole·degree, $H^\circ_{298.15} - H^\circ_0 = 2900 \pm 200$ cal/mole and $C^\circ_{p298.15} = 17{,}0$ cal/mole·degree was based on the corresponding data of the chlorides and oxides of Be, Mg and Ca. The value of $S^\circ_{298.15}$ was calculated by means of Karapet'yants' method [219] and verified by calculations with the help of the approximation method of Kireyev [224] (16.0), Drozin [180] (15.6) and Venner [127] (14.5 cal/mole·degree).*

The specific heat of $BeCl_2$ in the interval of from 298.15°K up to the melting point at 678°K [3508]** was estimated with the help of a linear equation, derived on the basis of the values of $C^\circ_{p298.15} = 17{,}0$ and $\Delta Hm_{678} = 3$ cal/mole·degree (see Table 235).

The value of the melting heat of $BeCl_2$, $C^\circ_{p678} = 21{,}0$ kcal/mole, was calculated from data obtained by Ralfs and Fischer [3350] on the saturated vapor pressure of solid and liquid $BeCl_2$. Owing to the low accuracy of these measurements (cf. page 1683), the value given has an error of ±1 kcal/mole. The specific heat of $BeCl_2$ was estimated as amounting to 24 cal/mole·degree.

The values of the thermodynamic functions of beryllium chloride in solid and liquid states, calculated for the temperatures of 293.15--1200°K, are given in Table 314 (II). The errors of the calculated values of Φ_T^* are given in Table 236.

The Table of the thermodynamic functions of crystalline and liquid $BeCl_2$ [Table 314 (II)] is identical with that given in the first edition of the present Handbook.

TABLE 236

Errors (in cal/mole·degree) of the Values of Φ_T^* of Beryllium and its Compounds in Solid and Liquid States

T°,K	298	1000	1500	2000	3000
Be	±0,02	±0,05	±0,07	±0,1	±0,25
BeO	±0,02	±0,05	±0,07	±0,1	±0,25
BeF_2	±0,5	±1,0	±1,5	±2,0	—
$BeCl_2$	±1,0	±2,0	—	—	—

§102. THE THERMODYNAMIC QUANTITIES

The standard state of beryllium is Be (cryst.).

Be (gas). The results of measurements of the saturated vapor pressure of beryllium, obtained by Baur and Brunner [691] (method of boiling point determination, 1850-2331°K) and Schuman and Garrett [3661, 3662] (method of evaporation from a surface, 1174-1336°K) are insufficiently accurate. As shown by Gulbransen and Andrew [1883], beryllium, under the conditions of the experiments of Schuman and Garrett [3661, 3662], coats itself with an oxide film which caused an essential drop of the vapor pressure measured. The vapor pressures measured in the paper of Baur and Brunner [961] show an irregular temperature dependence. In connection with this, the values of the heat of sublimation of beryllium, 78.3 ± 1.3 and 79.5 ± 0.6 kcal/g-atom, calculated from data of [691] and [3661, 3662], respectively, proved too high.

A more reliable value of the heat of sublimation of beryllium may be found from measurements of saturated vapor pressure, carried out by Holden, Speiser and Johnston [2105] and Gulbranson and Andrew [1883]. The results of the first paper, obtained with two samples of beryllium (1172-1552°K, effusion method and method of evaporation from a surface) yielded the values of $\Delta Hs_0 = 76{,}68 \pm 0{,}4$ and 77.02 ± 0.3 kcal/g-atom, respectively, for each of the samples. According to data of Gulbransen and Andrew obtained by the method of evaporation from a surface with two beryllium samples (1103-1229°K), the heat of sublimation of beryllium is equal to 77.18 ± 0.23 and 77.08 ± 0.2 kcal/g-atom. In the Handbook a mean value of these three has been accepted:

$$\Delta Hs_0(\text{Be, cryst.}) = 77 \pm 0{,}5 \text{ kcal/g-atom.}$$

BeO (cryst.). In the papers of Mielenz and Wartenberg [2903], Moose and Parr [2945], Neumann, Kroger and Kunz [3054] and Roth, Borger and Siemonsen [3524] the heat of combustion of beryllium in oxygen was measured. In these papers the values of —135,9, —134,5, —145,4 and -147.0 kcal/mole, respectively, were found. The insufficient purity of the initial samples of beryllium, their incomplete combustion and the simultaneous inflammation of the substances applied to facilitate the combustion reduce the accuracy of the quantities obtained in these papers.

The values of the heat of formation of beryllium oxide, calculated on the basis of measurements of the heat of its dissolution in hydrofluoric acid [1173, 1174, 2810], cannot be considered as accurate

[3524, 25], particularly owing to the fact that in these papers the thermal capacity of the calorimeter was calculated as the sum of the specific heats of all constituents of the calorimetrical system, which is not true for solutions.

Smirnov and Chukreyev [385] measured the emf of a galvanic element in which the reaction Be(cryst.) + 1/2CO_2 (gas) = BeO(cryst.) + + 1/2 C (solid) took place. The temperature dependence of the emf observed makes it possible to determine the value of the heat of this reaction: $\Delta H_{1134} = -93{,}9$ kcal/mole; a value of $\Delta H^\circ f_{298.15}$ (BeO, cryst.) = -141.1 kcal/mole corresponds to it. The authors of [385] suggested to assume that under the conditions of their experiments (955-1313°K) the reaction between CO_2 and carbon was insignificant. Thermodynamic calculations, however, show that under these conditions carbon oxide must be formed in large quantities. The possibility of side reactions reduces the reliability of the value obtained by the authors of [385].

Cosgrove and Snyder [1184] determined the heat of combustion of a pure sample of beryllium; they used a method of combustion which permitted complete combustion without the addition of substances facilitating the burning. The value of the heat of formation of beryllium oxide, obtained in this paper,

$$\Delta H^\circ f_{298.15}(\text{BeO, cryst.}) = -143{,}1 \pm 1{,}0 \text{ kcal/mole}$$

has been accepted in the Handbook.

BeO (gas). The saturated vapor pressure of beryllium oxide was measured by Erway and Seifert [1495] and Belykh and Nesmeyanov [315, 22]. The measurements reported in the first paper were carried out in the interval of 2250-2413°K by means of the effusion method with the application of radioactive beryllium. The measurements of the second paper were carried out by both the effusion method (integral variant) and the method of evaporation from an open surface. Special investigations [22] showed that in the temperature interval of 2103-2573°K in the effusion chamber no essential reduction of beryllium oxide occurs by virtue of the metallic tungsten of which the effusion cells used in papers [1495, 22] were made. The calculation of the heat of sublimation of BeO with data from [1495, 22], under the assumption that beryllium oxide evaporates in the form of BeO molecules, leads to values of 156.8 ± 0.2 and 160.0 ± 0.1 kcal/mole, to which BeO dissociation energies equal to 122 and 118 kcal/mole, respectively, correspond.

Calculations of the vapor pressure of beryllium above beryllium oxide, carried out by the authors of the Handbook, however, showed that the saturated vapor pressures above beryllium oxide obtained in papers [1495, 22], proved to be equal to or even lower than the calculated partial pressures of atomic beryllium above beryllium oxide. This speaks in favor of a virtually complete dissociation of beryllium oxide on evaporation. It is therefore not possible to calculate the value of the heat of sublimation of beryllium oxide on the basis of measurements of [1495, 315, 22].

The dissociation energy of beryllium oxide and, correspondingly, its heat of sublimation may be obtained from spectroscopic data. A linear extrapolation of the vibrational energy levels of the $X^1\Sigma$, state, carried out with the help of constants given in Table 231, yields a dissociation limit, equal to about 47,500 cm^{-1} (136 kcal/mole). Under the assumption that the BeO molecule in the $X^1\Sigma$ state dissociates into the atoms $Be(^1S) + O(^1D)$, this yields $D_0(BeO) = 90$ kcal/mole.

An extrapolation of the levels of the $A^1\Pi$ state is much more reliable since of this state the levels are wellknown for $v \leqslant 25$ (with the $X^1\Sigma$ state it is only the levels with $v \leqslant 16$) that have been investigated). The dissociation limit of the $A^1\Pi$ state is equal to 45,500 cm^{-1} (130 kcal/mole). The correlation of the electron states of BeO with the states of Be and O proves [2521] that BeO in the states $A^1\Pi$ and $X^1\Sigma$ may dissociate into the atoms Be(^1S) and O(^1D). Considering this, Lagerqvist in paper [2523] recommended a value of D_0(BeO) = 111 kcal/mole. If we take into account the inaccuracy of the estimates of dissociation energies by means of the method of linear extrapolation, the error of this value may amount to about ±10 kcal/mole.

Chupka, Berkowitz and Giese [1106] subjected beryllium oxide vapor to a mass-spectrometrical analysis. Atomic beryllium proved to be the main component of the vapor. The quantity of BeO only amounted to about 1/100 of the quantity of Be. Besides BeO, polymeric molecules of $(BeO)_3$, $(BeO)_4$, $(BeO)_5$, $(BeO)_2$ and $(BeO)_6$ (in the order of decrease) were observed. The fraction of polymeric molecules increases with the temperature and, by way of an extrapolation, one may arrive at the result that at the boiling point of BeO which is equal to about 4120°K [1106], $(BeO)_3$, $(BeO)_4$ and $(BeO)_5$ will be the chief components of the vapor.

Chupka et al [1106], using the values of vapor pressure of metallic beryllium above beryllium oxide, calculated from thermodynamic data, in their recalculation of ion currents to partial pressures, found the values of the equilibrium constants of the reactions $BeO_{(gas)} \rightarrow Be_{(gas)} + O_{(gas)}$ and $BeO_{(gas)} + O_{(gas)} \rightarrow Be_{(gas)} + O_{2(gas)}$. With these data Chupka et al calculated the values of D_0(BeO), equal to 104.4 and 106.6 kcal/mole, respectively. The value of $D_0(BeO) = 106,6 \pm 3$ kcal/mole is recommended as the better one; it was calculated from the results of investigating the second reaction, since its constant is nondimensional. Calculations based on the thermodynamic quantities accepted in the present Handbook and the data of paper [1106] yielded the values of 104.1 and 106.4 kcal/mole, respectively.* The value of the dissociation energy of beryl-

$$D_0(BeO) = 106,4 \pm 3 \text{ kcal/mole},$$

has been accepted in the Handbook; it was calculated from data of Chupka, Berkowitz and Giese [1106]. The value of $D_0(\text{BeO}) = 111 \pm 10$ kcal/mole, calculated by Lagerqvist [2523], coincides with it within the limits of error.

The values of

$$\Delta Hs_0(\text{BeO, cryst.}) = 171{,}868 \pm 3{,}2 \text{ kcal/mole},$$
$$\Delta H^\circ f_0(\text{BeO, gas}) = 29{,}587 \pm 3 \text{ kcal/mole}.$$

correspond to the value accepted for D_0(BeO).

BeH (gas). For the BeH dissociation energy Gaydon [1668] recommends a value of 2.3 ± 0.3 ev or 53 ± 7 kcal/mole, obtained from results of a graphical extrapolation for the states $X^2\Sigma$ (2.5 ev) and $A^2\Pi$ (2,2 ev), under the assumption that the BeH molecule in the state dissociates into the atoms Be(^3P) and H(^2S).*

This value is used in the Handbook:

$$D_0(\text{BeH}) = 53 \pm 7 \text{ kcal/mole},$$

to it corresponds

$$\Delta H^\circ f_0(\text{BeH, gas}) = 75{,}632 \pm 7 \text{ kcal/mole}.$$

BeF (gas). Experimental data on the dissociation energy or the heat of formation of BeF are lacking in literature. An estimation of this quantity based on a linear extrapolation of the vibrational levels of the $X^2\Sigma$ state of the BeF molecule with constants obtained in the papers [2251] and [414], yields values of 124 kcal/mole (43,370 cm^{-1}) and 126 kcal/mole (44,070 cm^{-1}), respectively. In Herzberg's book [2020] and in the Handbook [649] a value of $D_0(\text{BeF}) = 124$ kcal/mole has been accepted. Gaydon [1668] recommends a lower value, equal to 92 ± 23 kcal/mole, under the assumption that for molecules formed of atoms in the ^1S-state, a linear extrapolation yields too high results.

In the first edition of the present Handbook it has been assumed that, with BeF and also with a series of analogous molecules, the lower values of the dissociation energies obtained by linear extrapolation were incorrect and may rather be considered as the lower limits of the dissociation energies of the corresponding molecules. Tateyevskiy, Tunitskiy and Novikov [414], as the result of an analysis of the $A^2\Pi - X^2\Sigma$ band system of the BeF molecule, supported this assumption showing that the curve of $\Delta G_{v+1/2}$ as a function of v exhibits a positive curvature. An extrapolation of the vibrational levels of the states $X^2\Sigma$ and $A^2\Pi$ of the BeF molecule with the help of constants given in Table 231, yields values of 57,500 and 38,200 cm^{-1} for the dissociation energies of BeF in these states. It is, however, difficult to determine the BeF dissociation energy from these values as the correlation of the electron states of the molecule with the states of the Be and F atoms is unknown. According to the rules of correlation, the lower limit of dissociation of this molecule, $\mathrm{Be}(^1S) + \mathrm{F}(^2P)$, must be in correlation with the states: $^2\Sigma^+$ and $^2\Pi$. In zeroth approximation these states must be both repulsive since the Be atom in the ^{1}S-state has a closed electron shell.

If it is assumed that the states $A^2\Pi$ and $X^2\Sigma^+$, to be observed in the BeF spectrum, correlate with the dissociation limit of Be(^{3}P) + F (^{2}P),* the dissociation energy of the molecule in each of these states must be lower than the energy of the ^{3}P-state of the Be atom, i.e., lower than 22,000 cm^{-1}, because of the interaction with the repulsive states $^2\Pi$ and $^2\Sigma^+$

In the BeF spectrum, however, one may observe the levels of the states $^2\Sigma^+$ and $^2\Pi$ with energies, approximately equal to 21,600 and 18,100 cm^{-1}, respectively [414], and there are no indications as to a rapid convergence of the levels as their energy increases. The authors of paper [414] came therefore to the conclusion that the potential curves of the states $^2\Sigma^+$ and $^2\Pi$, correlating with the dissociation limit of $\mathrm{Be}(^1S) + \mathrm{F}(^2P)$, have deep minima owing to the perturbation by higher states of these types, that these states are stable and the system $^2\Pi \rightarrow {}^2\Sigma^+$ is connected with the transition between them. Two values of the dissociation energy of the BeF molecule, equal to 57,590 and $38\,200\ cm^{-1} + 33\,200\ cm^{-1} = 71\,400\ cm^{-1}$, will then correspond to the dissociation limits of the states $X^2\Sigma$ and $A^2\Pi$, calculated by extrapolating the energies of the vibrational levels of these states. The authors of paper [414] had no possibility of a reasonable choice between these two values so that they used a mean value, equal to 64,000 cm^{-1} or 183 kcal/mole.

In spite of the fact that the arguments used by the authors of paper [414] in favor of the assumption of a correlation between the observed states $X^2\Sigma^+$ and $^2\Pi$ of the BeF molecule and the atoms $Be(^1S)$ + + $F(^2P)$ are very persuasive, this is, however, insufficient for a determination of $D_0(BeF)$ from data, obtained by extrapolations of the levels of the $A^2\Pi$ state. In particular the potential curve of the $A^2\Pi$ state may have a maximum so that an extrapolation of the levels of this state yields too high a value of $D_0(BeF)$. If, in agreement with paper [414], we assume that the zeroth approximation of the $A^2\Pi$ state must be a repulsive state and the appearance of a minimum on the potential curve of this state is caused by the interaction with the $^2\Pi_i$ state, in correlation with the dissociation limit of $Be(^3P) + F(^2P)$, an extrapolation of the observed vibrational levels of the $A^2\Pi$ state must lead to a dissociation limit of a perturbing state (i.e., the limit of $Be(^3P) + F(^2P)$), in spite of the fact that the $A^2\Pi$ state is in correlation with the states of $Be(^1S) + F(^2P)$. In this case $D_0(BeF) =$ $= 71\,400\ cm^{-1} - 21\,900\ cm^{-1} = 49\,500\ cm^{-1}$, or 141 kcal/mole. It must be noted that with the molecules of MgF and CaF, which are analogous to BeF, an analysis of the correlation of the molecular and atomic states and a comparison of the dissociation energies, obtained by extrapolating the levels of a series of electron states of these molecules, verify the supposition that an extrapolation of the lower levels of the $A^2\Pi$ state yields the dissociation limit of $M(^3P) + F(^2P)$.

Hence we see that a substantiated choice of the value of dissociation energy of BeF from the data available at present is impossible and it may only be assumed that it must lie within the interval of from 140 to 180 kcal/mole.

In the Handbook the most likely value of

$$D_0(\mathrm{BeF}) = 160 \text{ kcal/mole},$$

has been chosen which is similar to the value obtained by extrapolation for the state $X^2\Sigma$. The error of this value can be estimated as ±20 kcal/mole.

It is interesting to indicate that the chosen value is close to the mean bond energy of Be – F in the BeF_2 molecule, though previously based on insufficiently reliable data, the mean bond energy in MX_2-type molecules was assumed to be much higher (cf. [242]) than $D_0(MX)$ (where M is a metal of group II and X a halogen).

A value of

$$\Delta H^\circ f_0(\mathrm{BeF, gas}) = -64{,}5 \pm 20 \text{ kcal/mole}.$$

corresponds to the value accepted.

BeF_2 (cryst.). Kolesov, Popov and Skuratov [234, 25] measured the heat of dissolution of beryllium oxide in 23% hydrofluoric acid and obtained $\Delta H_{293} = -24{,}17 \pm 0.12$ kcal/mole. The results of earlier measurements [1173, 1174, 2810] of the heat of this reactions are not accurate (cf. page 1672). Fricke and Wullhorst [1612] obtained a value of -24.35 kcal/mole for the heat of dissolution of beryllium oxide in 11.6% hydrofluoric acid, which is in good agreement with the results of measurements of [234, 25] if the difference in concentration of the acid is ignored.

The heat of dissolution of beryllium fluoride in 23% hydrofluoric acid measured by Kolesov, Popov and Skuratov [234, 25] by adiabatic and diathermic methods, proved to be equal to $\Delta H_{293} = -8{,}04 \pm 0{,}07$ kcal/mole. This quantity was measured for the first time. The BeF_2 sample investigated could not be examined with sufficient accuracy in a direct chemical analysis. The authors, however, made a careful analysis of the initial ammonium fluoroberyllate and showed that its decomposition, accompanying the formation of BeF_2, is complete and without any side reactions.

The following value of the heat of formation of crystalline beryllium fluoride

$$\Delta H^\circ f_{298,15}(BeF_2, \text{cryst.}) = -241{,}2 \pm 0{,}8 \text{ kcal/mole.}$$

corresponds to the heat of dissolution, obtained by Kolesov, Popov and Skuratov [234, 25].

This value has been accepted in the present Handbook.

In older literature the values of the heat of formation of beryllium fluoride published had been obtained with the help of approximate estimations. Thus, Brewer [1093] estimated the heat of formation of BeF_2 and found that it was equal to -277 ± 10 kcal/mole. Shishokin [464] estimated the heat of formation of beryllium fluoride to -203 kcal/mole. A much better result, -235 kcal/mole, was obtained by an estimation of Karapet'yants [221] according to a method proposed by himself.

BeF_2 (gas). The saturated vapor pressure of beryllium fluoride was measured by Khandamirova, Yevseyev, Pozharskaya, Borisov, Nesmeyanov and Gerasimov [434, 13] by means of an effusion method (864-949.5°K) and by means of the flow method by Sense, Snyder and Clegg [3686] (1019-1241°K) and Novoselova, Muratov, Reshetnikov and Gordeyev [323] (1040-1376°K). The results of the measurements are in good agreement with one another. A calculation of the heat of sublimation of BeF_2 at 0°K, according to data from [434, 3686 and 323] yields the values of 55.2 ± 0.2; 54.6 ± 0.3 and 54.5 ± 0.3 kcal/mole respectively. The mean of the values given above has been accepted in the Handbook for the heat of sublimation of BeF_2:

$$\Delta Hs_0(\mathrm{BeF_2},\ \text{крист.}) = 54{,}8 \pm 1{,}5\ \text{kcal/mole}.$$

The following values correspond to it:

$$\Delta H^\circ f_0(\mathrm{BeF_2},\ \text{газ}) = -185{,}721 \pm 1{,}7\ \text{kcal/mole},$$
$$D_0(\mathrm{BeF_2}) = 299{,}721 \pm 2\ \text{kcal/mole}.$$

BeCl (gas). In literature there are no experimental data on the dissociation energy or the heat of formation of BeCl. In Herzberg's monograph [2020] and in the Handbook [649] a value of $D_0(\mathrm{BeCl}) \approx 94$ kcal/mole is recommended which has been obtained as the result of a linear extrapolation of the vibrational levels of the state $X^2\Sigma$ with constants found in the paper of Fredrickson and Hogan [1603]. Based on the same consideration as in the case of BeF (cf. page 1676), Gaydon [1668] assumed a lower value, equal to 69 kcal/mole. However, as we may see from the example of the BeF molecule, such a reduction of the value, obtained by a linear extrapolation of the levels of the ground state, is not substantiated in the case of halogen compounds of elements of group II, but the values obtained by the linear extrapolation must be considered as a lower limit of the dissociation energy of the corresponding molecules. Novikov and Tunitskiy [321] estimated $D_0(\mathrm{BeCl})$ by extrapolating the vibrational levels of the $A^2\Pi$ state with respect to constants, given in Table 231; under the supposition that the states $X^2\Sigma$ and $A^2\Pi$ have a common dissociation limit, $\mathrm{Be}(^1S) + \mathrm{Cl}(^2P)$, they obtained $D_0(\mathrm{BeCl}) = 147 \pm 11$ kcal/mole (51,500 ± 4000 cm^{-1}). Taking into account that the potential curve of the $A^1\Pi$ state may possess maxima, the authors of paper [321] recommend a value of 135.8 kcal/mole for the dissociation energy of BeCl.

This value, however, seems to be a little too high. Just as in the case of BeF, it is possible that the extrapolation of the levels of the $A^2\Pi$ state yields the dissociation limit of $\mathrm{Be}(^3P) + \mathrm{Cl}(^2P)$, so that $D_0(\mathrm{BeCl}) \sim 30\,000\ cm^{-1}$, or 85 kcal/mole which is in satisfactory agreement with the value obtained in the linear extrapolation. A well-defined selection between the considered values of the dissociation energy of BeCl being impossible before new experimental values have been obtained, one may only assume that 90 kcal/mole $\leqslant D_0(\mathrm{BeCl}) \leqslant 130$ kcal/ /mole. Since the dissociation energy of $BeCl_2$ has a value of the order of 220 kcal/mole, and the dissociation energy of other diatomic compounds of metals of group II with halogens amounts to about half the value of $D_0(MX_2)$, in the Handbook we accept the value of

$$D_0(\mathrm{BeCl}) = 110 \pm 20 \text{ kcal/mole.}$$

The following value corresponds to it:

$$\Delta H^\circ f_0(\mathrm{BeCl}, \text{gas}) = -4{,}45 \pm \text{ kcal/mole.}$$

$BeCl_2$ (cryst.). Mielenz and Wartenberg [2903] determined the heat of combustion of beryllium in a stream of chlorine. The value obtained -112.6 kcal/mole, has been accepted by the authors of a series of Handbooks [1903, 267]. But since the initial sample contained a considerable quantity of impurities (30.55% of beryllium oxide) this work cannot be viewed as accurate.

As a result of measurements of the heat of combustion of beryllium (99%) in chlorine, carried out in an enameled calorimetrical bomb at a chlorine pressure of 7-8 atm, Siemonsen [3720] obtained a value of -109.2 kcal/mole for the heat of formation of beryllium chloride.

The most accurate measurement of the heat of formation of beryllium chloride was carried out by Johnson and Gilliland [2266a]. In this experiment beryllium (99.4%) was burnt in a chlorine current. The obtained value of

$$\Delta H^{\circ}f_{298.15}(\mathrm{BeCl_2},\ \text{cryst.}) = -118{,}03 \pm 0{,}56\ \text{kcal/mole}$$

is accepted in the present Handbook. The value obtained by Siemonsen [3720] just as in the case of $LiCl$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ (see Chapters XXVIII and XXVII) deviates considerably from the values obtained in other papers. Johnson and Gilliland assume that a systematic error was admitted in paper [3720].

BeCl (gas). Ralfs and Fisher [3350] measured the saturated vapor pressures above solid and liquid beryllium chloride in the temperature interval of 613-732.5°K. The values they obtained are not quite reliable because of the interaction of the $BeCl_2$ vapor with the quartz walls of the apparatus. The corrections for the partial pressures of $SiCl_4$ appearing, which were introduced by the authors of [3350], amounted to 50-80% of the total pressure. A calculation of the heat of sublimation of $BeCl_2$ according to data from [3350], under the assumption that beryllium chloride vapor consisted only of $BeCl_2$ molecules, yielded a value of $\Delta H_0 = 31{,}2 \pm 0{,}1$ kcal/mole.

Ralfs and Fisher [3350] also investigated the densities of $BeCl_2$ and $BeBr_2$ vapors and observed the presence of a considerable dimerization of these compounds. With the help of the estimated value of $\Delta\Phi^{*}$ for the reaction

$$(\mathrm{BeCl_2})_2 \rightleftarrows 2\mathrm{BeCl_2}$$

and the value of the equilibrium constant $K_{835} = 1{,}655$ [3350] the authors of the Handbook derived the approximate equation

$$\lg K_p = 9{,}84 - \frac{8030}{T}$$

in order to calculate the logarithm of the equilibrium constant of this reaction. Taking into account the dimerization of $BeCl_2$ in the vapor, the value of the heat of sublimation

$$\Delta Hs_0(\text{BeCl}_2,\ \text{cryst.}) = 33{,}0 \pm 1{,}5\ \text{kcal/mole},$$

was obtained which has been accepted in the Handbook.* The following values correspond to it:

$$\Delta H^\circ f_0(\text{BeCl}_2,\ \text{газ}) = -85{,}268 \pm 1{,}6\ \text{kcal/mole},$$
$$D_0(\text{BeCl}_2) = 219{,}368 \pm 1{,}7\ \text{kcal/mole}.$$

BeN (gas). In literature experimental data permitting a calculation of the value of the dissociation energy of BeN are lacking. An estimation of D_0(BeN) according to the method of Margrave and Stapitanonda [2777] (cf. page 1633) with $r_{\text{Be—N}} = 1{,}40 \pm 0{,}08$ Å, $I(\text{Be}) = 75192{,}29\ \text{см}^{-1}$ [2941] and $A(\text{N}) = 0$ [3331] yields $D_0(\text{BeN}) = 22 \pm 13$ kcal/mole.**

A comparison of the dissociation energy of diatomic nitrides of the elements of the second group of Mendeleyev's table yields the value

$$D_0(\text{BeN}) = 40 \pm 10\ \text{kcal/mole}.$$

This value proves to be more reliable than that calculated by means of the method of Margrave and Stapitanonda [2777] and used in the Handbook. The following corresponds to the value accepted:

$$\Delta H^\circ f_0(\text{BeN},\ \text{газ}) = 149{,}536 \pm 10\ \text{kcal/mole}.$$

TABLE 237

Accepted Values (in cal/mole) of the Thermodynamic Quantities of Beryllium and Its Compounds

Вещество 1	Состояние 2	D_0 или ΔHs_0	$\Delta H°f_0$	$\Delta H°f_{293.15}$	$\Delta H°f_{298.15}$	$H°_{293.15} - H°_0$	$H°_{298.15} - H_0$
Be	Крист. 3	77 000[a]	0	0	0	448	468
Be	Газ 4	—	77 000	78 008	78 013	1456	1481
BeO	Крист. 3	171 868[a]	—142 281	—143 093	—143 100	656	686
BeO	Газ 4	106 400	29 587	30 160	30 158	2041	2076
BeH	»	53 000	75 632	76 224	76 222	2032	2067
BeF	»	160 000	—64 500	—63 938	—63 942	2047	2082
BeF_2	Крист. 3	54 800[a]	—240 521	—241 202	—241 200	1840	1900
BeF_2	Газ 4	299 721	—185 721	—186 050	—186 063	2192	2237
BeCl	»	110 000	—4 450	—3 896	—3 898	2079	2117
$BeCl_2$	Крист. 3	33 000[a]	—118 268	—118 054	—118 030	2815	2900
$BeCl_2$	Газ 4	219 368	—85 268	—85 346	—85 351	2523	2579
BeN	»	40 000	149 536	150 112	150 109	2042	2077

[a] Value given of the heat of sublimation.

1) Substance; 2) state; 3) cryst.; 4) gas.

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1640	The low values of dissociation energies of the molecules of group II elements are caused by the fact that the atoms of these elements have a closed shell of valence electrons (s^2), and the formation of molecules occurs on account of Van-der-Waals forces and the influence of the excited states of these molecules.
1641	In the paper of Lagerkvist [2521] it was shown on the basis of an analysis of the possible electronic configurations that the least energy belongs to the state $^1\Sigma$ – the lowest of the electronic states observed in the emission spectrum of BeO. Recently this conclusion has been confirmed experimentally by Tresh who observed in the absorption spectrum of BeO bands of the system $B^1\Sigma - X^1\Sigma$ [3988b].
1644	This assertion is based solely on a theoretical analysis of the possible electronic configurations and the electronic states of the BeH molecule which correspond to them, because the absorption spectrum of BeH has not been observed.
1648	The third anharmonicity coefficient has been introduced into the expression for $G_0(v)$ of the state $X^2\Sigma$ of the BeCl molecule

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in order to match the energies of the vibrational levels and the dissociation limits of the states $X^2\Sigma$ and $A^2\Pi$ (see page 1681).

1650 It is noted in the Handbook [649] that the vibration frequencies found by Parker [3187] are too small for a molecule like BeCl.

1652 In the first edition of the present Handbook the frequencies of BeF_2 ($\nu_1 = 750$, $\nu_2 = 600$ and $\nu_3 = 1550$ см$^{-1}$) were calculated by Eqs. (P4.29) assuming the f_d force constant to be equal to k_e the force constant of the bond in the biatomic BeF molecule ($k_e = 5.77\cdot10^5$ dyn.cm^{-1}) and $f_{dd} = 0.1f_d$. The deformational constant f_α/d^2 was estimated quite roughly, similar to the estimation done by Stepanov [393] for the MgF_2 deformational constant, and was assumed to be $0.40\cdot10^5$ dyn·cm^{-1}. However, results of $BeCl_2$ spectrum investigations [1001] showed already, that such an estimation of the deformational force constant gives an understated value.

It should be noted, that the estimation of force constants of deformational vibrations of halogenide molecules of elements of the II group, carried out by Berry [771] based on the use of the ionic molecule model, led in case of BeF_2 also to a too low value $f_\alpha/d^2 = 0,46\cdot10^5$ dyn·cm^{-1}, whereas the value for this constant is $0.73\cdot10^5$ dyn·cm^{-1}, according to experimentally determined frequencies.

1654 Since no papers were before in literature dealing with the investigation of the $BeCl_2$ molecule spectrum in the first edition of the Handbook the values of $BeCl_2$ ground frequencies were calculated on the basis of approximative estimations of force constants of this molecule by Eqs. (P4.29). In the calculation was assumed that the force constant f_d of the bond in the $BeCl_2$ molecule is equal to the force constant of the bond of the corresponding biatomic molecule [k_e(BeCl) = $3.03\cdot10^5$ dyn.cm^{-1}] and the constant f_{dd} of bond interaction assumed to be $0.1f_d$. The value for the deformational constant f_α/d^2 was assumed to be $0.17\cdot10^5$ dyn·cm^{-1}, based upon the estimation by the method of stepanov, who applied it for the calculation of f_α/d^2 for MgF_2 [393]. As a result were found the following values of $BeCl_2$ frequencies: $BeCl_2$: $\nu_1 = 400$, $\nu_2 = 380$ and $\nu_3 = 1070$ см$^{-1}$. The value ν_3 of the frequency for the nonsym-

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metrical vibration is in good agreement with the experimentally determined value, while the estimated value for the frequency of the deformational vibration is extremely understated.

1664 According to data of Martin and Moore [2784a] the melting point of beryllium, purified by zone melting, is equal to 1565°K.

1666 When the calculations of the thermodynamic functions of BeO had been finished, a paper was published by Kandyba, Kantor, Krasovitskaya and Fomichev [204] who recommended somewhat different values of the coefficients of the enthalpy and the specific heat of BeO:

$$C_p^\circ = 9{,}471 + 2{,}09\cdot10^{-3}T\ (1200-2820^\circ\ K).$$

This equation yields lower values of the specific heat at 1200°K (by 2%) and higher values of C_p° at higher temperatures (at 2800°K by 7%). The values of S°_{2800} and Φ^*_{2800} deviate by 0.24 and 0.06 cal/mole·degree, respectively.
From the values of enthalpy in the interval of 2820-2840°K, given in paper [204] and referring to a sample that was partially molten, the lower limit can be found for the heat of melting of BeO, equal to 15 kcal/mole.

1667 As to the analogy between the crystalline forms and the polymorphous transformations of BeF_2 and SiO_2, see the paper of Novoselova and co-workers [322, 230, 321a].

1669 The values of $H_T - H^\circ_{298.15}$ for substances in crystalline and vitreous states (e.g., SiO_2, B_2O_3, $Na_2Si_2O_5$) differ from one another by less than 5-10%.

1670* The value of $S^\circ_{298.15} = 21{,}5 \pm 2{,}5$ cal/mole·degree of $BeCl_2$, determined by Kubaschewsky and Evans [2494] by means of Latimer's method [2565] is, obviously, incorrect. Estimations of the entropy of compounds of light elements at 298°K by means of this method usually yield much too high values.

1670** Furby and Wilkinson [1631a] obtained recently a value of 672°K for the melting point of $BeCl_2$.

1675 When calculating the experiment at T = 2242°K the authors of paper [1106] admitted an arithmetical error which mainly explains the differences between the values calculated in the Handbook and those of paper [1106].

1676 A less accurate linear extrapolation of the vibrational lev-

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els of the ground state $X^2\Sigma$ yields a value of $D_0(BeH) = 82{,}3$ kcal/mole.

1677 According to the Wigner-Wittmer correlation rule, the follow-12 electron states of BeF must be connected with the dissociation limit of $Be(^3P) + F(^2P)$, which is by 21,980 cm-1 higher than the limit of $Be(^1S) + F(^2P)$, $^2\Sigma^+(2)$, $^2\Sigma^-$, $^2\Pi(2)$, $^2\Delta$, $^4\Sigma^+(2)$, $^4\Sigma^-$, $^4\Pi(2)$ and $^4\Delta$.

1684* In the pape. of Ryabchikova and Tikhinskiy [356a], published when the compilation work with the present chapter had been finished, the ion current intensities of $BeCl_2^+$ and $Be_2Cl_4^+$ above beryllium chloride were measured in the interval of 496-578°K with the help of a mass-spectrometrical method. From the temperature dependence of the ion current intensities Ryabchikov and Tikhinskiy found the values of the heats of sublimation of $BeCl_2$ and Be_2Cl_4 at 537°K equal to 34 ± 1 kcal/mole and 44 ± 1 kcal/mole, respectively, and 24 ± 2 kcal/mole for the dissociation energy of dimeric molecules. A value of $\Delta H_{s_{537}}$ cryst.) = 32.3 ± 1 kcal/mole corresponds to the value of $\Delta H_{s_0}(BeCl_2$, obtained in this paper; it agrees with the value accepted in the Handbook within the limits of error.

1684** Margrave and Stapitanonda [2777] give two values for $D_0(BeN)$: 64 and 167 kcal/mole, obtained under the assumption that $I(Be) = 75\,192{,}29\ cm^{-1}$ [2941], $A(N) = -26$ kcal/mole [2769] and r_{Be-N} was calculated for two values of r_{N^-} equal to 0.70 and 1.08 A.

Chapter 26

MAGNESIUM AND ITS COMPOUNDS

(Mg, Mg^+, MgO, MgH, MgF, MgF_2, $MgCl$, $MgCl_2$, MgN)

In the present chapter we consider the thermodynamic properties of magnesium and its simplest compounds with oxygen, hydrogen, fluorine, chlorine and nitrogen. We will also consider the moatomic magnesium ion which may be formed in systems containing magnesium at temperatures of 5000-6000°K. The data available permit us to consider the magnesium-oxygen system as more simple as the analogous system of beryllium-oxygen. Mass-spectrometrical investigations of the composition of the evaporation products of MgO [3305] showed that the vapor contains only Mg and MgO. The absence of stable gaseous magnesium hydroxides [2626] make it possible to assume that the system magnesium-oxygen-hydrogen will also be described sufficiently completely by the data given. The low value of the dissociation energy of the Mg_2 molecule (7.2 kcal/ /mole [3813,29]) permits the exclusion of this molecule from the number of the components under considerationl In the Handbook all known compounds of magnesium with fluorine and chlorine, **MgF, MgF_2, MgCl** and $MgCl_2$, are considered. Indications as to the existence of polymeric molecules of the type $(MgX_2)_n$ are lacking in literature.

Among the compounds of magnesium with nitrogen, only MgN (gas) will be considered. We also know a magnesium nitride (Mg_3N_2) in solid state, but it disintegrates at 1300°K.

The composition of the reaction products of magnesium with oxygen, hydrogen, fluorine and chlorine is much simpler than in the case of beryllium and the data given in the Handbook permit calculations of various systems comprising magnesium with great reliability.

§103. THE MOLECULAR CONSTANTS

Mg. In its ground state the magnesium atom has the electron configuration $1s^22s^22p^63s^2$, to which the one term ^1S corresponds. On exciting one 3s-electron a group of singlet and triplet terms, $3s(^2S)nl$ with the values of $L = \ell$ appear. The first excited state of this group, $3p\,^3P$, has an excitation energy of about 22,000 cm^{-1}.

Table 238 gives the energy levels of the Mg atom pertaining to the group of terms with the configuration $3s(^2S)nl$ and possessing excitation energies lower than 50,000 cm^{-1}. These levels correspond to the transition of a 3s-electron to the states 3p, 3d, 4s and 4p. Levels of this group with higher excitation energies and also levels connected with the excitation of two 3s-electrons or electrons with n = 2 could not be taken into account in the following calculations (cf. page 1704).

TABLE 238

Energy Levels of the Magnesium Atom

1 Номер уровня	2 Состояние		5 Статистический вес	6 Энергия, см$^{-1}$
	3 электронная конфигурация	4 терм		
0	$1s^22s^22p^63s^2$	^1S	1	0
1	$1s^22s^22p^63s\,(^2S)\,3p$	$^3P_0$	1	21850,368
2	$1s^22s^22p^63s\,(^2S)3p$	$^3P_1$	3	21870,426
3	$1s^22s^22p^63s\,(^2S)3p$	$^3P_2$	5	21911,140
4	$1s^22s^22p^63s\,(^2S)\,3p$	^1P	3	35051,36
5	$1s^22s^22p^63s\,(^2S)\,4s$	^3S	3	41197,37
6	$1s^22s^22p^63s\,(^2S)\,4s$	^1S	1	43503
7	$1s^22s^22p^63s\,(^2S)\,3d$ $1s^22s^22p^63s\,(^2S)\,4p$	$^1D,\ ^3D$ ^3P	29	47650
8	$1s^22s^22p^63s\,(^2S)\,4p$	^1P	3	49346

1) Number of level; 2) state; 3) electron configuration; 4) term; 5) statistical weight; 6) energy, cm^{-1}.

The excitation energies of the Mg levels given in Table 238 are based on recommendations of Moore [2941] and levels whose excitation energies are similar in magnitude were united to a single one, with a summary statistical weight and a mean excitation energy.

Mg$^+$. The positive magnesium ion has an electron configuration of $1s^22s^22p^63s$ in its ground state and is isoelectronic with the natrium atom. Just as with the Na atom (cf. page 1863), the ground state of the Mg$^+$ ion is of the type ^2S and the excited states are connected with transitions of a 3s-electron to higher states. In Table 239 only one excited state of Mg$^+$ (Moore [2941]) is considered, the other states have energies of 70,000 cm^{-1} and more and cannot be taken into account in the following calculations.

TABLE 239

Energy Levels of the Mg$^+$ Ion

1 Номер уровня	2 Состояние		5 Статистический вес	6 Энергия, см$^{-1}$
	3 электронная конфигурация	4 терм		
0	$1s^22s^22p^63s$	^2S	2	0
1	$1s^22s^22p^63p$	$^2P_{1/2}$	2	35669,42
2	$1s^22s^22p^63p$	$^2P_{3/2}$	4	35760,97

1) Number of level; 2) state; 3) electron configuration; 4) term; 5) statistical weight; 6) energy, cm^{-1}.

MgO. Two band systems were investigated in the spectrum of the MgO molecule, which lie in the red and green ranges of the spectrum. Mahanti [2739, 2742] was the first who analyzed the vibrational structure of these two systems. His analyses of the rotational structures of the 0-1, 0-0, 1-0 and 2-0 bands of the red system [2742] led him to the conclusion that this system was connected with the electron transition $^1\Sigma - {}^1\Sigma$. Later on Lagerqvist [2519] investigated the bands 0-0 and 1-1 of the green system and showed that they belong to a system connected with transitions between the electron states $^1\Sigma$. The vibrational constants of the lower states of both systems are in good agreement with one another, the rotational constants, however, proved to be essentially different. This disagreement was the cause of a new investigation of the red bands of MgO, carried out by Lagerqvist and Uhler [2534, 2533]. The radiation source used by the authors of paper [2534, 2533] was an arc discharge burning in air between cooled magnesium electrodes. The spectrum was photographed in first order of grating (dispersion 1.2 A/mm); the errors in wave number measurements did not exceed ±0.04 cm^{-1}. In contrast to Mahanti's data [2742], the spectrograms obtained in paper [2533] showed clearly the lines of the Q-branch. An analysis of the band structure showed that the green bands are actually connected with $^1\Sigma \rightarrow {}^1\Sigma$, transitions and the bands of the red system with the $^1\Pi \rightarrow {}^1\Sigma$, transitions, the lower states $^1\Sigma$ of both systems being identical. It was thus also shown that Manhanti's analysis [2742] was incorrect. The molecular constants of MgO in the three electron states investigated, obtained as a result of an analysis of the five bands of the system $^1\Pi - {}^1\Sigma$ and the three bands of the system $^1\Sigma - {}^1\Sigma$, are compiled in Table 240 and used in the present Handbook. The same values of the constants are recommended in Herzberg's book [2020] and in the Handbook [649].

It is necessary to consider in particular the problem of the electron ground state of the MgO molecule. As follows from what has been said above, the MgO emission band systems investigated correspond to transitions between singlet electron states. On the other hand, since the ground state of the Mg atom is of the type $^1S_0$, a combination with the nonperturbed oxygen atom in the ^3P state may, according to the Wigner-Witmer correlation rule, result in the formation of molecules only in triplet states. In the past years a series of papers was published in literature, in which, based on theoretical considerations [917] and also on direct experimental data [929, 2526], the assumption was supported that the electron ground state of the MgO molecule cannot be a singlet but must be a triplet state. Since the question whether the lowest known state $^1\Sigma$ was the ground state could not be answered definitely without investigating the absorption spectrum of MgO vapor, it was tried to obtain MgO absorption spectra and to discover new bands in the MgO spectrum which corresponded to transitions between triplet states. In particular, Barrow and Crawford [650] obtained the first absorption spectrum with a flame containing magnesium compounds. The complex band system appearing in the ultraviolet range of the spectrum, which was previously observed by many authors in the emission spectrum, under various conditions of excitation, [2339, 4098, 1452], was assumed by Barrow and Crawford to pertain to the MgO molecule, though they did not succeed in analyzing the spectrum obtained because of the complexity of the structure and the insufficient resolution of the bands.

These bands were then obtained by Brewer and Porter [929] in the absorption spectrum of vapor in equilibrium with solid magnesium oxide heated in a King furnace up to temperatures of 2500-2600°K. In spite of the fact that a spectrograph with diffraction grating with a second-order dispersion of 0.67 A/mm was used as a spectral apparatus, the rotational structure of the bands could not be resolved completely. As a result of an approximate analysis of the vibrational structure of the ultraviolet system which, according to Brewer and Porter, corresponds to transitions between the triplet states of MgO, one of which being viewed as the ground state, the values of the vibrational constants in these states were determined. The authors, however, noted that the data obtained by them do not permit an unambiguous attribution of the band system observed to the magnesium oxide spectrum. In papers [124, 1670] it was in fact supposed that the bands observed in the ultraviolet range of the spectrum might be connected with the emission of the triatomic MgOH molecule.*

Thus, since there are no direct experimental data specifying the type of the electron ground state of MgO and since, on the other hand, it is well-known that the electron ground states of the molecules of BeO, CaO, SrO and BaO (see the corresponding sections of Chapters XXV and XXVII) are $^1\Sigma$ states, it has been assumed in the Handbook that the MgO ground state is of the type $^1\Sigma$, corresponding to the lower state o the red and green systems, investigated in detail in the paper of Lagerqvist and Uhler.

It must be noted that after the compilation work of this chapter had been finished, the results of investigations of Bulewicz and Sugden [1012] were published, who had studied the stability of the MgO and MgOH molecules by the method of flame photometry. Studying the temperature dependence of the relative intensity of the 0-0 band edge of the green system of MgO, Bulewicz and Sugden found that the excitation energy of the upper state of the green system is equal to about 97 kcal/ /mole, and the lower state $^1\Sigma$ must be at least by 45 kcal/mole higher than the MgO ground state. This value agrees with the value of 55 ± 15 kcal/mole obtained by Brewer and Porter as the result of measurements, carried out on exciting the MgO spectrum in a King-type furnace [929]. Concluding from these data and from the coincidence of the values of D_0(MgO), calculated with the help of the second and third laws of thermodynamics under the assumption that the ground state of MgO is a $^3\Sigma$ type state, Bulewicz and Sugden [1012], just as also Brewer and Porter [929] assume that the MgO ground state must be a triplet.

In 1960 a paper of Tresch [3988b] was also published which was devoted to the problem of the type of the BeO ground state. Besides an investigation of the BeO absorption spectrum, Tresch studied the absorption spectrum of a pulsed discharge between magnesium electrodes in an oxygen atmosphere and observed in it only a triplet system of MgO, on which Brewer and Porter [929] had reported. These observations might be considered as a support of the assumption that the ground state of MgO was of the type of $^3\Sigma$ provided the conditions of excitation in the pulsed discharge were in equilibrium, which is not quite evident.

<u>MgH</u>. The electron ground state of the MgH molecule is a $^3\Sigma$ state. In the MgH spectrum five band systems have been analyzed, lying in the range of from 2300 to 6100 A and observed in both the emission spectru and the absorption spectrum **[4187, 3208, 3209, 1893, 1894, 1868, 1869, 4027, 4028, 1895, 1896, 1897]**. The most detailed and complete investigation of the known systems of MgH bands was carried out by Guntsch [1897]. As results from the tables published in the Handbook [649],* in the system $A^2\Pi \rightarrow X^2\Sigma$ Guntsch [1897] measured and analyzed ten bands (v' and $v'' \leqslant 3$), in the system $C^2\Pi \rightarrow A^2\Pi$ two bands [(0-0) and (1-1)] and in the system $C^2\Pi \rightarrow X^2\Sigma$ five bands $(v' \leqslant 1, v'' \leqslant 2)$. An analysis of the system of bands $A^2\Pi \rightarrow X^2\Sigma$ was carried out according to the edges of the P-branches of the band system $C^2\Pi \rightarrow A^2\Pi$ according to the beginnings of the bands and of the system $C^2\Pi \rightarrow X^2\Pi$ according to the edges of the Q-branches. An investigation of the band structure showed that the $A^2\Pi$ state is a normal $^2\Pi$ state with A = 35 cm^{-1}. The splitting of the $C^2\Pi$ state could not be measured. In the systems $B^2\Sigma - X^2\Sigma$ and $D^2\Sigma - A^2\Pi$ only the 0-0 bands were investigated. The values of the molecular constants of MgH obtained in paper [1897] are recommended in Herzberg's monograph [2020] and in the Handbook [649]. These constants are accepted in the present Handbook and given in Table 240.

TABLE 240

Accepted Values of the Molecular Constants of MgO, MgH, MgF, MgCl and MgN

Моле-кула[1]	Состо-яние[2]	T_e	ω_e	$\omega_e x_e$	B_e	$\alpha_1 \cdot 10^2$	$D_0 \cdot 10^6$	r_e
		см⁻¹						Å
MgO	$X^1\Sigma^{а}$ $A^1\Pi$ $B^1\Sigma$	0 3563,3 19984,0	785,1 664,1 824,1	5,18 3,91 4,76	0,5743 0,5056 0,5822	0,50 0,46 0,45	1,23 1,18 1,15	1,749 1,864 1,737
MgH	$X^2\Sigma$ $A^2\Pi_r$ $B^2\Sigma$ $C^2\Pi$ $D^2\Sigma$	0 $19223^{г}$ 38730 41120 42070	1495,7 1611,3 $990^{ж}$ 1740 $1620^{ж}$	$31,5^{б}$ $40,7^{д}$ — 56 —	5,8181 6,1779 $5,448^{з}$ 6,161 $6,296^{з}$	$16,68^{в}$ $18,83^{е}$ — 14,4 —	330 360 270 340 380	1,7306 1,6795 $1,789^{и}$ 1,682 $1,664^{и}$
MgF	$X^2\Sigma^+$ $A^2\Pi$ $B^2\Sigma$ $C^2\Sigma$	0 $27832^{и}$ 37151,7 42528	$717,0^{к}$ 746,0 757,8 821,9	$3,84^{к}$ 3,97 6,24 4,82	$0,518^{з}$ $0,529^{з}$ $0,537^{з}$ —	$0,39^{л}$ $0,39^{л}$ $0,55^{л}$ —	$1,09^{м}$ — — —	$1,75^{и}$ $1,73^{и}$ $1,72^{и}$ —
MgCl	$X^2\Sigma$ $A^2\Pi$	0 $26493^{и}$	$465,4^{о}$ $491,5^{п}$	$2,05^{о}$ $2,52^{и}$	$0,25^{п}$ —	— —	— —	$2,16^{п}$ —
MgN	$X^2\Sigma^{р}$	0	$860^{п}$	—	$0,25^{п}$	—	—	$1,55^{п}$

1) Molecule;
2) state;

a) It cannot be considered as definitely established that this state is the electron ground state of MgO. It is possible that the ground state is of the type of $^3\Sigma$ [917, 929, 2526, 1012, 3988b].

b) $\omega_e y_e = -0{,}15\ \text{см}^{-1}$.

c) $\alpha_2 = -0{,}0073\ \text{см}^{-1}$.

d) $A = 35\ \text{см}^{-1}$. The value of T_e given is a mean value of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$.

e) $\omega_e y_e = 1{,}48\ \text{см}^{-1}$.

f) $\alpha_2 = -0{,}0013\ \text{см}^{-1}$.

g) Calculated from the value of $\Delta G_{1/2}$ for MgH and MgD.

h) Value of B_0 given.

i) Value of r_0 given.

k) mean value given, averaged from the results of measuring the bands of the A → X, B → X and C → X systems.

l) Calculated from Eq. (1.38).

m) Calculated from Eq. (1.36).

n) mean given of the values of the constants of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$.

o) mean value of the quantities obtained for the transitions $A^2\Pi_{1/2} \rightarrow X^2\Sigma$ and $A^2\Pi_{3/2} \rightarrow X^2\Sigma$.

p) estimate.

q) chosen according to the correlation rules.

<u>MgF</u>. The electron ground state of the MgF molecule is of the type $^2\Sigma$. Three band systems have been investigated in the MgF spectrum: $A^2\Pi - X^2\Sigma$, $B^2\Sigma - X^2\Sigma$ and $C^2\Sigma - X^2\Sigma$ [1265, 2250, 2262, 2233, 1587]. The first MgF bands were obtained by Datta [1265] in the emission spectrum of an arc, containing MgF_2. The MgF spectrum was recorded with a spectrograph of a dispersion of 2.75 A/mm. The author of paper [1265] did not analyze the MgF spectrum.

An analysis of the vibrational structure of the band systems $A^2\Pi - X^2\Sigma$, $B^2\Sigma - X^2\Sigma$ and $C^2\Sigma - X^2\Sigma$ was carried out by Jevons [2250], Johnson [2262] and Fowler [1587]. The most reliable values of the molecular constants of MgF in the states $X^2\Sigma$, $A^2\Pi$ and $C^2\Sigma$ were obtained by Fowler [1587] when investigating the MgF absorption spectrum. The spectrum was excited by heating MgF_2 in a King furnace to temperatures of 1300-1900°C, for recording a spectrograph with a dispersion of 1.3A/ /mm was used. Comparing the molecular constants in the state $X^2\Sigma$, obtained on analyzing the system $C^2\Sigma - X^2\Sigma$, with the constants obtained previously by Johnson [2262] in investigations of the $A^2\Pi - X^2\Sigma$. band system, showed that Johnson's analysis [2262] was incorrect. Therefore Fowler [1587] analyzed the band system $A^2\Pi - X^2\Sigma$ once again, using the spectrograms obtained by Datta [1265]. The analysis based on the edges of the Q_2 branches of the bands with $v' \leqslant 7$ and $v'' \leqslant 8$.

The vibrational structure of the band system $B^2\Sigma - X^2\Sigma$ was investigated by Jevons [2250]. As in paper [1265], the spectrum was excited in a carbon arc, burning in an MgF_2 atmosphere. The spectrum was photographed in a quartz spectrograph with a dispersion of 2.81 to 3.22 A//mm, in the range of $\lambda\lambda$ 2740—2630 Å. The bands with $v' \leq 6$ and $v'' \leq 7$. were analyzed.

The paper by Jenkins and Grinfeld [2233] is the only one in which the rotational structure of the MgF bands could partly be resolved. In spite of using an apparatus with a 21-foot grating, the authors of paper [2233] succeeded in measuring only a few lines in the R- and Q--branches of the 0-0 bands of the systems $A^2\Pi - X^2\Sigma$ and $B^2\Sigma - X^2\Sigma$. This enabled them to find the values of the rotational constants B_0 in the states $X^2\Sigma$, $A^2\Pi$ and $B^2\Sigma$. The authors of paper [2233] came to the conclusion that the $A^2\Pi$ state of the MgF molecule, just as the $A^2\Pi$ state of the BeF molecule is an inverse state with a coupling constant $A = -34{,}3$ см$^{-1}$. The rotational structure of the bands of the $C^2\Sigma - X^2\Sigma$ system was not analyzed.

Table 240 gives the vibrational constants of MgF, obtained in the papers of Fowler [1587] and Jevons [2250]. Since in the analysis of the systems $C - X$, $A - X$ and B – X somewhat different values were obtained for the constants of the state $X^2\Sigma$, the mean of these values was chosen for Table 240. The values of the rotational constants, given in Table 240, were obtained in the paper of Jenkins and Grinfeld [2233].

In Herzberg's monograph [2020]* and in the Handbook [649] the same values of the constants of MgF are recommended.

<u>MgCl.</u> The electron ground state of the MgCl molecule is of the type of $X^2\Sigma$. In the emission and absorption spectra of MgCl, investigated by a series of authors [3131, 4147, 3345, 3188, 2948, 1957], three band systems were identified, lying in the ultraviolet range of the spectrum.

The vibrational structure of the band systems of MgCl was analyzed by Parker [3188], Morgan [2948] and Harrington [1957]. Parker investigated the emission spectrum of MgCl. As a result of an analysis of the bands lying in the near ultraviolet and forming the sequence $\Delta v = 0. +$ ± 1, ± 2, he obtained the serial formula $\nu = 26\,441{,}5 + [474{,}8\,(v' + 1/2) - 2{,}5\,(v' + 1/2)^2] - [447{,}4\,(v'' + 1/2) - 1{,}6\,(v'' + 1/2)^2]$, which gives a satisfactory description of the wave numbers of the edges of the bands observed. The same band system was obtained by Morgan [2948] in the absorption spectrum of MgCl. The necessary vapor pressure of magnesium chloride was produced by conducting a current of chlorinve over metallic magnesium arranged in an open graphite tube in a King furnace whose temperature was kept at a level of 1600°C. The absorption spectrum was recorded in second order of a curved grating (dispersion 2.7 A/mm). Based on the results of an analysis of the bands with $v' \leqslant 7, v'' < 8$, forming the sequence $\Delta v = 0, \pm 1, \pm 2$, Morgan [2948] found that within the limits of error of measurement, the positions of the edges of the Q-branches can be described by the Equation $\nu = 26\,521{,}0 + [491{,}6\,(v' + 1/2) - 2{,}54\,(v' + 1/2)^2 - 0{,}025\,(v' + 1/2)^3] - [466{,}0\,(v'' + 1/2) - 2{,}10\,(v'' + 1/2)^2]$. In paper [2948] it was also shown that the band system of MgCl in the near ultraviolet is connected with the transition $A^2\Pi - X^2\Sigma$, and that the analysis carried out by Parker [3188] was incorrect owing to a wrong attribution of the band system observed to the transition $^2\Sigma - {}^2\Sigma$ or $^2\Pi - {}^2\Pi$. The most complete investigation of the spectrum of MgCl was carried out by Harrington [1957].* The band system $A^2\Pi - X^2\Sigma$ was obtained by the author of paper [1957] in both the emission and the absorption spectra. An analysis of the vibrational structure of 23 bands of this system, forming the sequence $\Delta v = 0, \pm 1$ (v' and $v'' \leqslant 8$), made it possible to obtain the values of the molecular constants of MgCl which coincide virtually with the constants found by Morgan [2948]. Besides the system $A^2\Pi - X^2\Sigma$, Harrington [1957] observed another two band systems in the MgCl absorption spectrum which are connected with transitions between the excited states $B^2\Sigma$ ($T_e \sim 37\,006$ cm^{-1}) and $C^2\Pi$ ($T_e \sim 40\,847$ cm^{-1}) and the electron ground state $X^2\Sigma$. The vibrational structure of these band systems were not analyzed.

In the present Handbook the vibrational constants of MgCl, found in paper [1957] and given in the Handbook [649] have been accepted.

The rotational constants of the MgCl molecule have not been determined by experiment since the rotational structure of the bands observed could not even be resolved in fourth order of a 10-foot curved grating. The value of the rotational constant of MgCl in the $X^2\Sigma$ state was therefore calculated from the relation $r_{Mg-Cl} = 2{,}16 \pm 0{,}02$ Å, obtained by way of comparing the interatomic distances in the molecules of MgF (1,75 Å) [2233], MgF_2 (1,77 Å) [69] and $MgCl_2$ (2,18 Å) [69].

MgN. In literature there are no data on the molecular constants of MgN. An estimate of the corresponding values, given in Table 240, was carried out by the authors of the Handbook just as also for the BeN molecule (cf. §99). The possible error of the value of $r_{Mg-N} = 1{,}55$ Å may amount to ± 0.08 A, and the error in the value of the vibration frequency may reach ±180 cm^{-1}. In the Handbook, in agreement with the correlation rules, the electron ground state of MgN was assumed to be a $^2\Sigma$ state.

MgF_2. The structure of the magnesium fluoride vapor molecules was investigated by Akishin, Spiridonov and Naumov [69] by the method of electron diffraction. In the results of the investigations of these authors it was established that the MgF_2 molecule has a structure of linear symmetry (point group $D_{\infty h}$) and that the interatomic distance was $r_{Mg-F} = 1{,}77 \pm 0{,}02$ Å. The value of the moment of inertia of MgF_2, calculated from these data, is given in Table 241.

In literature there is not any information about investigations of the spectrum of magnesium fluoride vapor. In the first edition of the

Handbook the fundamental frequencies of the MgF_2 molecule were therefore calculated from Eq. (P4. 31) on the basis of estimated values of the force constants. The force constant of bond f_d in the MgF_2 molecule was assumed to be equal to the force constant of bond k_e in the diatomic molecule, and the value of the constant of bond interaction was taken as $f_{dd} = 0{,}1 f_d$. The deformation constant f_α/d^2 was estimated by means of a method suggested by Stepanov [393] , by way of comparison with the AlF_3 molecule. In this connection it was assumed that the value of f_α/d^2 of MgF_2 lies between the values of f_α/d^2 and f_Δ/d^2 of AlF_3. The accuracy of the value of f_α/d^2 obtained in this way was estimated by Stepanov to amount to 50% which results in an error of the value of ν_2 amounting to 25-30%. Based on the estimated values of the force constants the fundamental frequencies (in cm^{-1}) were calculated: $\nu_1 = 565$, $\nu_2 = 325$, $\nu_3 = 815$*.

The investigation of the infrared spectrum of $BeCl_2$, carried out by Buchler and Klemperer [1001] showed that an estimation of the value of the constant of deformation, f_α/d^2 according to the method of Stepanov, leads to incorrect values.** The values of the force constants of the MgF_2 molecule, estimated under the assumption that the relationships linking the force constants of the MgX_2 molecules remain unchanged, just as in the case of the force constants of $BeCl_2$, are equal to (in dyne·cm^{-1}): $f_d = 3{,}5 \cdot 10^5$, $f_{dd} = 0{,}35 \cdot 10^5$ and $f_\alpha/d^2 = 0{,}3 \cdot 10^5$. The fundamental frequencies of MgF_2 corresponding to these constants are given in Table 241 and accepted in the present Handbook.*** The frequency values found in this way are approximate and may contain errors of the order of 10-15%.

$MgCl_2$. An electron-diffraction analysis of the structure of vapor molecules of magnesium chloride showed that the $MgCl_2$ molecule has a linear symmetrical form (point group $D_{\infty h}$) with an intermolecular distance of $r_{\mathrm{Mg-Cl}} = 2{,}18 \pm 0{,}02$ Å [69]. The value of the moment of inertia of the $MgCl_2$ molecule, calculated from the structural parameters found in paper [69], has been accepted in the present Handbook and is given in Table 241.

Since the $MgCl_2$ molecule pertains to the point group of symmetry $D_{\infty h}$, it must have three normal modes of vibration, the symmetric (ν_1) and asymmetric (ν_3) valence oscillations and the doubly degenerate deformation oscillation (ν_2). The modes ν_2 and ν_3 must be active in the infrared spectrum, the mode ν_1 in the Raman spectrum.

The infrared absorption spectrum of gaseous magnesium chloride was studied by Buchler and Klemperer [1001, 1002] and Randall, Green and Margrave [3369]. The Raman spectrum of $MgCl_2$ was not investigated.

Buchler and Klemperer [1002] investigated the infrared spectrum of $MgCl_2$ at a temperature of $T \sim 1000°\mathrm{C}$ in the range from 700 to 220 cm^{-1}. The spectrum was recorded with a Perkin-Elmer spectrometer. The frequencies of the antisymmetric and deformation oscillations were found: $\nu_3 = 597$ and $\nu_2 = 295$ cm^{-1}.

Randall, Green and Margrave [3369], working with a Beckman device, obtained the absorption spectrum of gaseous $MgCl_2$ in the infrared, at a temperature of 1000°C. Since the long-wave end of the device used by the authors was at 400 cm^{-1}, they could only observe one frequency, connected with the antisymmetric valence oscillation, for which a value of $\nu_3 = 588$ cm^{-1} was found, which deviates by only 9 cm^{-1} from the value obtained by Buchler and Klemperer [1002]. The frequency ν_1, not observed in experiments, may be calculated from the estimated values of the force constants of $MgCl_2$. Randall et al [3369] estimated the value of ν_1 and obtained 297 cm^{-1} (calculation carried out according to Eq. (P4.32), with a value of $f_d = 1{,}84 \cdot 10^5$ dyne·cm^{-1}, calculated from the value of $\nu_3 = 588$ см$^{-1}$ under the assumption that the constant of interaction of the bonds $f_{dd} = 0$). A virtually coincident value of $\nu_1 = 301$ cm^{-1} is obtained by calculating with the help of Eq. (P4. 32), using the constant $f_d = 1{,}9 \cdot 10^5$ dyne·cm^{-1} obtained by Buchler and Klemperer [1002], also under the assumption that $f_{dd} = 0$. The latter supposition is based on results of investigating the spectra of mercury halides [2441, 2442] which show that the force constant of interaction of the bonds in these compounds are very small. If we assume that $f_{dd} = 0.1\ f_d$, a calculation with the helo of Eq. (P4. 31) (with the values of $f_d = 2.11 \cdot 10^5$ and $f_{dd} = 0.21 \cdot 10^5$ dyne·cm^{-1}, calculated from the wellknown value of ν_3) leads to $\nu_1 = 334$ cm^{-1}. In the present Handbook a value of 310 ± ± 30 cm^{-1} is taken for ν_1, the mean of the values given above. The values chosen for ν_2 and ν_3 were borrowed from the paper of Buchler and Klemperer [1002]. The possible error of these frequencies amounts to ±3%.

TABLE 241

Accepted Values of the Molecular Constants of MgF_2 and $MgCl_2$

1 Молекула	ν_1	ν_2 (2)	ν_3	I	σ
	$cм^{-1}$ 2			3 10^{-40} $г \cdot cм^2$	
MgF_2	590	370	860	19,8	2
$MgCl_2$	310	295	597	55,9	2

1) Molecule; 2) cm^{-1}; 3) g·cm^2.

It must be noted that a calculation of the frequencies of the $MgCl_2$ molecule from Eqs. (P4.31) with the force constants $f_d = 2{,}0 \cdot 10^5$, $f_{dd} = 0{,}2 \cdot 10^5$ and $f_\alpha/d^2 = 0{,}18 \cdot 10^5$ dyne·cm^{-1} [the latter were estimated in the same way as in the case of MgF_2 (see above)] leads to the following values of frequencies: $\nu_1 = 325$ $\nu_2 = 260$ and $\nu_3 = 580$ $cм^{-1}$. The values of ν_2 and ν_3 are in good agreement with the values found in experiments.

§104. THE THERMODYNAMIC FUNCTIONS OF THE GASES

The thermodynamic functions of magnesium and its compounds considered in the present Handbook, in the state of a perfect gas at the temperatures of 293.15 to 6000°K are given in the Tables **318, 319, 321—323, 325, 326, 328, 329** of Volume II of the Handbook. The thermodynamic functions of all compounds of magnesium were calculated for a natural mixture of magnesium isotopes and other elements' isotopes, without taking into account the differences of the constants of the individual isotope modifications of the molecules. In connection with the absence of corresponding data, no information is given in the present Handbook on the constants of intermolecular interaction with magnesium and its compounds.

Mg. The thermodynamic functions of monatomic magnesium, given in Table 318 (II), were calculated from Eqs. (II.22) and (II.23) The progressive components in the values of the thermodynamic functions of gaseous monatomic magnesium were calculated from Eqs. (II.8) and (II.9) with $A_\Phi = 2{,}2294$ and $A_S = 7{,}1976$ cal/g-atom·degree. The sum over the electron states of the Mg atom and its derivative with respect to temperature was calculated by direct summation based on data given in Table 238. At temperatures below 4000°K the accuracy of the calculated values of thermodynamic functions of magnesium is only determined by the accuracy of the physical constants used, and the errors of Φ_T° and S_T° do not exceed 0.003-0.005 cal/g-atom·degree. At higher temperatures the errors become essential because of the fact that in the calculations the electron states of the magnesium atom with excitation energies higher than 50,000 cm^{-1} and a principal quantum number in $n \leqslant 11$ have not been taken into account. The contribution of these levels to the sum over the states and its derivative is small and the error caused by their neglection does not exceed 0.03 cal/g-atom·degree in the value of

S°_{6000}.

Tables of thermodynamic functions of atomic magnesium were previously calculated by Overstreet [3158] (Φ^*_T for $T \leqslant 1500°$ K), Kolsky et al [2462] ($T \leqslant 8000°$ K) Katz and Margrave [2334] ($T \leqslant 2000°$ K), Stull and Sinke [3894] ($T \leqslant 3000°$ K) and Veyts, Gurvich and Rtishcheva [126] ($T \leqslant 3500°$ K). The deviations between the data given in Table 318 (II) and in the papers [126, 2334, 2462, 3894], and also in the first edition of the Handbook, are only determined by the differences of the universal constants used in the calculations.

Mg^+. The thermodynamic functions of ionized magnesium, given in Table 319 (II) were calculated from Eqs. (II.22) and (II.23) (A_Φ = = 2.2294 and A_S = 7.1976 cal/g-atom·degree), with the levels listed in Table 239 taken into account in the statistical sum and its derivative. The neglection of levels with higher excitation energies in the calculation does not give rise to errors in the values of the thermodynamic functions of Mg^+ with $T \leqslant 6000°$ K.

The thermodynamic functions of Mg^+ were calculated in the paper of Margrave and co-workers [1851a] for $T \leqslant 50\,000°$ K. The results of this investigation are in good agreement with the data given in Table 319 (II).

MgO. The thermodynamic functions of gaseous magnesium oxide given in Table 321 (II) were calculated by means of the Gordon-Barnes method, using the constants given in Table 240. Since the MgO molecule has two electron states with low excitation energies ($A^1\Pi$ and $B^1\Sigma$) Eqs, (II.131) and (II.132) were used in the calculation. The progressive components of the quantities Φ^*_T and S°_T were calculated from Eqs. (II.8) and (II.9), the components of the electron states $X^1\Sigma$, $A^1\Pi$ and $B^1\Sigma$ from the quantities M_1 and N_1, obtained from Eqs. (II.117) and (II.118), without introducing a correction for the limitedness of the number of rotational levels of these states. Table 242 gives the values of θ and x for the states $X^1\Sigma$, $A^1\Pi$ and $B^1\Sigma$ of the MgO molecule and also the coefficients of Eqs. (II.137) and (II.138) used to calculate the quantities M_1 and N_1. The values of the constants A_Φ and A_S of Eqs. (II.8) and (II.9) are also given.

TABLE 242

Values of the Constants Used to Calculate the Thermodynamic Functions of Gaseous MgO, MgH, MgF, MgCl and MgN

1 Вещество	θ	$x \cdot 10^3$	$\beta_1 \cdot 10^3$	$\beta_2 \cdot 10^4$	$\frac{\gamma_0}{T}$	$\frac{d_0 \cdot 10^4}{T}$	$\frac{f_0 \cdot 10^{10}}{T^2}$	C_Φ	C_S
	2 град				3 град$^{-1}$		град$^{-2}$ 3	4 кал/моль·град	
MgO $X^1\Sigma$	1129,4	6,5979	0,8744	0,76	1,21576	5,23	—	3,7372^a	8,7051^a
$A^1\Pi$	955,74	5,8850	0,9140	0,84	1,38122	6,48	—	—	—
$B^1\Sigma$	1185,5	5,7760	0,7759	0,60	1,19867	4,75	—	—	—
MgH	2151,6	21,060	2,9032	21,20^b	0,121221	14,0	—2,2	—0,4639	6,4916
MgF	1031,4	5,3556	0,7528	0,58	1,34203	5,65	—	5,9131	12,5686
MgCl	669,5	4,4048	—	—	—	—	—	8,3193	15,2748
MgN	1237,4	—	—	—	—	—	—	5,3064	12,2619

a) Values of A_Φ and A_S given; b) calculated from Eq. (II.58).

1) Substance; 2) degree; 3) deg^{-1}; 4) cal/mole·degree.

The main errors in calculating the values of the thermodynamic functions of magnesium oxide are connected with the accuracy of the data on the energy of the vibrational levels of the MgO molecule and the neglection of corrections for the limitedness of the number of rotational levels of energy. None the less, if the ground state of MgO is a $^1\Sigma$ state, as this was assumed in 103, the errors in the values of $\Phi^\circ_{298,15}$ and Φ°_{3000} do not exceed 0.01 and 0.05 cal/mole·degree, respectively.

The thermodynamic functions of MgO were previously calculated by Kelley [2363] (S°_T for $T \leqslant 3000°$ K), this calculation, however, was carried out in the approximation of the rigid rotator-harmonic oscillator model, with incorrect values of the constants, proposed by Mahanti

[2739]. Owing to these facts the data of [2363] differ essentially from the values given in Table 321 (II). The corresponding divergences reach 2 cal/mole·degree. The thermodynamic functions of MgO, given in the first and the present editions of this Handbook and in the article by Veyts, Gurvich and Rtishcheva [126] are identical.

MgH. The thermodynamic functions of magnesium hydride, given in Table 322 (II), were calculated from Eqs. (II.161) and (II.162). The values of $\ln \Sigma$ and $T \frac{\partial}{\partial T} \ln \Sigma$ in these equations were calculated by the Gordon-Barnes method [Eqs. (II.137) and (II.138)] with the constants given in Table 240. The calculations were carried out without corrections for the limitedness in number of the rotational energy levels. In Table 242 the values of the constants C_Φ and C_S of Eqs. (II.161) and (II.162) are given, as well as the values of θ, x and the coefficients of Eqs. (II.137) and (II.138). Since the MgH molecule has a $^2\Sigma$ -type ground state, the quantities C_Φ and C_S comprise terms of R ln 2. The components of the excited state $A^2\Pi$ of the MgH molecule were calculated from Eqs. (II.126) and (II.127), i.e., taking into account the differences in the constants of MgH in the states $X^2\Sigma$ and $A^2\Pi$, the components of the state $B^2\Sigma$ were calculated from Eqs. (II.120), (II.121), i.e., without taking this difference into account. The higher electron states with excitation energies exceeding 40,000 cm^{-1}, are not considered in the calculation as their contribution to the values of the thermodynamic functions is negligibly small with $T \leqslant 6000° K$

The main error of the calculated values of the thermodynamic functions of magnesium hydride are due to the absence of sufficiently accurate data on the vibrational energy levels of the MgH molecule,* and also to the application of an approximate method of calculation. In particular, the neglection of correction for the limitedness in number of rotational levels of MgH causes errors of 0.02 and 0.4 cal/mole·degree with the values of Φ°_{3000} and Φ°_{6000} respectively. The total errors of the values of $\Phi^{\circ}_{298.15}$, Φ°_{3000} and Φ°_{6000} of magnesium hydride amount to ±0.01 ±0.03 and ±0.5 cal/mole·degree, respectively.

The thermodynamic functions of magnesium hydride, given in the first and the present editions of the Handbook are identical with those given in the paper of Veyts, Gurvich and Rtishcheva [126]. In literature there is no information on other calculations of thermodynamic functions of this gas.

MgF and MgCl. The thermodynamic functions of magnesium monofluoride and monochloride, given in Tables 323 (II) and 326 (II) were calculated from Eqs. (II.161) and (II.162) and the molecular constants given in Table 240. The values of $\ln \Sigma$ and $T\frac{\partial}{\partial T} \ln \Sigma$ in these equations were calculated according to the Gordon-Barnes method [Eqs. (II.137) and (II.138)]. In Table 242 we find the values of the constants C_{Φ} and C_S, necessary to calculate the components of the rigid rotator and progressive motion, and also the values of θ and x and the coefficients of Eqs. (II.137) and (II.138). Since the constants of centrifugal distortion and vibration-rotation interaction in MgCl are unknown, a series of constants in Eqs. (II.137) and (II.138) has been set equal to zero in the calculation of the thermodynamic functions of this gas.

The molecules of MgF and MgCl have ground states of the type $^2\Sigma$, so that the terms of R ln 2 have been included in the quantities C_{Φ} and C_S. The components of the states $A^2\Pi$ and $B^2\Sigma$ of the MgF molecule were calculated from Eqs. (II.126) and (II.127), (taking into account that the constants of these states are different) and Eqs. (II.120) and (II.121), respectively, (without taking the difference of the constants into account). Owing to the absence of data accounting for the centrifugal distortion of MgCl and the interaction between rotation and vibration in this molecule, the components of the state $A^2\Pi$ of the MgCl molecule were calculated from Eqs. (II.120) and (II.121).

The main error in the values of the thermodynamic functions of MgF calculated in this way are due to the absence of data on the energies of high vibrational levels of this molecule and an accurate value of its dissociation energy. But thanks to the fact that the dissociation energy of MgF is high, these errors are small, being of the order of 0.02 and 0.05 cal/mole·degree for the values of $\Phi_T^{\bullet}$ at 3000 and 6000°K.

In the case of MgCl, the errors caused by the absence of experimental data on the rotational constant will also contribute to these errors (±0.05 cal/mole·degree in the values of $\Phi_T^{\bullet}$ and S_T°) and the same is true for those caused by the neglection of the centrifugal distortion and the rotation-vibration interaction in the MgCl molecule, which reach 0.07 and 0.16 cal/mole·degree with the values of $\Phi_{3000}^{\bullet}$ and $\Phi_{6000}^{\bullet}$ respectively. The errors of the values of $\Phi_{298.15}^{\bullet}$, $\Phi_{3000}^{\bullet}$ and $\Phi_{6000}^{\bullet}$ calculated amount to ±0.1, ±0.2 and ±0.3 cal/mole·degree.

The thermodynamic functions of MgF and MgCl given in the first and in the present editions of the Handbook are identical. Other calculations of the thermodynamic functions of these gases have not been published in literature.

MgN. The thermodynamic functions of magnesium nitride, given in Tables 329 (II) were calculated from Eqs. (II.161) and (II.162) in the approximation of the rigid rotator-harmonic oscillator model, based on molecular constants considered in the previous section. In table 242 we find the values of the constants C_{Φ} and C_S of Eqs. (II.161) and (II.162), and also the values of θ used to calculate the components of the harmonic oscillator. Since in §103 it has been assumed that the ground state of MgN is of the type $^2\Sigma$, terms R ln 2 are comprised in the quantities C_{Φ} and C_S. Owing to the fact that the calculation of the thermodynamic functions of MgN was carried out with the help of constants obtained from a rough estimation and in the approximation of the rigid rotator-harmonic oscillator model, the calculated values of these functions have large errors. The errors due to the estimate of the quantity r_{Mg-N} amount to about ±0.4 cal/mole·degree with the values of Φ^{*}_{T} and S°_{T}, respectively, and the errors due to the inaccurate values of the MgN vibration frequency amount to about ±0.03, ±0.35 and ±0.4 cal/mole·degree with the values of $\Phi^{*}_{298.15}$, Φ^{*}_{3000} and Φ^{*}_{6000}. The errors caused by the neglection of the anharmonicity of the vibrations, of centrifugal distortion and rotation-vibration interaction in these quantities are of the order of 0.01, 0.3 and 0.6 cal/mole·degree, respectively, while the errors caused by ignoring the necessity of limiting the number of rotational levels of MgN amount to about 0.05 and 0.5 cal/mole·degree with the values of Φ^{*}_{3000} and Φ^{*}_{6000} respectively. The total errors in the values of Φ^{*}_{T} at 298.15, 3000 and 6000°K amount to ±0.3, ±1 and ±2 cal/mole·degree.

The thermodynamic functions of MgN in the first and the present editions of the Handbook are identical. Indications as to other calculations of thermodynamic functions of these gases are lacking in literature.

$\underline{MgF_2 \text{ and } MgCl_2}$. The thermodynamic functions of magnesium fluoride and chloride, given in Tables 325 (II) and 328 (II), were calculated in the approximation of the rigid rotator-harmonic oscillator model from Eqs. (II.241) and (II.242) with the help of the constants given in Table 241. Table 243 contains the values of the constants C_{Φ} and C_S in these equations and also the values of θ_n used to calculate the components of the harmonic oscillators, calculated from the accepted molecular constants of MgF_2 and $MgCl_2$.

TABLE 243

Values of the Constants Used to Calculate the Thermodynamic Functions of Gaseous MgF_2 and $MgCl_2$

Вещество 1	θ_1	θ_2	θ_3	C_Φ	C_S
	2 град			3 кал/моль·град	
MgF_2	848,89	532,35 (2)	1237,4	6,8218	13,7773
$MgCl_2$	446,03	424,44 (2)	580,96	10,1485	17,1040

1) Substance; 2) degree; 3) cal/mole·deg.

The main errors in the calculated values of the thermodynamic functions of MgF_2 and $MgCl_2$ are caused by the inaccuracy of the values taken for the fundamental frequencies and the fact that the calculations were carried out in the approximation of the rigid rotator-harmonic oscillator model. Since in the case of MgF_2 the values of all three fundamental frequencies have been chosen by way of approximate estimations, the errors in the calculated values of $\Phi^\circ_{298,15}$, Φ°_{3000} and Φ°_{6000} amount to ±0.5, ±2.5 and ±4 cal/mole·degree. With $MgCl_2$ they amount to about ±0.3, ±2 and ±3 cal/mole·degree.

The differences in the values of the thermodynamic functions of both gases given in the first and the present editions of the Handbook are caused by the application of somewhat different values of the fundamental frequencies of their molecules and reach 0.5-1.3 cal/mole·degree with the values of Φ°_T and S°_T. Indications as to other calculations of thermodynamic functions of magnesium fluoride and chloride are not encountered in literature.

§105. THE THERMODYNAMIC PROPERTIES OF Mg, MgO, MgF_2 and $MtCl_2$ IN SOLID AND LIQUID STATES

The thermodynamic functions of Mg, MgO, MgF_2 and $MgCl_2$ in solid and liquid states (Tables 317, 320, 324 and 327 of Vol. II) were calculated from Eqs. (III.9)-(III.11), based on the values of the thermodynamic quantities given in Table 244. The errors of the calculated values of Φ°_{T} at the temperatures of 298, 1000, 1500, 2000, 3000° K, estimated on the basis of an analysis of the possible errors of the initial data, are given in Table 245.

TABLE 244

Accepted Values of the Thermodynamic Quantities of Magnesium and Its Compounds in Solid and Liquid States

1 Вещество	2 Состояние	$H^{\circ}_{298,15}-H^{\circ}_{0}$	$S^{\circ}_{298,15}$	$C^{\circ}_{p298,15}$	5 Коэффициенты в уравнении для C°_{p} [a]			6 Интервал температуры	Tm	ΔHm
		3 кал/моль	4 кал/моль·град		a	$b \cdot 10^{3}$	$c \cdot 10^{-5}$	°K	°K	кал/моль
Mg	Крист.	1190	7,78	5,95	5,33	2,45	0,103	298,15—923	923	2 140
Mg	Жидк.	—	—	—	7,9	—	—	923—2400	—	—
MgO	Крист.	1233	6,43	9,03	10,18	1,74	1,48	298,15—2100	—	—
MgO	»	—	—	—	13,37	0,205	—	2100—3075	3075	18 500
MgO	Жидк.	—	—	—	16,0	—	—	3075—4800	—	—
MgF_2	Крист.	2370	13,68	15,21	16,93	2,52	2,20	298,15—1536	1536	13 900
MgF_2	Жидк.	—	—	—	22,6	—	—	1536—5000	—	—
$MgCl_2$	Крист.	3300	21,4	17,01	18,90	1,42	2,06	298,15—987	987	10 300
$MgCl_2$	Жидк.	—	—	—	22,1	—	—	987—3700	—	—

[a] $C^{\circ}_{p}=a+bT-cT^{-2}$ (cal/mole·deg).

1) Substance; 2) state; 3) cal/mole; 4) cal/mole·degree; 5) coefficients in the equation for C°_{p}; 6) Temperature interval.

The structure of magnesium is of the type of hexagonal closest packing. Polymorphous transformations do not occur with magnesium.

Based on measurements of the specific heat of magnesium, carried out by Clusius and Vaughen [1137] (11-229°K) and Eastman and Rodebush [1442] (74-289°K), Kelley [2364] recommended a value of $S^{\circ}_{298,15}=7,77\pm0,05$ cal/g-atom·degree.

Later measurements of the specific heat of magnesium at low temperatures were made by Craig, Krier, Coffer, Bates and Wallace [1210] (12--320°K), Smith [3793] (1-20°K) and Esterman, Friedberg and Goldman [1495a] (1.8-4.2°K). A calculation with the data of these authors leads to values of $S^\circ_{298,15} = 7{,}78 \pm 0{,}03$ cal/g-atom·degree and $H^\circ_{298,15} - H^\circ_0 = 1190 \pm 5$ cal/g-atom, which are accepted in the present Handbook.*

Measurements of the specific heat and the enthalpy of magnesium in the interval of 298 to 1050°K were considered by Kelley [2363] and Kubashevskiy [2492] who recommended the following equations for the specific heat of solid magnesium:

$$C^\circ_p = 6{,}14 + 1{,}50 \cdot 10^{-3}T - 0{,}78 \cdot 10^{5}T^{-2}\ [2363], \qquad \text{(XXVI.1)}$$

$$C^\circ_p = 5{,}33 + 2{,}45 \cdot 10^{-3}T - 0{,}103 \cdot 10^{5}T^{-2}\ [2492]. \qquad \text{(XXVI.2)}$$

In the Handbook the second equation has been chosen to calculate the thermodynamic functions of magnesium since recently published measurements of the true specific heat of Mg (Saba, Sterrett, Craig, Wallace [3572] (293-548°K) coincide virtually with the curve obtained by Kubashewski [2492] and differ at room temperature by 4% from the value calculated with Kelley's equation [2363]. Stull and MacDonald [3893] measured the enthalpy of crystalline magnesium at five temperatures of from 720 to 890°K. The equation he derived for the specific heat of magnesium,

$$C^\circ_p = 4{,}463 + 3{,}697 \cdot 10^{-3}T + 0{,}33 \cdot 10^{5}T^{-2} \qquad \text{(XXVI. 3)}$$

yields near the melting point of Mg to values of the specific heat that are somewhat higher compared to other data, though the values of the enthalpy differ from the corresponding values calculated with the equation accepted in the Handbook by no more than 0.5% (at 900°K).

For the heat of melting of magnesium and its specific heat in liquid state different values are found in literature. Kelley [2363], based on data of Zalesinski and Zulinsky [4373] and Awbery and Griffiths [590] recommended a value of $\Delta H_{923} = 2{,}16 \pm 0{,}14$ kcal/g-atom and $C^\circ_p = 7{,}4 \pm \pm 0{,}7$ cal/g-atom·degree. Kubaschewski, taking into account unpublished data of Reinharts on the enthalpy of liquid magnesium, calculated the values of $\Delta H_{923} = 2{,}1 \pm 0{,}1$ kcal/g-atom [2494] and $C_p = 8{,}1 \pm 0{,}3$ cal/g-

-atom·degree [2492]. The most reliable value of the melting heat of magnesium, equal to 2.14 ± 0.05 kcal/g-atom, was obtained by Stull and MacDonald [3893] from measurements of the enthalpy of solid and liquid magnesium in the interval of 720-1055°K. The following equation has been introduced for the specific heat of liquid magnesium (Stull and MacDonald, [3893]):

$$C_p^\circ = 5{,}292 + 2{,}60 \cdot 10^{-3} T - 0{,}118 \cdot 10^5 T^{-2}. \qquad \text{(XXVI.4)}$$

According to this equation the specific heat of Mg in the interval of 923-1100°K increases almost linearly from 7.68 to 8.14 cal/g-atom·degree. Since the data on the enthalpy of liquid magnesium obtained by the authors of [3893] in a comparatively narrow temperature interval (955-1055°K) display a certain scatter (maximum deviation from mean values reaches ±7%), the authors of the Handbook consider it more justified to use these data to calculate the value of the mean specific heat, $C_p^\circ = 7{,}9 \pm 0{,}2$ kcal/g-atom·degree. This value has been accepted in the Handbook to calculate the thermodynamic functions of liquid magnesium in the interval 923-1100°K and also at temperatures higher than 1100°K.*

The values of the thermodynamic functions of magnesium in solid and liquid states, calculated for temperatures of 293.15-2400°K, are given in Table 317 (II). The values of the errors of the calculated values of Φ_T° are given in Table 245.

The differences between the values of the thermodynamic functions of magnesium, given in Table 317 (II) and those of the first edition of our Handbook, are caused by an improvement of the heat of melting of magnesium and do not exceed 0.05 and 0.15 cal/g-atom·degree with the values of Φ_T° and S_T°, respectively.

MgO. Magnesium oxide is only known in the form of a cubic modification (structural type of NaCl). Measurements of the specific heat of magnesium oxide at low temperatures were carried out by Gunther [1889]

(21-84°K), Parks and Kelley [3192] (94-291°K), Giauque and Archibald [1711] (20-301°K) and Barron, Berg and Morrison [640] (10-270°K). A calculation of the entropy of MgO at 298.15°K, according to data from [3192, 1711 and 640] yields the values $6{,}4 \pm 0{,}1$; $6{,}66 \pm 0{,}02$ and 6.43 ± 0.05 cal/mole·degree, respectively. The strong deviation of the value calculated from the data of Giauque and Archibald [1711] is explained by the fact that the authors of paper [1711] investigated an MgO preparation that had been obtained by dehydrating $Mg(OH)_2$ at 200-300°C and was, as to its state, essentially different from the other crystalline samples of MgO investigated by other authors.* Most accurate are the data of Barron, Berg and Morrison [640], according to which the values of $S^{\circ}_{298.15} = 6{,}43 \pm 0{,}05$ cal/mole·degree and $H^{\circ}_{298.15} - H^{\circ}_{0} = 1233 \pm 5$ kcal/mole were chosen for the Handbook.

The most accurate measurements of the enthalpy of MgO at high temperatures were carried out by Magnus [2732] (288-1040°K) and Wilks [4268] (303-2073°K). Based on these data, an equation, given in Table 244, was derived by Kelley [2363] for the specific heat of MgO in the interval of 298-2100°K. In the interval of from 2100°K to the melting point at $3075 \pm 30°$ K [917] the specific heat of MgO was estimated with the help of a linear equation, under the assumption that $C^{\circ}_{p_{2100}} = 13{,}80$ [2363] [2363] and $C^{\circ}_{p_{3075}} = 14{,}0$ cal/mole·degree (estimate, cf. page 258).

The heat of melting of MgO, equal to 18.5 ± 1 kcal/mole, was borrowed from Kelley [2356] who calculated this quantity from the phase diagram of a binary system containing MgO. The specific heat of liquid MgO was estimated as equal to 16 cal/mole·degree.

The values of the thermodynamic functions of magnesium oxide in solid and liquid states, calculated for temperatures of 293.15-4800°K are given in Table 320 (II). The errors of the calculated values of Φ°_{T} are given in Table 245.

The differences between thermodynamic functions of magnesium oxide, given in Table 320 (II) and those given in the first edition of the present Handbook, do not exceed 0.12 cal/mole·degree in the values of Φ_T° and S_T° and are caused by improved values of $S_{298.15}^\circ$.

MgF_2. Up to the past years there was no information as to the polymorphism of magnesium fluoride in literature. In 1961 Breusov [96a] showed that MgF_2 may exist in two different tetragonal modifications, a low-temperature α-MgF_2 and a high-temperature β-MgF_2 with melting points at 1255 and 1400°C, respectively. Besides these two modifications Breusov obtained also an unstable modification (α'-MgF_2), whose structure was not established and which, when heated up to 900°C, goes over to the high-temperature modification β-MgF_2. Experimental data on the specific heat and the enthalpy of magnesium fluoride were only obtained with α-MgF_2, the temperature and the heat of equilibrium transition of α-MgF_2 to β-MgF_2 were not determined; in the present Handbook the thermodynamic functions of crystalline MgF_2 were therefore calculated for the α-modification.

The specific heat of magnesium fluoride at temperatures of from 54 to 297°K was measured by Todd [3993] who calculated the value of $S_{298.15}^\circ = 13{,}68 \pm 0{,}07$ cal/mole·degree. Since an extrapolation of the specific heat below 51°K contributes essentially to the value of the entropy of MgF_2 ($S_{51}^\circ = 0{,}54$ cal/mole·degree), the possible error of this value at 298.15°K must be raised to ±0.1 cal/mole·degree. A calculation of $H_{298.15}^\circ - H_0^\circ$ according to Todd's data [3993] yields 2370 ± 10 cal/mole.

The most reliable determinations of the enthalpy of crystalline and liquid MgF_2 were made by Nealor [3035] (298-1760°K). Kelley [2363] estimates the accuracy of these measurements as amounting to ±0.5%. In Table 244 we find the equation for the specific heat of MgF_2 in the interval of from 298°K to the melting point at 1536°K [3508], and also the values of the melting heat of MgF_2, $\Delta H_{1536} = 13{,}9 \pm 0{,}2$ kcal/mole, and the specific heat of liquid MgF_2 $C_p^{\circ} = 22{,}6$ cal/mole·degree, obtained by Nealor [3035]. The latter value was used in the calculation of the thermodynamic functions of liquid MgF_2 at temperatures higher than 1760°K.

The values of the thermodynamic functions of magnesium fluoride in solid and liquid states, calculated for temperatures of 293.15-5000°K, are given in Table 324 (II). The magnitudes of the errors of the calculated values of Φ_T° are given in Table 245.

The tables of the thermodynamic functions of MgF_2 given in the first and the present editions of the Handbook are identical.

$MgCl_2$. Magnesium chloride is known in the form of a rhombohedral modification (laminated structure of the type of $CdCl_2$).

Kelley and Moore [2366] measured the specific heat of $MgCl_2$ in the interval of 54-295°K and calculated $S_{298.15}^{\circ} = 21{,}4 \pm 0{,}2$ cal/mole·degree. The error of this value is mainly due to a considerable contribution of the entropy at T = 54°K which was estimated by an extrapolation of the specific heat of $MgCl_2$ below 50°K ($S_{50}^{\circ} = 1.74$ cal/mole·degree). The value of the enthalpy, $H_{298.15}^{\circ} - H_0^{\circ} = 3300 \pm 20$ cal/mole, was calculated according to data of Kelley and Moore [2366].

The enthalpy of $MgCl_2$ at temperatures above 298°K was measured by a series of authors (as to references see in Kelley [2363]), the most reliable data, however, were obtained by Moore [2942] in the interval of 298-1428°K. The recommendations of the author of [2942] as to the equation for the specific heat in crystalline $MgCl_2$ (see Table 244), the value of the heat of melting of $MgCl_2$ $\Delta H_{987} = 10{,}3 \pm 0{,}3$ kcal/mole and the value of the specific heat of liquid $MgCl_2$ $C_p^{\circ} = 22{,}1$ cal/mole·degree, are accepted in the present Handbook. The latter value is used to calculate the thermodynamic functions of liquid $MgCl_2$ at temperatures higher than 1400°K.

TABLE 245

Errors (in cal/mole·degree) of the Values of Φ_T^* of Magnesium and Its Compounds in Solid and Liquid States

T, °K	298	1000	1500	2000	3000
Mg	±0,03	±0,06	±0,12	±0,3	—
MgO	±0,05	±0,15	±0,2	±0,3	±0,6
MgF_2	±0,1	±0,15	±0,2	±0,5	±1,0
$MgCl_2$	±0,2	±0,3	±0,4	±0,7	±1,2

The values of the thermodynamic functions of magnesium chloride in solid and liquid states, calculated for the temperatures of 293.15-3700°K, are given in Table 327 (II). The errors of the calculated values of Φ_T^* are given in Table 245.

The tables of the thermodynamic functions of $MgCl_2$, given in the first and the present editions of the Handbook are identical.

§106. THE THERMODYNAMIC QUANTITIES

The standard state of magnesium is Mg (cryst.).

Mg (gas). Table 246 contains the values of the heat of sublimation of magnesium, calculated with the help of the values of the thermodynamic functions of Mg accepted in the present Handbook, based on measurements of the saturated vapor pressure of magnesium, carried out by various authors. The values calculated with the help of data obtained by means of the boiling point method, the flow method and the effusion method, are in good agreement.

In the present Handbook we use a rounded mean value of the heat of sublimation of magnesium:

$$\Delta Hs_0(\text{Mg, cryst.}) = 35{,}0 \pm 0{,}2 \text{ kcal/g-atom.}$$

The highest value of the heat of sublimation, $\Delta Hs_0 = 35{,}38 \pm 0{,}05$ kcal/g-atom, was calculated from the results of a paper by Hartmann and Schneider [1967]. It must be noted that the authors of a series of Handbooks [2355, 3508, 3894] consider this paper as the most reliable.

TABLE 246

Results of Calculating the Heat of Sublimation of Magnesium

1 Авторы	2 Год	3 Метод	4 Интервал температуры °K	5 Число измерений	6 ΔHs_0, ккал/г-атом
7 Руфф, Хартманн [3554] . .	1924	Метод кипения	911—1359	11	34,65±0,1
8 Хартманн, Шнейдер [1967] .	1929	17 » »	1023—1271	13	35,38±0,05
9 Лейтгебель [2588]	1931	» »	1370	1	34,93
10 Баур, Бруннер [691] . . .	1934	» »	926—1283	8	34,96±0,4
11 Колман, Эджертон [1155] . .	1935	Эффузионный 18 метод	700—738	8	35,01±0,02
12 Шнейдер, Эш [3642] . . .	1939	Метод кипения 17	1376	1	35,06
13 Шнейдер, Штолль [3644] . .	1941	Метод протока	817—1067	3	35,02±0,12
14 Веттер, Кубашевский [4105]	1953	19 » »	973—1073	2	34,92±0,12
15 Прицелков, Цепляева, Сапожников [27а]	1957	Эффузионный 18 метод	668—782	18	34,74±0,05
16 Смит, Смит [3785]	1959	»	626—818	—	34,9

1) Authors
2) year
3) method
4) temperature interval
5) number of measurements
6) kcal/g-atom
7) Ruff, Hartmann
8) Hartmann, Schneider
9) Leitgeb
10) Baur, Brunner
11) Coleman and Egerton
12) Schneider, Esch
13) Schneider, Stoll
14) Vetter, Kubaschewski
15) Priselkov, Tseplyayeva, Sapozhnikov,
16) Smith, Smith
17) Boiling-point method
18) effusion method
19) flow method.

Mg^+ (gas). According to Moore [2941], the ionization potention of the magnesium atom is equal to 91,669.14 cm^{-1} or

$$I(\text{Mg}) = 176{,}328 \text{ kcal/g-atom.}$$

The error of this value amounts to about 1 cal/g-atom. This value is accepted in the Handbook; the following corresponds to it:

$$\Delta H^\circ f_0(\text{Mg}^+, \text{gas}) = 211{,}328 \pm 0{,}2 \text{ kcal/g-atom.}$$

MgO (cryst.). The heat of combustion was determined repeatedly. The results of many measurements, carried out until 1936, are compiled in the Handbook by Bychowsky and Rossini [813]. The most accurate measurements of the heat of combustion were made by Holley and Huber [2108] and Vorob'yev and Skuratov [129, 129b]. In these papers the values of $\Delta H^\circ f_{298{,}15}$(MgO, cryst.) equal to -143.70 ± 0.12 kcal/mole and -143.92 ± ± 0.26 kcal/mole, respectively, were obtained.

Schomate and Huffmann [3649] measured very accurately the heat of dissolution in hydrochloric acid of metallic magnesium (-111.322 ± 0.041 kcal/g-atom) and magnesium oxide (-35.799 ± 0.021 kcal/mole) and obtained $\Delta H^\circ f_{298{,}15} = -143{,}84$ ± 0.05 kcal/mole for the heat of formation of magnesium oxide. This value coincides within the limits of possible error with the results of measurements of Holley and Huber [2108] and Vorob' 'yev and Skuratov [129, 129b].

In the Handbook the following value has been accepted:

$$\Delta H^\circ f_{298{,}15}(\text{MgO, cryst.}) = -143{,}84 \pm 0{,}1 \text{ kcal/mole.}$$

MgO (gas). The vapor pressure of magnesium oxide was measured by Ruff and Schmidt [3564] by the method of boiling point determination (2723-2903°K) and Brewer and Porter [929] by the effusion method (2040--2200°K). A recalculation [296] of the results of these papers, taking into account the formation of O, O_2, Mg and MgO (ground state $^1\Sigma$) in the vapor yielded the following values of the heat of sublimation of magnesium oxide: $\Delta Hs_0 = 144$ [3564] and 129 kcal/mole [929] or $D_0(\text{MgO}) = 93$ and 108 kcal/mole, respectively. The dissociation of magnesium oxide in vapor seizes 70% according to data from [3564] and 20-70% according to data of [929] (as dependent on temperature). The results of these papers, however, cannot be viewed as reliable because of the reducing conditions in the effusion cell and errors in the temperature scale [932].

In the paper of Brewer and Porter [929] the temperature dependence of the emission intensity of the green band system of MgO was also investigated and the value of the heat of sublimation of magnesium oxide in an excited state was obtained as $\Delta Hs_0 = 185 \pm 15$ kcal/mole. To recalculate it for the ground state of MgO, the authors of [929] compared the intensities of the green and ultraviolet band systems and found $\Delta Hs_0 = 115 \pm 35$ kcal/mole. As shown in papers [3225, 122, 1670], however, the ultraviolet band system must not be attributed to the MgO spectrum (see page 1693).

Porter, Chupka and Ingrham [3305] investigated the composition of the products of evaporation of magnesium oxide by means of a mass-spectrometrical method and came to the conclusion that the main evaporation product of magnesium oxide were magnesium atoms (ratio Mg:MgO in vapors exceeds 1000) and that $\Delta Hs_0(\mathrm{MgO,\ cryst.}) > 149{,}4$ kcal/mole, while $D_0(\mathrm{MgO}) < 90$ kcal/mole (under the assumption that the ground state of the magnesium oxide molecule was of the type $^3\Sigma$). A recalculation of the data of [3305] under the assumption that the MgO ground state was a $^1\Sigma$, type state yields $D_0(\mathrm{MgO}) < 94$ kcal/mole. As shown by Medvedev [298] (see also the sections on the choice of the values of dissociation energies of CaO, SrO and BaO), however, mass-spectrometrical measurements yielded lower values of D_0(MgO) which is caused by the dissociation of MgO molecules on ionization.

Much more accurate information on the dissociation energy of MgO may be obtained by means of spectroscopic measurements of the equilibrium constants of magnesium oxide dissociation in flames. Huldt and Lagerqvist [2149] investigated the dissociation equilibrium of magnesium oxide in an acetylene-air flame and obtained $D_0(\mathrm{MgO}) = 120$ kcal/mole. In papers [917, 122] it was, however, noticed that in the paper of Huldt and Lagerqvist [2149] an error had been admitted. Veyts and Gurvich [122] determined the MgO dissociation equilibrium constants from measurements of the absolute and relative line intensities of magnesium in acetylene-air, acetylene-oxygen and hydrogen-oxygen flames whose temperature varied between 2430 and 3250°K. The value of the dissociation energy of magnesium oxide, found in this paper under the supposition that the MgO ground state is a $^1\Sigma$ -type state (see page 1693),

$$D_0(MgO) = 100 \pm 3 \text{ kcal/mole},$$

has been accepted in the Handbook. This value is in satisfactory agreement with the results of a theoretical calculation, carried out by Gaspar and Csaviszky [1656] who obtained $D_0(MgO) = 103{,}7$ kcal/mole.

The following corresponds to the value accepted:

$$\Delta Hs_0(MgO,\text{cryst.}) = 136{,}833 \pm 3 \text{ kcal/mole},$$
$$\Delta H^\circ f_0(MgO,\text{gas}) = -6{,}013 \pm 3 \text{ kcal/mole}.$$

When the calculations of the tables of thermodynamic properties of the substances considered in this chapter were finished, the paper of Bulewicz and Sugden [1012] was published in which the dissociation of magnesium oxide was investigated with the method of flame photometry, developed in Sugden's laboratory [2206, 3898, 1011, 1010]. Under the assumption that the MgO electron ground state is a triplet state of the type $^3\Sigma$, the authors of paper [1012] recommend a value of 98 ± 2 kcal/mole for $D_0(MgO)$ which is a mean of the values obtained in three different ways. A recalculation of the results of paper [1012] under the assumption that the ground state of the MgO molecule is of the type $^1\Sigma$ yields the value $D_0(MgO) = 102 \pm 2$ kcal/mole which, within the limits of error, agrees with that accepted in the Handbook. It must be noted that the authors of paper [1012] stressed particularly that the value of $D_0(MgO)$ they had found was in best agreement with the value of $D_0(MgO) = 100$ kcal/mole, obtained in paper [122] and accepted in the present Handbook.

MgH (gas). A graphic extrapolation of the vibrational energy levels of the $X^2\Sigma$ state of the MgH molecule yields a value of $D_0(\mathrm{MgH}) \sim$ $\sim$ 16 000 см^{-1}, or 46 kcal/mole. This value was used by Gaydon [1668]. Guntsch [1897], with the help of an observation of the predissociation in the $C^2\Pi$ state of this molecule and under the assumption that the $C^2\Pi$ state of the MgH molecule dissociates into the atoms $\mathrm{Mg}(^3P) + \mathrm{H}(^2S)$, obtained $D_0(\mathrm{MgH}) \leqslant 20\,000$ см^{-1}, or $\leqslant 58$ kcal/mole.

A more accurate value of the dissociation energy may, obviously, be obtained when investigating the $B^2\Sigma$ state of the MgH molecule which, thanks to the low value of ω_e, must have a potential curve with a flat minimum. Up to present days, however, in the MgH spectrum it was only transitions from this state to the lower vibrational level ($v' = 0$) that were observed. Nonetheless, even under the assumption that the level with $v' = 1$ of the $B^2\Sigma$ state did not exist, a value of 16,600 cm^{-1} or 47.5 kcal/mole was obtained for the lower limit of the dissociation energy of MgH.

An unambiguous choice among the three values considered is rendered difficult, particularly because of the unreliability of the graphic extrapolation for the $X^2\Sigma$, state in which only levels with $v \leqslant 3$ are to be observed. We therefore chose the following value for the Handbook:

$$D_0(\mathrm{MgH}) = 51 \pm 5 \text{ kcal/mole},$$

which is close to the mean value (18,000 cm^{-1}) of the above values. The following corresponds to it:

$$\Delta H^\circ f_0(\mathrm{MgH, газ}) = 35{,}632 \pm 5 \text{ kcal/mole}.$$

MgF (gas). In literature there are no experimental data on the value of the dissociation energy of the MgF molecule. An estimate of this value by means of a linear extrapolation of the vibrational levels of the $X^2\Sigma$ state of the MgF molecule, with the constants chosen above (cf. page 1698) yields a value of the order of 35,000 cm^{-1} or 95 kcal/

/mole. This value was accepted by Herzberg [2020] and in the Handbook [649]. Gaydon [1668], on the basis of the same considerations as in the case of BeF (cf. page 1676) assumed a value lower than that obtained by linear extrapolation and recommended 74 kcal/mole. In the first edition of the present Handbook it was noted that such a reduction is not justified and the value obtained in the linear extrapolation may only be viewed as a lower limit of the dissociation energy of MgF. If we assume that with halides of the elements of group II the ratio between the dissociation energy of the molecule and the value obtained by linear extrapolation of the ground state levels is virtually kept constant, analogously as in the case of compounds of the elements of group III, the dissociation energy of MgF must be close to 125 kcal/ /mole.

The correlation of the electron states of the atoms of Mg and F and the MgF molecule shows that the first three dissociation limits of this molecule correspond to the atoms $Mg(^1S)+F(^2P)$, $Mg(^3P)+F(^2P)$ and the ions $Mg^+(^2S)+F^-(^1S)$, while the second and third dissociation limits lie higher by 21,900 and 32,700 cm^{-1} than the first. The two states of MgF, $^2\Sigma$ and $^2\Pi$, correspond to the lower dissociation limit of $Mg(^1S)+F(^2P)$ states which, in zeroth approximation, must possess repulsive potential curves. If, however, we consider the perturbation of these states by the states $^2\Sigma^+$ and $^2\Pi$, correlating with the higher dissociation limits, in particular the state $^2\Sigma^+$, in correlation with the states $Mg^+(^2S)+F^-(^1S)$,* we may suggest to view them as the stable lower states of MgF.

Since the band systems $B^2\Sigma - X^2\Sigma$ and $C^2\Sigma - X^2\Sigma$ in the MgF spectrum are sufficiently intense, the upper states $^2\Sigma$ of these systems are, obviously, of the type $^2\Sigma^+$. The state $B^2\Sigma^+$ of the MgF molecule may only correlate with the dissociation limit $Mg(^3P)+F(^2P)$, while the state $C^2\Sigma$ may be linked with both this dissociation limit and a higher one, corresponding to $Mg^+(^2S) + F^-(^1S)$. The dissociation energies of MgF in the states $B^2\Sigma^+$ and $C^2\Sigma^+$, obtained by linear extrapolation with the constants accepted above, are equal to 22,500 and 36,000 cm^{-1}, respectively. The following values of the dissociation energy of MgF in the ground state correspond to them: about 38,000 and 56,000 cm^{-1} (if MgF in the $C^2\Sigma^+$ state dissociates into the ions $Mg^+(^2S)+ F^-(^1S)$) * or 45,000 cm^{-1} (if MgF in the state $C^2\Sigma$ dissociates into $Mg(^3P) + F(^2P)$).

The dissociation energy of MgF in the $A^2\Pi$, state, found by linear extrapolation, is equal to 34,5000 cm^{-1}. If MgF in the $A^2\Pi$ state is assumed to dissociate into the atoms $Mg(^1S) + F(^2P)$ and extrapolation is carried through toward this dissociation limit, the dissociation energy of MgF must be close to 62,000 cm^{-1}. Such a value of D_0(MgF) seems too high** and one may assume that, as in the case of BeF, a linear extrapolation of the vibrational levels of MgF in the $A^2\Pi$ state leads us to a dissociation limit that would correspond to an excited state of the Mg atom. The energy of dissociation of MgF, obtained as a result of an estimation by way of an extrapolation of the vibrational levels of MgF in the states $A^2\Pi$, will then be equal to $62\,000 - 21\,900 \approx 40\,000$ см$^{-1}$, which is in good agreement with the value calculated above with the help of an extrapolation of the levels of the state $B^2\Sigma$.

The latter fact obviously supports the assumption that a linear extrapolation of the lower vibrational levels of the states $A^2\Pi$ and $B^2\Sigma$ of the MgF molecule leads us to the common dissociation limit. An analogous position is also encountered in the case of CaF.

It is obvious from what has been discussed above that the values of the dissociation energies of the MgF molecule, obtained as a result of an extrapolation of the vibrational levels of four states of this molecule, must lie within the limits of 35,000 and 56,000 cm^{-1} or 95 and 160 kcal/mole. Since it is impossible at present to reasonably select one among these values, a value of

$$D_0(\mathrm{MgF}) = 120 \pm 20 \text{ kcal/mole},$$

has been accepted in the Handbook for the dissociation energy of MgF, which is close to the mean of the values mentioned above. Note that it coincides virtually with the mean value of the bond energy in the MgF molecule. The following corresponds to the value accepted:

$$\Delta H^\circ f_0\,(\mathrm{MgF, gas}) = -66{,}5 \pm 20 \text{ kcal/mole}.$$

MgF_2 (cryst.). The thermal effects of the reaction of precipitation of magnesium fluoride from magnesium chloride and magnesium sulfate solutions, measured by Petersen [3227] and Guntz [1898] are equal to -29.1 and +1.7 kcal/mole, respectively. Bichowsky and Rossini [813] used these data and obtained a value of -263.8 kcal/mole for the heat of formation of magnesium fluoride.

A recalculation of Domanges data [1361] with the help of the equation

$$\mathrm{MgF_2\,(тв.) + H_2O\,(gas) = MgO\,(тв.) + 2HF\,(gas)} \qquad \text{(XXVI.5)}$$

yields a value of $\Delta H_0 = 50{,}9$ kcal/mole for the thermal effect of this reaction; a value of $\Delta H^\circ f_{298,15} = -266{,}2$ kcal/mole of the heat of formation of magnesium fluoride corresponds to it.

Brewer [1093] estimated the entropy of MgF_2 and, with the help of data on the product of solubility and entropy of the magnesium ion [2564], he calculated the value of the heat of formation of magnesium fluoride: $\Delta H^\circ f_{298,15} = -261{,}6$ kcal/mole.

Torgeson and Sahama [4001] measured the heat of dissolution of magnesium hydroxide in hot hydrofluoric acid ($\Delta H_{73,7^\circ C} = -29{,}09 \pm 0{,}02$ kcal/mole) and the heat of transformation of magnesium oxide in hydroxide $\Delta H_{298,15} = -8{,}85 \pm 0{,}025$ kcal/mole). With the help of these values and taking the results of the papers of Petersen [3227] and Guntz [1898] into account, the authors of the Handbook [3508] calculated the value of the heat of formation of magnesium fluoride: $\Delta H^\circ f_{298,16} = -263{,}5$ kcal/mole.

In the paper of Gross, Hayman and Levi [1864] the heat of reaction of metallic aluminum and lead fluoride was measured. As a side result these authors obtained also the heat of formation of magnesium fluoride, -268 kcal/mole. The measurement of the heat of formation of MgF_2 was not the principal aim of this work and the authors of [1864] themselves assumed, for various reasons, that the value they had found might be too high.

In the present Handbook a value of

$$\Delta H^\circ f_{298,15}(MgF_2,\text{cryst.}) = -263{,}5 \pm 1 \text{ kcal/mole,}$$

has been accepted for the heat of formation of crystalline magnesium fluoride, which was calculated by the authors of the Handbook [3508], based on measurements of heats of dissolution.

MgF_2 (gas). The saturated vapor pressure of magnesium fluoride was measured Ruff and Le Boucher [3559] (1934-2129°K) by the method of boiling point determination and by Yevseyev and Pozharskaya [22] (1282-1462°K) by means of the effusion method. A calculation of the heat of sublimation of MgF_2 from these data yields the values 85.9 ± 0.4 and 86.04 ± 0.1 kcal/mole, respectively. Results of electron-diffraction studies [8] and also the good agreement of the values of the heat of sublimation, calculated from the results of vapor pressure measurements in a wide temperature interval (1300-2100°K), speak in favor of the absence of a noticeable association or dissociation of MgF_2 vapor under the experimental conditions of papers [3559, 22].

In the Handbook we accept the following value of the heat of sublimation of magnesium fluoride:

$$\Delta Hs_0(MgF_2,\text{cryst.}) = 86 \pm 2 \text{ kcal/mole,}$$

$$D_0\,(MgF_2) = 248{,}569 \pm 2{,}5 \text{ kcal/mole},$$
$$\Delta H^\circ f_0\,(MgF_2,\text{gas}) = -176{,}569 \pm 2{,}2 \text{ kcal/mole}.$$

correspond to it.

MgCl (gas). A linear extrapolation of the vibrational levels of the state $X^2\Sigma$ with constants, given in Table 240, yields the value of $D_0(MgCl) \sim 74$ kcal/mole, recommended by Herzberg [2020] and in the Handbook [649]. Gaydon [1668] uses a lower value (58 kcal/mole), obtained by a graphical extrapolation of the levels of the state $A^2\Pi$ based on the assumption that the $A^2\Pi$ state is in correlation with the states of $Mg(^3P) + Cl(^2P)$. At the same time, if one estimates the dissociation energy of MgCl on the basis of a graphical extrapolation of the values of $\Delta G_{v+1/2}$ in the state $A^2\Pi$ as a function of v or $G_0(v)$, in this case assuming that the states $X^2\Sigma$ and $A^2\Pi$ have a common dissociation limit so that the corresponding value will be equal to about 100 kcal/mole.

A well-defined choice between the values given is rendered difficult by the insufficiency of the data available for a reliable graphic extrapolation of the levels of the state $A^2\Pi$. Based on the data considered and a comparison of the dissociation energies of the molecules of BeF, MgF and BeCl with the values obtained by a linear extrapolation for the state $X^2\Sigma$, and the mean bond energies in the molecules of the type MeX_2, the following has been accepted in the Handbook:

$$D_0\,(MgCl) = 90 \pm 15 \text{ kcal/mole}.$$

Corresponds to the value accepted

$$\Delta H^\circ f_0\,(MgCl,\text{газ}) = -26{,}45 \pm 15 \text{ kcal/mole}.$$

$MgCl_2$ (cryst.). It was impossible [3720] to determine the heat of formation of magnesium chloride by the method of burning magnesium in chlorine, since magnesium does not burn well because of the high boiling point of magnesium chloride.

Sano [3579] investigated the equilibrium of

$$MgCl_2\,(\text{sol.}) + H_2O\,(\text{gas}) = MgO\,(\text{sol.}) + 2HCl\,(\text{gas}) \qquad (XXVI.6)$$

and found that the heat of this reaction was equal to $\Delta H_{298,16} = 20{,}2$ kcal/mole; a value of -150.4 kcal/mole of the heat of formation of magnesium chloride corresponds to it.

A more accurate value of the heat of formation of magnesium chloride may be obtained from data on the heats of dissolution of metallic magnesium and magnesium chloride in hydrochloric acids. Among the great number of papers devoted to this problem (for literature references see Handbooks [813, 3508]), the paper of Schomate and Huffman [3649] is the best. These authors measured very accurately the heat of dissolution of magnesium in 1 N hydrochloric acid and obtained $\Delta H_{298,16} = -111\,322 \pm 41$ cal/mole (this value was varified by measurements of Westrum and Ayring [4223]) and $\Delta H_{298,16} = -36\,566 \pm 18$ cal/mole for the heat of dissolution of magnesium chloride in hydrochloric acid. These data were used to calculate the value of the heat of formation of magnesium chloride:

$$\Delta H^{\circ}f_{298,15}\,(MgCl_2, \text{cryst.}) = -153{,}4 \pm 0{,}2 \text{ kcal/mole},$$

which has been accepted in the Handbook. In the calculation of the differential heat of dissolution of hydrogen chloride the authors of the Handbook used more accurate values [3508] which explains the difference between the value obtained and the value of -153.2 kcal/mole calculated by the authors of [3649].

$MgCl_2$ (gas). The saturated vapor pressure of magnesium chloride was measured by Maier [2744] in the temperature interval of 1056-1401°K (cf. [148], page). A calculation of the heat of sublimation of $MgCl_2$ with the help of these data yields the value of $\Delta Hs_0 = 52{,}8$ kcal//mole. A value of

$$\Delta Hs_0\,(MgCl_2, \text{cryst.}) = 52{,}8 \pm 2 \text{ kcal/mole},$$

had been accepted in the Handbook for the heat of sublimation of $MgCl_2$;

the following corresponds to it:

$$\Delta H^\circ f_0(\mathrm{MgCl_2, gas}) = -100{,}516 \pm 2\ \mathrm{kcal/mole},$$
$$D_0(\mathrm{MgCl_2}) = 192{,}616 \pm 2\ \mathrm{kcal/mole}.$$

MgN (gas). In literature there are no experimental data which could be used as a basis for calculating the dissociation energy of MgN.

Margrave and Stapitanonda [2777] proposed to use an ion model to calculate the dissociation energy of nitrides of the first three groups of the periodic system. This model was previously used to calculate the dissociation energy of oxides, hydrides and halides of metals [1344, 2443, 2770, 928]. The interatomic distances in nitrides ($r_{\mathrm{Me-N}}$) were in this case estimated with the help of the ionic radii. With the electron affinity of the nitrogen atom being assumed to amount to -26 kcal/mole [2769], the value of the ionization energy of magnesium to 61,669.14 cm^{-1} [2941] and with the two values of 1.08 and 0.7 A for the ionic radius of nitrogen, Margrave and Stapitanonda obtained values of 45 and 101 kcal/mole, respectively, for $D_0(\mathrm{MgN})$. Using a value of $r_{\mathrm{Mg-N}} = 1{,}55 \pm 0{,}08$ Å for the interatomic distance in the MgN molecule, which is accepted in the Handbook, an assuming that the electron affinity of the nitrogen atom is equal to zero (as recommended by Pritchard and Skinner [3331]) a value of $D_0(\mathrm{MgN}) = 38 \pm 11$ kcal/mole is obtained by applying the method of Margrave and Stapitanonda.

An estimation of $D_0(\mathrm{MgN})$ by way of comparing the dissociation energies of the nitrides of the elements of group two of the periodic system results in a similar value, amounting to 35 kcal/mole.

The following value is used in the further calculations in the Handbook:

$$\Delta H^\circ f_0(\mathrm{MgN, gas}) = 112{,}536 \pm 10\ \mathrm{kcal/mole}.$$
$$D_0(\mathrm{MgN}) = 35 \pm 10\ \mathrm{kcal/mole}.$$

corresponds to the value accepted.

TABLE 247

Accepted Values (in cal/mole) of the Thermodynamic Quantities of Magnesium and Its Compounds

1 Вещество	2 Состояние	D_0, I или ΔH_{s_0}	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293,15}$	$\Delta H^\circ f_{298,15}$	$H^\circ_{293,15} - H^\circ_0$	$H^\circ_{298,15} - H^\circ_0$
Mg	Крист.	35 000[а]	0	0	0	1160	1190
Mg	Газ	—	35 000	35 296	35 291	1456	1481
Mg^+	»	176 328[б]	211 328	213 080	213 100	1456	1481
MgO	Крист.	136 833[а]	—142 846	—143 838	— 143840	1188	1233
MgO	Газ	100 000	— 6 013	— 6 102	— 6 112	2091	2129
MgH	»	51 000	35 632	35 519	35 507	2039	2074
MgF	»	120 000	— 66 500	— 66 592	— 66 603	2105	2143
MgF_2	Крист.	86 000[а]	—262 569	—263 508	—263 500	2294	2370
MgF_2	Газ	248 569	—176 569	—177 217	—177 227	2585	2643
MgCl	»	90 000	— 26 450	— 26 494	— 26 503	2193	2234
$MgCl_2$	Крист.	52 800[а]	—153 316	—153 414	—153 400	3215	3300
$MgCl_2$	Газ	192 616	—100 516	—100 930	—100 934	2899	2966
MgN	»	35 000	112 536	112 434	112 423	2076	2113

a) Heat of sublimation given; b) ionization potential given.

1) Substance; 2) state; 3) or.

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[Footnotes]

1694 This assumption was verified later on in a paper of Pesic and Gaydon [3225] who investigated the spectrum of magnesium oxide and hydroxide in the range of 3600-4000 A. A comparison of the spectra excited in a hydrogen-oxygen flame with the spectrum of an arc burning in an oxygen atmosphere containing vapor of light and heavy water, and the complexity of structure of the bands observed, led the authors of paper [3225] to the conclusion that the ultraviolet bands observed previously [929, 650] attributed to the MgO molecule, are actually produced by a superposition of MgOH bands and the bands of multiatomic magnesium oxides (Mg_2O_2, Mg_2O or MgO_2).

1695 Guntsch's thesis is not available in the libraries of USSR. The results of the investigations of [1897] are given in the Handbook [649].

1698 In the book [2020] there is, obviously, a misprint: a value of $\omega_e(X^1\Sigma) = 717{,}6$ $см^{-1}$ is given.

1699 Harrington's thesis [1957] has not been published. The re-

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	sults of the investigations of [1957] are contained in the Handbook [649].
1701*	The MgF_2 frequencies were previously obtained by Stepanov [393] whose calculations yielded the following values: $\nu_1 = 540 \pm 30, \nu_2 = 320 \pm 80$ и $\nu_3 = 770 \pm 40$ см$^{-1}$. In paper [393], however, the values of the dynamic constants f_d and f_{dd} were chosen on the basis of an incorrect value of ω_e(MgF), obtained by Jenkins and Grinfeld [2233].
1701**	Cf. footnote on page 1654.
1701***	In the paper of Klemperer and Buchler [1002] the fundamental frequencies ν_2 and ν_3 were found as a result of investigating the infrared absorption spectrum of $MgCl_2$; they are in excellent agreement with the frequency values calculated in the same way as in the case on the MgF_2 frequencies. This agreement between the estimated values of the fundamental frequencies of $MgCl_2$ and those found by experiment supports the validity of the assumptions made when estimating the dynamic constants of MgF_2.
1707	It must be noted that a neglection of the constant $\omega_e y_e$ of the MgH molecule in calculations using the Gordon-Barnes method does not give rise to essential errors because of the small amount of this constant. An extrapolation of the vibrational level energies of MgH by means of equations of second and third orders yields slightly different results (cf. page 1723).
1713	Based on a private communication by Wallace (1955), Stull and Sinke [3894] recommend somewhat higher values of $S^\circ_{298.15} = 7.81$ cal/g-atom·degree and $H^\circ_{298.15} - H^\circ_0 = 1195$ cal/g-atom; in the subsequent papers of Wallace and co-workers [4134, 3572], however, it is noticed that the values of the specific heat of magnesium they had measured neat room temperatures were lower by 0.2% than those obtained previously [1210].
1714	The extrapolation of the equation of specific heat of magnesium toward the boiling point of magnesium at 1390°K ($C^\circ_p = 8.9$ cal/g-atom·degree) made by Stull and Sinke [3894] is not justified since, according to data obtained in the past years for a series of metals (cf. page 262), the specific heat of molten metals decreases slightly as the temperature increases.

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1715 The influence of the dimensions of the MgO crystals on their specific heat was also studied by Lien and Phillips [2614] who measured the specific heat of an MgO sample consisting of finest grains of dimensions of about 100 A in the interval of 1.5-4°K, and obtained values of the specific heat which were about ten times as high as the corresponding values for MgO microcrystals.

1724 According to the Wigner-Witmer rule the following correlations of electron states of atoms (and ions) with states of the MgF molecule may occur:

$$\begin{array}{ll} \mathrm{Mg}\,(^1S) + \mathrm{F}\,(^2P) & \mathrm{MgF}: {}^2\Sigma^+,\ {}^2\Pi \\ \mathrm{Mg}\,(^3P) + \mathrm{F}\,(^2P) & \mathrm{MgF}: {}^2\Sigma^+\,(2),\ {}^2\Sigma^-,\ {}^2\Pi\,(2),\ {}^2\Delta,\ {}^4\Sigma^+\,(2),\ {}^4\Sigma^-,\ {}^4\Pi\,(2),\ {}^4\Delta \\ \mathrm{Mg}^+\,(^2S) + \mathrm{F}^-\,(^1S) & \mathrm{MgF}: {}^2\Sigma^+ \end{array}$$

1725* If the $C^2\Sigma$ state correlates with Mg^+ and F^- ions, a linear extrapolation for these states must yield too low a value.

1725** With $D_0\,(\mathrm{MgF}) \sim 62\ 000\ \mathrm{cm}^{-1}$ the MgF dissociation energy in the $B^2\Sigma^+$ state must be of the order of 47,000 cm^{-1}, i.e., it must be more than twice as high as the value obtained by linear extrapolation.

Chapter 27

CALCIUM, STRONTIUM, BARIUM AND THEIR OXIDES

(Ca, Ca^+, CaO, Sr, Sr^+, SrO, Ba, Ba^+, BaO)

In the present chapter, we consider the thermodynamic properties of calcium, strontium, barium, their singly charged ions and their oxides. No compounds other than the metal and the diatomic oxide have been detected in significant quantities in the calcium-oxugen and strontium-oxygen systems [3213]. The barium-oxygen system is somewhat more complex. $(BaO)_2$, Ba_2O and Ba_2O_3 may occur in this system [2170]. The lack of data on the structure and molecular constants of these compounds is an obstacle to calculation of their thermodynamic properties.

The halogen compounds of calcium, strontium and barium and compounds of these elements with hydrogen are not considered in the Handbook. It includes the ionized gases Ca^+, Sr^+ and Ba^+, since the ionization of the corresponding atoms becomes substantial even at temperatures of 4000-6000°K.

§107. MOLECULAR CONSTANTS

Atoms and Monatomic Ions

Ca. Basically, the Ca atom has the electron configuration $1s^22s^22p^63s^23p^64s^2$, to which corresponds a single ^1S term. On excitation of one 4s-electron, the term group $\ldots 3p^64s(^2S)nl$, whose serial boundary occurs 49,304 cm^{-1} above the lowest term, makes its appearance. This group consists of singlet and triplet terms with $L = \ell$. On excitation of the second 4s-electron of the Ca atom, series groups of the type $\ldots 3s^23p^6nl(^2L)n'l'$ form. The terms of the first series of this type,

$...3s^23p^63d(^2D)nl'$ have moderate excitation energies (beginning at 35,000 cm^{-1}), and its serial boundary is approximately 63,000 cm^{-1} above the lowest ^1S state. This group consists of singlet and triplet terms with L O 2 for $\ell' = 0$, L = 1, 2, 3 for $\ell' = 1$ and L ' ℓ', $\ell' \pm 1$ and $\ell' \pm 2$ for $\ell' \geq 2$. The terms of the other series of the type $...4p(^2P)nl, ...5s(^2S)nl$ etc., have considerably higher excitation energies. The same applies for terms related to excitation of inner-shell Ca electrons with the principal quantum numbers 2 and 3.

Table 248 lists energy levels of the Ca atom that belong to groups of terms $...4s(^2S)nl$ and $...3d(^2D)nl'$ and terms with the electron configuration $...4p^2$ and $...3d^2$. The energies of these levels are takn on the basis of data recommended by Moore, [2941], and levels with closely similar excitation energies have been combined into single levels with a resultant statistical weight and the excitation energies averaged. Since Moore does not give data for all terms of the group $...3p^64s(^2S)nl$ and gives them for only a few terms of the group $...3p^63d(^2D)nl'$, the energies of all remaining terms were estimated by the technique described earlier (see page 56). Thus, the energy of terms with L = 3 and the given value of n was assigned to terms of the group $...4s(^2S)nl$ with $L > 3$ and $n \leqslant 11$ In view of the lack of data needed for more accurate estimation, terms of the group $...3d(^2D)nl'$ with $n \geqslant 5$ were assigned to the boundary of the series.

In Table 248, the terms taken as a basis for the estimates are marked with the asterisk. The maximum errors in estimating the excitation energies by the method used are incurred for the $...4s(^2S)5g\,^2G$ and $...3d(^2D)6d'\,^3P;$ states; they may be of the order of 1500 and 3500 cm^{-1}, respectively.

TABLE 248

Energy Levels of the Calcium Atom

Номер уровня A	B Состояние электронная конфигурация C	 D терм	E Статистический вес	F Энергия, $см^{-1}$
0	$...4s^2$	^1S	1	0,00
1	$...4s\ (^2S)\ 4p$	$^3P_0$	1	15157,91
2	$...4s\ (^2S)\ 4p$	$^3P_1$	3	15210,067
3	$...4s\ (^2S)\ 4p$	$^3P_2$	5	15315,948
4	$...4s\ (^2S)\ 3d$	^3D	15	20356,6
5	$...4s\ (^2S)\ 3d$	^1D	5	21849,61
6	$...4s\ (^2S)\ 4p$	^1P	3	23652,32
7	$...4s\ (^2S)\ 5s$	^3S	3	31539,51
8	$...4s\ (^2S)\ 5s$	^1S	1	33317,25
9	$...3d\ (^2D)\ 5p'$	$^3F,\ ^1D$	26	35832
[illegible]	$...4s\ (^2S)\ 5p$ $...3d\ (^2D)\ 4p'$	^3P ^1P	12	36607
11	$...4s\ (^2S)\ 4d$	$^1D,\ ^3D$	20	37640
12	$...3d\ (^2D)\ 4p'$ $...4p^2$	^3D ^3P	24	38336
13	$...3d\ (^2D)\ 4p'$	^3P	9	39338
14	$...4s\ (^2S)\ 6s$ $...3d\ (^2D)\ 4p'$ $...4p^2$	^3S ^1F $^1S,\ ^1D$	16	40592
15	$...4s\ (^2S)\ 6s$ $...4s\ (^2S)\ 5p$	^1S ^1P	4	41705
16	$...4s\ (^2S)\ 4f$ $...4s\ (^2S)\ 6p$	$^1F,\ ^3F$ ^3P	37	42290
17	$...4s\ (^2S)\ 5d$	$^3D,\ ^1D$	20	42789
18	$...4s\ (^2S)\ 6p$ $...4s\ (^2S)\ 7s$ $...3d^2$	^1P $^3S,\ ^1S$ ^3F	28	44000

Номер уровня A	B Состояние		E Статистический вес	F Энергия, см⁻¹
	электронная конфигурация C	D терм		
19	...4s (^2S) 5f, 5g ...4s (^2S) 7p ...4s (^2S) 6d	$^3F, ^1F; ^3G, ^1G$ $^3P, ^1P$ $^3D, ^1D$	96	44920
20	...4s (^2S) 6f — 6h ...4s (^2S) 7d ...4s (^2S) 8s, 8p ...4s (^2S)9s	$^1F, ^3F; ^1G^*, ^3G^*;$ $^1H^*, ^3H^*$ $^3D, ^1D$ $^3S, ^1S; ^3P^*, ^1P$ $^3S, ^1S$	148	46210
21	...4s (^2S) 7f — 7i ...4s (^2S) 9p ...4s (^2S) 8d ...4s (^2S) 10s ...3d (^2D) 5s′	$F, G^*, \ldots, I^*$ $^3P^*, ^1P$ $^3D^*, ^1D^*$ $^3S, ^1S$ $^3D, ^1D^*$	216	47070
22	...4s (^2S) 8f — 8k ...4s (^2S) 10p ...4s (^2S) 9d ...4s (^2S) 11s	$F, G^*, \ldots, K^*$ $^3P^*, ^1P$ $^3D, ^1D^*$ $^3S, ^1S$	256	47580
23	...4s (^2S) 9f — 9l ...4s (^2S) 11p ...4s (^2S) 10d	$F, G^*, \ldots, L^*$ $^3P^*, ^1P$ $^3D, ^1D^*$	320	47930
24	...4s (^2S) 10f — 10m ...4s (^2S) 11d — 11n ...3d^2	$F, G^*, \ldots, M^*$ $^3D, ^1D^*, F, G^*, \ldots, N^*$ $^1S, ^1D, ^1G, ^3P$	856	48300
25	...3d (^2D) 5p′, 6d′ ...3d (^2D) 4d′, 5d′	D, P. D, F S, P, D, F, G	280	53860
26	...3d (^2D) nl′	L^a	9480	62955

* This state has not been observed experimentally.

[a] All states with the electron configuration 3d(^{2}D)nℓ', corresponding to n ≤ 11 and not taken into account in the levels with lower excitation energies.

A) Number of level; B) state; C) electron configuration; D) term; E) statistical weight; F) energy, cm-1.

Ca$^+$. The positive calcium ion in the ground state has the electron configuration $1s^22s^22p^63s^23p^64s$, to which corresponds the single term ^{2}S. Table 249 gives the energy levels of the positive calcium ion with excitation energies under 50,000 cm^{-1}, adopted from Moore [2941].

Most of the electron levels of the Ca^+ ion have high excitation energies, and its ionization limit is situated 95,748 cm^{-1} above the ground state. Because of this, the levels with excitation energies over 50,000 cm^{-1} are not discussed in the present Handbook. Neglecting of these levels does not cause any important errors in the results of the subsequent calculations.

TABLE 249

Energy Levels of the Ca^+ Ion

A Номер уровня	B Состояние		E Статистический вес	F Энергия, $см^{-1}$
	C электронная конфигурация	D терм		
0	$...3s^2 3p^6 4s$	^2S	2	0,00
1	$...3s^2 3p^6 3d$	^2D	10	13687
2	$...3s^2 3p^6 4p$	^2P	6	25340

A) Number of level; B) state; C) electron configuration; D) term; E) statistical weight; F) energy, cm^{-1}.

Sr. The strontium atom in the ground state ^1S has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$. As with the other elements of group 2, excitation of one valency electron of Sr forms the group of terms $...4s^2 4p^6 5s(^2S)nl$, whose series edge has the energy 45,925.6 cm^{-1}. This group consists of singlet and triplet terms with $L = \ell$. The second group of terms, connected with the excitation of the second valency electron of Sr into the 4d-state, $...4s^2 4p^6 4d(^2D)nl'$, also consists of singlet and triplet terms with $L = 2$ at $l' = 0$, $L = 1, 2, 3$ at $\ell' = 1$ and $L = \ell'$, $\ell' \pm 1$ and $\ell' \pm 2$ at $l' \geqslant 2$. The first levels of this group of terms have an energy of about 33,000 cm^{-1}, and its edge is situated approximately 60,000 cm^{-1} above the ground state ^1S. The terms of the Sr atoms, connected with the transition of the second valency electron to higher states (5p, 6s, 5d, etc.), and also the terms connected with excitation of internal electrons (with $n < 5$), have high energies and are not considered in the Handbook.

TABLE 250

Energy Levels of the Strontium Atom

A Номер уровня	B Состояние		E Статистический вес	F Энергия, см⁻¹
	C электронная конфигурация	D терм		
0	$\ldots 5s^2$	^1S	1	0,00
1	$\ldots 5s\,(^2S)\,5p$	$^3P_0$	1	14317,52
2	$\ldots 5s\,(^2S)\,5p$	$^3P_1$	3	14504,35
3	$\ldots 5s\,(^2S)\,5p$	$^3P_2$	5	14898,56
4	$\ldots 5s\,(^2S)\,4d$	^3D	15	18253,7
5	$\ldots 5s\,(^2S)\,4d$	^1D	5	20149,7
6	$\ldots 5s\,(^2S)\,5p$	^1P	3	21698,5
7	$\ldots 5s\,(^2S)\,6s$	^3S	3	29038,8
8	$\ldots 5s\,(^2S)6s$	^1S	1	30591,8
9	$\ldots 4d\,(^2D)\,5p'$	$^3F_2, {}^3F_3$	12	33455,2
10	$\ldots 4d\,(^2D)\,5p'$ $\ldots 5s\,(^2S)\,6p$	$^3F_4, {}^1D$ $^3P, {}^1P$	26	33924
11	$\ldots 4d\,(^2D)\,5p'$ $\ldots 5s\,(^2S)\,5d$	$^1P^\circ$ ^1D	8	34727,5
12	$\ldots 5s\,(^2S)\,5d$ $\ldots 5p^2$	^3D ^3P	24	35217
13	$\ldots 4d\,(^2D)\,5p'$	^3D	15	36441
14	$\ldots 5p^2$ $\ldots 4d\,(^2D)\,5p'$ $\ldots 5s\,(^2S)\,7s$	$^1D, {}^1S$ ^3P ^3S	18	37229
15	$\ldots 4d\,(^2D)\,5p'$ $\ldots 5s\,(^2S)\,7s, 7p$ $\ldots 5s\,(^2S)\,4f$	^1F $^1S, {}^1P$ ^3F	32	38595
16	$\ldots 5s\,(^2S)\,7p$ $\ldots 5s\,(^2S)\,4f$ $\ldots 5s\,(^2S)\,6d$	^3P ^1F $^3D, {}^1D$	36	39607
17	$\ldots 5s\,(^2S)\,8s, 8p$ $\ldots 5s\,(^2S)\,5f, 5g$	$S; {}^1P, {}^3P^\circ$ $F; G^\circ$	80	41393

18	$...5s\,(^2S)\,7d$ $...5s\,(^2S)\,9s,\,9p$	D $S;\,^1P,\,^3P^*$	36	42131
19	$...5s\,(^2S)\,6f-6h$ $...5s\,(^2S)\,8d$	$F,\,G^*,\,H^*$ D	128	42864
20	$...5s\,(^2S)10s,10p$ $...5s\,(^2S)\,7f-7l$ $...5s\,(^2S)\,9d$	$S;\,^1P,\,^3P^*$ $F,\,G^*,\,H^*,\,I^*$ D	196	43643
21	$...5s\,(^2S)11s,11p$ $...5s\,(^2S)\,8f-8k$ $...5s\,(^2S)\,10d$	$S;\,^1P,\,^3P^*$ $F,\,G^*,\,\ldots,\,K^*$ $^3D,\,^1D^*$	256	44192
22	$...4d^2$ $...5s\,(^2S)\,9f-9l$ $...5s\,(^2S)\,11d$	$^1S^*,\,^1D^*,\,^1G^*,\,^3P,\,^3F^*$ $F,\,G^*,\,\ldots,\,L^*$ D	353	44580
23	$...5s\,(^2S)10f-10m$ $...5s\,(^2S)\,11f-11n$	$F,\,G^*,\,\ldots,M^*$ $F,\,G^*,\,\ldots,\,N^*$	812	44925
24	$...\,4d\,(^2D)\,nl'$	L^a	9440	64815

* This state has not been observed experimentally.

a) All states with the electron configuration $3d\,(^2D)nl'$, corresponding to $n \leq 11$ and not taken into account in the levels with lower excitation energies. A) Number of level; B) state; C) electron configuration; D) term; E) statistical weight; F) energy, cm^{-1}.

Table 250 gives the levels of the Sr atom, including the terms of the two groups: $...5s(^2S)nl$ and $...4d(^2D)nl'$, and also the corresponding electron configurations $...5s^2$ and $...5p^2$. The energies of the terms were taken from Moore [2941]; the terms with similar excitation energies were combined into a single level. Inasmuch as Moore [2941] presents data only for the S-, P- and D-terms of the group $...5s(^2S)nl$ and for several terms of the group $4d(^2D)nl'$, the excitation energies of the other terms were adopted on the basis of estimates. In this case the energy of the F-terms with the same values of n were ascribed to the terms of the first group with $L > 3$ and to the ^1D terms with $n > 9$ and the ^3P

terms with $n > 7$ the energy of the corresponding ^3D and ^1P terms. The energies of the unobserved terms of the second group with $n = 5$ were estimated on the basis of the excitation energies of the levels of the Sr^+ ion and the Ca atom, and the terms with $n > 5$ were ascribed to the ionization limit. The inaccuracies thus produced do not cause any great errors in the results of the subsequent calculations.

Sr^+. The strontium ion in the ground state ^2S has the electron configuration $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s$. Upon excitation of the 5s-electron the group of $\ldots(^1S)n\ell$ terms is formed whose edge is 88,964 cm^{-1} above the lower state ^2S.

TABLE 251

Energy Levels of the Sr^+ Ion

Номер уровня A	B Состояние		E Статистический вес	F Энергия, $см^{-1}$
	C электронная конфигурация	D терм		
0	$\ldots4s^24p^65s$	^2S	2	0
1	$\ldots4s^24p^64d$	^2D	10	14724,2
2	$\ldots4s^24p^65p$	^2P	6	24249,5
3	$\ldots4s^24p^66s$	^2S	2	47736,53

A) Number of level; B) state; C) electron configuration; D) term; E) statistical weight; F) energy, cm^{-1}.

Table 251 gives the three first excited terms of this group corresponding to the transition of the 5s-electron into the 4d-, 5p- and 6s-states, adopted from Moore [2941]. The higher levels of the Sr^+ ion will not be considered in the present Handbook.

Ba. The barium atom in the ground state ^1S has the electronic configuration $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^2$. Excitation of one 6s-electron gives rise to the group of terms $\ldots5s^25p^66s(^2S)nl$, whose series limit is situated 42,032.4 cm^{-1} above the ground state ^1S. This group consists of singlet and triplet terms with $L = \ell$.

In addition to the terms of this group, another two groups of terms are treated in the Handbook: $...5s^2 5p^6 5d(^2D)nl'$ and $...5s^2 5p^6 6p(^2P)nl''$ with series limits situated 47,390 and 63,420 cm^{-1}, respectively, higher than the ground state. The group $...5d(^2D)nl'$ consists of singlet and triplet terms with $L = 2$ at $l' = 0$, $L = 1, 2, 3$ at $\ell' = 1$ and $L = \ell'$, $' \pm$ ± 1; $\ell' \pm 2$ at $l' \geqslant 2$; the group $...5p(^2P)nl''$ consists of the singlet and triplet terms with $L = 1$ at $\ell'' = 0$ and $L = l''$; $l'' \pm 1$ at $l' \geqslant 1$. The other groups of terms of the barium atom are not considered in the Handbook because their levels have excitation energies over 60,000 cm^{-1}.

Table 252 gives the energy levels of the barium atom corresponding to the above-indicated groups of terms, adopted on the basis of the data recommended by Moore [2941]. The levels with closely similar excitation energies are combined into a single one with summary statistical weight and mean excitation energy. The summary [2941] presents data only for a relatively small number of terms, mainly for the S-, P-, D- and F-terms of the groups $...6s(^2S)nl$ and $...5d(^2D)nl'$; the remaining terms, including the terms of the group $...6p(^2P)nl''$, have not been observed experimentally and were estimated during the preparation of the Handbook.

Thus, the ^{1}S-, ^{1}G- and ^{3}F-terms, corresponding to the configuration $...5s^2 5p^6 5d^2$, were ascribed to the $^3P_2$ term of the same electron configuration. In the group $...6s(^2S)nl$ terms with large values of n at small ℓ are absent; these terms were ascribed to the levels of the same group in correspondence with the arrangement of the analogous terms with smaller values of n. The excitation energies of the terms with values of $L > 3$ were assumed to be equal to the excitation energies of the terms with $L = 3$ (for the same value of n). The unobserved state with the configurations $...5d(^2D)nl'$ and $...6p(^2P)nl''$ were ascribed to the corresponding ionization limits.*

TABLE 252

Energy Levels of the Barium Atom

A Номер уровня	B Состояние		E Статистический вес	F Энергия, $см^{-1}$
	C электронная конфигурация	D терм		
0	$...6s^2$	^1S	1	0,00
1	$...6s\,(^2S)\,5d$	$^3D_1$	3	9033,985
2	$...6s\,(^2S)\,5d$	$^3D_2$	5	9215,518
3	$...6s\,(^2S)\,5d$	$^3D_3$	7	9596,551
4	$...6s\,(^2S)\,5d$	^1D	5	11395,4
5	$...6s\,(^2S)\,6p$	$^3P_0$	1	12266,0
6	$...6s\,(^2S)\,6p$	$^3P_1$	3	12636,6
7	$...6s\,(^2S)\,6p$	$^3P_2$	5	13514,7
8	$...6s\,(^2S)\,6p$	^1P	3	18060,3
9	$...5d\,(^2D)\,6p'$	$^3F_2$	5	22065
10	$...5d\,(^2D)\,6p'$	$^3F_3$	7	22947
11	$...5d\,(^2D)\,6p'$	$^3F_4$	9	23757
12	$...5d^2$ $...5d\,(^2D)\,6p'$	^1D ^1D	10	23068
13	$...5d^2$	$^3P_0$	1	23209
14	$...5d^2$	$^3P_1$	3	23480
15	$...5d^2$	$^3P_2,\ ^1S^\circ,\ ^3F^\circ,\ ^1G^\circ$	36	23919
16	$...5d\,(^2D)\,6p'$	$^3D_1$	3	24192
17	$...5d\,(^2D)\,6p'$	$^3D_2$	5	24532
18	$...5d\,(^2D)\,6p'$	$^3D_3$	7	24980
19	$...5d\,(^2D)\,6p'$	$^1P_0,\ ^3P_1$	4	25688
20	$...5d\,(^2D)\,6p'$	$^3P_2$	5	25957
21	$...6s\,(^2S)\,7s$	^3S	3	26160
22	$...5d\,(^2D)\,6p'$	^1F	7	26816
23	$...6s\,(^2S)\,7s$	^1S	1	28230
24	$...5d\,(^2D)\,6p'$	^1P	3	28554
25	$...6s\,(^2S)\,6d$	^1D	5	30237
26	$...6s\,(^2S)\,6d$ $...6s\,(^2S)\,7p$	^3D ^3P	24	30822
27	$...6s\,(^2S)\,7p$	^1P	3	32547
28	$...5d\,(^2D)\,7s'$	$^3D_1,\ ^3D_2$	8	32892
29	$...5d\,(^2D)\,7s'$	$^3D_3$	7	33526
30	$...5d\,(^2D)\,7s'$ $...6s\,(^2S)\,8s$	^1D ^3S	8	33837
31	$...6p^2$ $...6s\,(^2S)\,4f$	$^1S,\ ^3P_0,\ ^3P_1$ $^3F,\ ^1F$	33	34652
32	$...6p^2$	$^3P_2,\ ^1D$	10	35481
33	$...6s\,(^2S)\,7d$ $...6s\,(^2S)\,8p$ $...5d\,(^2D)\,6d'$	^3D $^1P,\ ^3P^\circ$ $^3G_3,\ ^3D'$	37	35844

A Номер уровня	B Состояние		E Статистический вес	F Энергия, см⁻¹
	C электронная конфигурация	D терм		
34	$\ldots 5d\,(^2D)\,6d'$ $\ldots 5d\,(^2D)\,7p'$	$^3G_4$, $^3D_2$, ^1F $^3F_3$	26	36249
35	$\ldots 5d\,(^2D)\,6d'$ $\ldots 5d\,(^2D)\,7p'$	$^3D_3$, ^3S $^3F_2$, $^3D_1$	20	36540
36	$\ldots 5d\,(^2D)\,6d'$ $\ldots 5d\,(^2D)\,7p'$ $\ldots 6s\,(^2S)\,8s$ $\ldots 6s(^2S)9s$	$^3G_3$, ^1P, $^3F_3$ $^3P_{0,1}$, $^3D_2$, ^1D, $^3F_4$ ^1S ^3S	46	37010
37	$\ldots 5d\,(^2D)\,7p'$ $\ldots 5d\,(^2D)\,6d'$ $\ldots 6s\,(^2S)\,5f,\ 5g$ $\ldots 6s\,(^2S)\,7d$	$^3P_2$, $^3D_3$ $^3F_2$ $F,\ G$ ^1D	88	37470
38	$\ldots 5d\,(^2D)\,6d'$ $\ldots 5d\,(^2D)\,7p'$ $\ldots 6s(^2S)\,9p$	$^3P_0$, $^3F_4$, ^1D ^1F ^1P, $^3P^*$	34	37763
39	$\ldots 6s\,(^2S)\,8d$ $\ldots 6s\,(^2S)\,9s$ $\ldots 5d\,(^2D)\,6d'$	^3D ^1S $^3P_1$, ^1G, $^3P_2$	33	38089
40	$\ldots 5d\,(^2D)\,7p'$ $\ldots 6s\,(^2S)\,8d$ $\ldots 6s\,(^2S)\,10s$ $\ldots 6s\,(^2S)\,6f$	^1P ^1D ^3S ^3F	32	38735
41	$\ldots 6s\,(^2S)\,6f - 6h$ $\ldots 6s\,(^2S)\,9d$ $\ldots 6s\,(^2S)\,10s,\ 10p$	$^1F,\ G^*,\ H^*$ D $^1S^*$, ^1P, $^3P^*$	120	38984
42	$\ldots 6s\,(^2S)\,11s$ $\ldots 6s\,(^2S)\,7f - 7l$ $\ldots 5d\,(^2D)\,4f'$ $\ldots 6s\,(^2S)\,10d$	^3S $F,\ G^*, \ldots, I^*$ ^3F ^3D	199	39722
43	$\ldots 6s\,(^2S)\,11s,\ 11p$ $\ldots 6s\,(^2S)\,8f - 8k$ $\ldots 6s\,(^2S)\,10d$	$^1S^*$, ^1P, $^3P^*$ $F,\ G^*, \ldots, K^*$ ^1D	238	40241
44	$\ldots 6s\,(^2S)\,11d$ $\ldots 6s\,(^2S)\,9f - 9l$	^3D, $^1D^*$ $F,\ G^*, \ldots, L^*$	308	40615
45	$\ldots 6s\,(^2S)\,10f - 10m$ $\ldots 6s\,(^2S)\,11f - 11n$	$F,\ G^*, \ldots, M^*$ $F\ G,^* \ldots, N^*$	812	41009
46	$\ldots 5d\,(^2D)\,nl'$	L^a	9160	47300
47	$\ldots 6p\,(^2P)\,nl^*$	L^a	5700	63420

* This state has not been observed experimentally.

a) All states with this electronic configuration, corresponding to $n \leq 11$ and not taken into account in the preceding levels. A) Number of level; B) state; C) electron configuration; D) term; E) energy, cm^{-1}.

The terms in Table 252 for which Moore [2941] did not give any data, are marked with an asterisk.

Because the accuracy of estimation of the energies of the lower levels is the most important for the subsequent calculations, an approximate estimate of the energy of the term $\ldots 5d^2\ {}^3F$ gives the basic error in it. It should be pointed out that it is impossible to carry out a reliable estimate of the excitation energy precisely for this level and that the error in the adopted value can attain 8000-10,000 cm^{-1}. The maximum error in the estimate of the energy of the levels, formed by the non-equivalent electrons, is that made in the term $\ldots 6s({}^2S)5g\ {}^3G$ and amounts to approximately 3500 cm^{-1}.

Table 252 does not give the terms formed by the equivalent $4f^2$ electrons; it is to be expected that they are close to the first ionization limit and that the error in the subsequent calculations, due to neglecting these levels, will be very slight (see page 1755).

Ba$^+$. The positive barium ion in the ground state ${}^2S$ has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s$. Excitation of the 6s-electron forms the group of doublet terms $\ldots({}^1S)\ nl$, whose limit is situated 80,686.87 cm^{-1} above the ground state of Ba$^+$.

Table 253 gives the terms of this group with energies up to 50,000 cm^{-1} adopted from Moore [2941]. The error connected with the fact that levels with higher energy were neglected, is slight.

TABLE 253

Energy Levels of the Ba^+ Ion

A Номер уровня	B Состояние		E Статистический вес	F Энергия, $см^{-1}$
	C электронная конфигурация	D терм		
0	$...5s^2 5p^6 6s$	^2S	2	0,00
1	$...5s^2 5p^6 5d$	$^2D_{3/2}$	4	4873,850
2	$...5s^2 5p^6 5d$	$^2D_{5/2}$	6	5674,824
3	$...5s^2 5p^6 6p$	$^2P_{1/2}$	2	20261,6
4	$...5s^2 5p^6 6p$	$^2P_{3/2}$	4	21952,4
5	$...5s^2 5p^6 7s$	^2S	2	42355
6	$...5s^2 5p^6 6d$	^2D	10	46073
7	$...5s^2 5p^6 4f$	^2F	14	48387
8	$...5s^2 5p^6 7p$	^2P	6	49804

A) Number of level; B) state; C) electron configuration; D) term; E) statistical weight; F) energy, cm^{-1}.

Oxides of Calcium, Strontium and Barium

The spectra of the oxides of the alkaline earth elements have several features typical for this group of molecules. As a result of many years of research, carried out by different authors, the different band systems in the emission spectra of CaO, SrO and BaO_2, situated within a board spectral region from the far ultraviolet to the near infrared, have been fairly adequately studied to date. All the band systems observed in the spectra of the monoxides of Ca, Sr and Ba are connected with transitions between the singlet states $^1\Sigma$ and $^1\Pi$, the state $^1\Sigma$ being the lower state for all these molecules. The ease with which excitation of the spectra at relatively low temperatures and under conditions in which thermal excitation takes place can be achieved, led to the natural conclusion that the lower $^1\Sigma$ states of the corresponding transitions are the electron ground states of the molecules of the alkaline earth element molecules. This conclusion, however, is in contradiction to the Wigner-Witmer correlation rules, according to which the ground states of these oxides should be the triplet states $^3\Sigma$ or $^3\Pi$, provided that they, as is usually the case with other molecules, are connected with the ground states of the corresponding atoms. Hence many authors, in particular Gaydon [1668] and Brewer [917], assumed in their works that the ground states of CaO and SrO are triplet states, transition to which have not yet been observed in the spectra of these molecules. A final solution of the problem concerning the type of ground state is impossible without a careful study of the absorption spectra of Ca and SrO have not been studied to date, an attempt has been made in the work of Veyts and Gurvich [124] to resolve this question indirectly. As a result of an investigation of the temperature dependence of the logarithm of the equilibrium constant of the dissociation of CaO and SrO within 2300-3200°K in the work [124], the dissociation energies of these molecules have been determined. On the basis of a comparison between the values of D_0 found in this manner and the values calculated by means of the equation $D_0 = T(\Delta\Phi^* - R\ln K_p)$, the authors of the work [124] inferred that the ground state of the molecules of these two oxides should be the state $^1\Sigma$. In the work [124] it has been shown that this conclusion does not contradict the correlation rules, if the ground states of the molecules are correlated with the excited state ^3P of the metal atom, and the potential curves of the triplet states, formed from the ground states of the metal and oxygen atoms $M(^1S) + O(^3P)$ are curves of the repulsion type. In accordance with the conclusions of the work [124], it is assumed in the present Handbook that the ground states of the molecules of the alkaline earth element oxides are the states $^1\Sigma$.*

Another typical feature of the spectra of these molecules is that perturbations occur in the excited electron states. An analysis of the corresponding perturbations in the band structure, carried out by the method of Kovacs and Budo [2468] showed that in the molecules of the alkaline earth metal element oxides should exist hitherto unobserved excited electron states with energies of the order of 10,000-15,000 cm^{-1} and make it possible to estimate the values of the molecular constants of the oxides in these states.

CaO. The emission spectrum of CaO, situated in the region from 11,000 to 3000 A and appearing when different calcium compounds are introduced into a flame or arc, has been studied by many authors [2739, 967, 2835, 968, 3483, 2589, 2590, 2155, 2154, 3196, 2522, 2524].

The most detailed investigations of the CaO spectrum has been carried out by Lagerqvist and Hultin [2155, 2154, 2522, 2524]. The spectrum was excited either in a carbon arc, whose positive electrode contained $CaCl_2$ or in an arc with electrodes of pure calcium and was recorded in the first order of the grating (dispersion about 1.25 A/mm). The position of the lines was determined with an accuracy of ± 0.05 cm^{-1}. An analysis of the bands in the infrared system, connected with the transition $A^1\Sigma - X^1\Sigma$, of four bands of the blue system ($B^1\Pi - X^1\Sigma$) and six bands of the ultraviolet system, corresponding to a transition between the electronic states $C^1\Sigma$ and $X^1\Sigma$ has shown that the lower states of all these systems are identical and are $^1\Sigma$ states. This state has been taken in the present Handbook as the electron ground state of CaO.

An investigation of the band structure and also of the perturbations in the upper states of the above-enumerated systems enabled the authors of the works [2154, 2524] to recommend the values for the molecular constants of CaO in different electronic states, given in Table 254 and adopted in the present Handbook.

Herzberg [2020] recommends several different values for the molecular constants of CaO, found as a result of the investigations [967, 2835, 2589, 2590, 2401]* carried out before the appearance in print of works of Lagerqvist and Hultin [2155, 2154, 2522, 2524].

TABLE 254

Adopted Values of the Molecular Constants of CaO, SrO and BaO

Моле-кула	Состояние	T_e	ω_e	$\omega_e x_e$	B_e	$\alpha_1 \cdot 10^3$	$D_0 \cdot 10^6$	r_e
		см⁻¹						Å
CaO	$X^1\Sigma$	0	732,11	4,81	0,44447	3,35^а	0,684^б	1,822
	$A^1\Sigma^в$	11556,2	716	1,6	0,4063	1,41	0,54	1,906
	$B^1\Pi$	25991,9	574,4^г	—	0,3882	5,5	0,7	1,950
	$C^1\Sigma$	28857,7	560,9	4,0	0,3731	3,2	0,7	1,989
SrO	$X^1\Sigma$	0	653,49	3,96	0,33779	2,04^д	0,354^е	1,920
	$A^1\Sigma^ж$	10886,6	619,58	0,80^з	0,30471	1,12	0,32	2,027
	$B^1\Pi$	24702,8	519,9	3,24	0,29377	1,55	—	2,061
	$C^1\Sigma$	28632,7	480,2	2,6	0,2742	2,1	0,35	2,132
BaO	$X^1\Sigma$	0	669,81	2,054	0,31249	1,30^и	0,265	1,940
	$A^1\Sigma^к$	16812,2	499,7	1,64	0,2584	1,11	0,28	2,133

A) Molecule

B) state.

a) $\alpha_2 = 0{,}000005$ см⁻¹.

b) $\beta_1 = -0{,}003 \cdot 10^{-6}$ см⁻¹.

c) An analysis of the perturbations in the excited electron states leads to the hypothesis that there are six perturbing electron states or substates with energies of the order of 11,000-12,000 cm^{-1} and approximately equal rotational and vibrational constants $\omega_e \sim 500-600$, $B_e \sim 0{,}33-0{,}38$ см⁻¹.

d) The value $\omega_e - 2\omega_e x_e$. is given.

e) $\alpha_2 = -0{,}000006$ см⁻¹.

f) $D_v'' = [0{,}354 + 0{,}0024(v + {}^1/_2) - 0{,}002(v + {}^1/_2)^2] \cdot 10^{-6}$.

g) analysis of the perturbations observed in the bands of the infrared system has shown that there exist four closely contiguous electron states with energies of the order of 10,900--11,300 cm^{-1}, whose vibrational and rotational constants are close to ($\omega_e \sim 440-450$; $B_e \sim 0{,}242-0{,}252$ см⁻¹). The type of these states is unknown.

h) $\omega_e y_e = -0{,}054$ см⁻¹.

i) $\alpha_2 = -0{,}00002$ см⁻¹.

k) analysis of the perturbations in the vibrational levels of the state $A^1\Sigma$ has shown that there exist another four electron states, components of the states $^3\Sigma^-$ and $^3\Pi$. It was found that the excitation energies of these states are of the order of 17,00-1800 cm^{-1}, $\omega_e \sim 450$ and $B_e \sim 0{,}225$ см⁻¹.

The Handbook [649] presents the constants of CaO in the states $X^1\Sigma$ and $A^1\Pi$, recommended by Lagerqvist and Hultin [2155, 2154], the approximate values of the vibrational and rotational constants of six states with energies of the order of 11,000-12,000 cm^{-1}, found in the same works [2155, 2154] as a result of an analysis of the perturbations observed in the spectrum, and also the vibrational constants of another eight electronic states with energies over 37,000 cm^{-1}, calculated by Lejeune and Rosen [2590]. Because it is pointed out in the Handbook [649] that the assignment and analysis of the bands, carried out in the work [2590] are doubtful, the corresponding constants are not given in Table 254 of the present Handbook.

SrO. The spectrum of the strontium oxide molecule has been investigated repeatedly by different authors [2832, 2739, 2743, 520, 519, 521, 522, 2468, 2469, 1278, 2525, 2532]. Three band systems were observed in the emission spectrum: the infrared system connected with the electron transition $A^1\Sigma - X^1\Sigma$, the blue system, corresponding to the transition $B^1\Pi - X^1\Sigma$, and the system $C^1\Sigma - X^1\Sigma$, situated in the ultraviolet region of the spectrum. Analysis of the vibrational and rotational structure of the bands of the different systems shows that their lower states are identical and are the $^1\Sigma$ state which is regarded as the electron ground state of the molecule SrO in the present Handbook.

The analysis of the vibrational structure of the bands in the blue system, carried out by Mahanti [2739], the analysis of the vibrational and rotational structure of the infrared system, carried out by Almkvist and Lagerqvist [519, 521] and Lagerqvist and Selin [2532] and also the analysis of the vibrational and rotational structure of the blue system, carried out by Kovacs and Budo [2468, 2469] and Dcezsi, Koczkas and Matrai [1278] gives excellent agreement between the constants of the state $X^1\Sigma$ of the SrO molecule. The constants of SrO in the state

$X^1\Sigma$, found in the work of Lagerqvist and Selin [2532] were adopted in the Handbook. The rotational and vibrational constants of SrO in the state $X^1\Sigma$ recommended in the work [2532] were obtained on the basis of the results of the investigation of the bands 0—2, 1—3, 2—4, 3—5 of the system $A^1\Sigma - X^1\Sigma$ and the earlier analysis [521] of the bands 4—1, 3—0, 3—1, 2—0, 1—0, 0—0 and 0-1 of this same system.

The constants of the first excited state $A^1\Sigma$ of the SrO molecule, adopted in the present Handbook and presented in Table 254 were found by Almkvist and Lagerqvist [519, 521]. An analysis of seven bands with $v<4$ of the system $A^1\Sigma - X^1\Sigma$ has been carried out in these works. An analysis of the perturbations, observed in the bands of the infrared system $A^1\Sigma - X^1\Sigma$, enabled the authors of the work [521] to infer the existence of four closely spaced electronic states with energies of the order of 10,900-11,300 cm^{-1} whose vibrational and rotational constants are practically identical $(\omega_e \sim 440-450,\ B_e \sim 0{,}242-0{,}252$ см$^{-1})$. The type of these states has not been determined in the work [521].

Analysis of the bands 0—1, 0—2, 0—3, 1—1, 1—4, 1—5, 1—0, 1—6 and 2-6 of the system $B^1\Pi - X^1\Sigma$, carried out by Kovacs and Budo [2468, 2469] and Dcezsi, Koczkas and Matrai [1278] enabled the molecular constants of SrO in the state $B^1\Pi$, given in Table 254, to be found.

The same Table gives the molecular constants of SrO in the state $C^1\Sigma$ found by Lagerqvist and Almkvist as a result of an analysis of the bands with $v'<4$ and $v''<1$ of the ultraviolet system $C^1\Sigma - X^1\Sigma$.

<u>BaO</u>. The BaO bands have been observed in emission [2832, 2741, 2209, 2527, 2467, 2466], as well as absorption [3191].* The scheme of the band edges of BaO was first established by Mecke and Guillery [2832]. Later one, Mahanti [2741] showed that the bands, situated in the region between λλ 4300 and 8000 A, are connected with a transition between $^1\Sigma$ singlet states and carried out an analysis of the structure of these

bands.

Because the interatomic distance in the lower $^1\Sigma$ state found by Mahanti proved to be too low as compared with the magnitude of r_e in analogous molecules and because several inaccuracies existed in the data given by Mahanti, which had been commented on by James [2209], Lagerqvist, Lind and Barrow [2527] in 1950 again investigated the spectrum of the barium oxide molecule. An acetylene-air flame, into which $BaCl_2$ solution was introduced, was used as source for the excitation of the spectrum. The spectrum was recorded in the first order of the grating (dispersion 1.2 A/mm). The accuracy of the determination of the line positions in the spectrum was about ±0.03 cm^{-1}. Analysis of the structure of 11 bands with $v' \leqslant 5$ and $v'' \leqslant 4$ showed that they are connected with the electron transition $A^1\Sigma - X^1\Sigma$ and enabled the molecular constants of BaO in these two states to be determined. These constants were adopted in the Handbook and are given in Table 254.

Analysis of the observed bands showed that all the vibrational levels of the excited $^1\Sigma$ state with $v > 1$ are perturbed. A careful study of these perturbations [2467, 2466] enabled them to be connected with the perturbing influence of four electronic states, two of which are substantes of the $^3\Sigma$ state, and the two others, substantes of the $^2\Pi$ state. The work [2466] gives the constants of one of the perturbed states (the components of the $^3\Sigma$ state: $\nu_{00} = 17\,476{,}4\ см^{-1}$, $G_v = 450{,}4\,(v + 1/2) - 2{,}9(v + 1/2)^2$ and $B_v = 0{,}2254 - 0{,}00135\,(v + 1/2)$. The constants of the other three substates, determined with less accuracy, are similar to those given above.

§108. THERMODYNAMIC FUNCTIONS OF GASES

The thermodynamic functions of atomic and ionized calcium, strontium and barium and also their oxides in the ideal gas state were calculated within the temperature range 293.15-6000°K on the basis of the constants adopted in the preceding section. The calculations were carried out without allowing for the differences of the constants of the isotope modifications of the molecules CaO, SrO and BaO; the calculation results are given in Tables 331, **332, 334, 336, 337, 339, 341, 342, 344 II** of Vol. 2.

Ca, Sr and Ba. The thermodynamic functions of the three above-mentioned monatomic gases, given in Table 331 (II), 336 (II) and 341 (II), were calculated by means of the relations (II.22) and (II.23). Table 255 gives the values of the constants A_Φ and A_S in these equations, used in the calculations of the thermodynamic functions of Ca, Sr and Ba. The electron components in the values of the thermodynamic functions of Ca, Sr and Ba were calculated by means of Eqs. (II.20) and (II.21) by direct summation of the electron energy levels, given in Tables 248, 250 and 252. The summation was carried out on a high-speed electronic computer with limitation of the number of electron states of these atoms in accordance with the method described in §6 [see Eq. (II.18)]. To simplify the calculation, the maximum value of the principal quantum number n_{max} was taken as equal to 11 and the same for all temperatures.

TABLE 255

Values (in cal/g-atom·degree) of the Constants for the Calculation of the Thermodynamic Functions of Ca, Ca^+, Sr, Sr^+, Ba and Ba^+.

A Вещество	A_Φ	A_S
Ca, Ca^+	3,7186	8,6868
Sr, Sr^+	6,0504	11,0186
Ba, Ba^+	7,3902	12,3584

A) Substance.

The uncertainty in the thermodynamic functions of calcium and strontium at temperatures up to 4000-5000°K thus calculated is determined only by the inaccuracy of the values used for the physical constants, because at these temperatures taking into account the excess electron states with values of $n_{max}<n<11$, where n_{max} has been calculated by means of Eq. (II.18), does not introduce any errors.

These errors do not exceed ±0.005 cal/g-atom•degree in the values of Φ^*; in the case of barium, additional errors are introduced because of the absence of experimental data concerning the energy of the state $\ldots 5d^2\ {}^3F$ (up to ±0.03 cal/g-atom•degree in the of Φ^*_{3000}).

At higher temperatures the errors due to the use of an approximate method of limiting the number of electron states of the atoms and also the absence of experimental data on the excitation energies of several levels begin to exert an effect. However, the total error in the values of Φ^*_{6000} of the above-considered gases do not exceed ±0.02 cal//g-atom•degree for Ca and Sr and ±0.1 cal/g-atom•degree for Ba.

The thermodynamic functions of Ca have been calculated earlier by Overstreet [3158] (Φ^*_T for $T \leqslant 3000°$ K), for Ca and Sr by Katz and Margrave [2334] ($T \leqslant 2000°$ K), for Ca, Sr and Ba by Veyts, Gurvich and Ritishcheva [126] ($T \leqslant 3500°$ K) and Kolsky, Gilmer and Gilles [2462] ($T \leqslant 8000°$ K).

At $T < 4000°$ K the differences between the data of [2334, 126, 2462] and the values given in Tables 331, 336 and 341 of Vol. 2 do not exceed 0.003 cal/g-atom•degree and are due only to the difference between the values of the physical constants used in the calculations. At higher temperatures the data of [2462] differ considerably from those given in the present Handbook. At 6000°K these differences attain 0.037; 0.064 and 0.156 cal/g-atom•degree in the values of Φ^*_T for Ca, Sr and Ba, respectively, and are due to the fact that in the calculations of Kolsky et al. all the levels given by Moore [2941] were taken into account without limitation of the magnitude of the principal quantum number, and because the states for which experimental data are lacking, have not been taken into account.

Ca^+, Sr^+ and Ba^+. The thermodynamic functions of Ca^+, Sr^+ and Ba^+, given in Tables 332 (II), 337 (II) and 342 (II), respectively, were calculated by means of Eqs. (II.22) and (II.23). The values of the constants A_Φ and A_S in these equations, used in the calculations, are given in Table 255. The electron components were calculated by means of direct summation of the energy levels, given in Tables 249, 251 and 253. The main errors in the values of the thermodynamic functions of Ca^+, Sr^+ and Ba^+ thus calculated are determined mainly by the fact that the electron levels with excitation energies over 50,000 cm^{-1} have been neglected. Owing to the fact, however, that the ionization limits of all three ions are fairly high (approximately 90,000 cm^{-1}), the errors in the values of Φ^*_{6000} are less than the errors due to the inaccuracy of the physical constants.

The thermodynamic functions of ionized calcium, given in the first and present editions of the Handbook, agree within the limits of 0.002 cal/g-atom·degree; within the same limits the thermodynamic functions of Ca^+, Sr^+ and Ba^+ agree with the calculation results of Margrave and co-workers [1851a].

CaO, SrO and BaO. The thermodynamic functions of the oxides of calcium, strontium and barium, given, respectively, in the Tables 334 (II), 339 (II) and 344 (II), were calculated by means of Eqs. (II.161) and (II.162). The values of $\ln\Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ in these equations were calculated by the method of Gordon and Barnes [Eqs. (II.137) and (II.138)] on the basis of the molecular constants, presented in Table 254. The calculation of $\ln\Sigma$ and $T\frac{\partial}{\partial T}\ln\Sigma$ was carried out without limitation of the number of rotational energy levels and without correlation of the adopted vibrational constants of the above molecules with their dissociation energies. Table 256 gives the values of the constants C_Φ and C_S in Eqs. (II.161) and (II.162), the values of θ and x for the interpolation by means of the anharmonic oscillator Tables and also the values of the coefficients in Eqs. (II.137) and (II.138), calculated on the basis of the adopted molecular constants for CaO, SrO and BaO.

The components of the excited states of the molecules CaO, SrO and BaO given in Table 254, were calculated by means of Eqs. (II.120) and (II.121), i.e., without taking account of the difference between the vibrational and rotational constants of these molecules in their ground and excited electron states.

The errors in the calculated values of the thermodynamic functions of CaO, SrO and BaO at temperatures up to 1500-2000°K are mainly due to the inaccuracy of the values of the physical and molecular constants used in the calculations and do not exceed 0.02-0.03 cal/mole·degree in the values of Φ_T^*. At higher temperatures the errors due to the approximate manner of taking into account the excited electron states of CaO, SrO and BaO given in Table 254, the neglect of the need for limiting the number of rotational states and also the neglect of several lower electron states which have not been observed directly, but have been detected by means of the perturbations in the spectra of these molecules (see page 839), begin to take effect. These last-mentioned errors can attain 0.2-0.5 cal/mole·degree in the values of Φ_{6000}^* of these gases. The total uncertainty in the values of $\Phi_{298.15}^*$, Φ_{3000}^* and Φ_{6000}^* of the oxides of calcium, strontium and barium is of the order of ±0.01, ±0.1 and ±0.5 cal/mole·degree.

The thermodynamic functions of CaO, SrO and BaO had been calculated earlier in the work of Veyts, Gurvich and Rtishcheva [126] for $T \leqslant 3500°$ K. The results, given in this work and in Tables 334 (II), 339 (II) and 344 (II), agree within the limits of 0.005 cal/mole·degree. The existing differences are accounted for by a certain difference between the values of the physical and molecular constants which have been used. Other calculations of the thermodynamic functions of CaO, SrO and BaO are not known in the literature.

TABLE 256

Values of the Constants for the Calculation of the Thermodynamic Functions of Gaseous CaO, SrO and BaO

Вещество a	θ	$x \cdot 10^3$	$\beta_1 \cdot 10^3$	$\beta_2 \cdot 10^4$	$\frac{q_0}{T}$	$\frac{d_0}{T} \cdot 10^6$	C_Φ	C_S
	град				b град⁻¹		c кал/моль·град	
CaO	1053,4	6,5701	0,7566	0,460	1,56964	4,65	5,6157	12,5712
SrO	940,24	6,0598	0,6058	0,545	2,06381	4,35	7,9901	14,9456
BaO	963,72	3,0665	0,4169	0,815	2,22883	3,79	9,3114	16,2669

a) Substance; b) degree; c) cal/mole·degree.

§109. THERMODYNAMIC PROPERTIES OF Ca, CaO, Sr, SrO, Ba and BaO IN THE SOLID AND LIQUID STATE

The thermodynamic functions of Ca, CaO, Sr, SrO, Ba and BaO in the solid and liquid state (Tables 330, 333, 335, 338, 340 and 343 of Vol. (II) were calculated by means of Eqs. (III.9)-(III.11) on the basis of the values of the thermodynamic quantities given in Table 257. The errors in the calculated values of Φ_T^* at the temperatures 298, 1000, 1500 2000 and 3000°K were estimated on the basis of an analysis of the possible errors in the initial data, given in Table 258.

Ca. Three polymorphous modifications of Ca are known: α-Ca — the cubic, dense packed modification (structure of the Cu type), β-Ca — a modification with a complex, as yet undetermined structure and γ-Ca, which has a hexagonal close packed structure (structure of the Mg type). As the heat of transformation of α-Ca into β-Ca is unknown, only the polymorphous transformation of β-Ca into γ-Ca at 713°K has been taken into account in the calculation of the thermodynamic functions of calcium.

Kelley [2364] examined the results of several studies on the heat capacity of calcium at low temperatures and, based mainly on the data of Clusius and Vaughen [1137] (10-201°K), recommended the value $S^\circ_{298.15}$

= 9.95 ± 0.10 cal/g-atom·degree. The data of Roberts [3450] (1.5-20°K), published in 1957, gave a value of S°_{20} = 0.134 cal/g-atom·degree which is 0.02 cal/g-atom·degree greater than the corresponding value obtained on the basis of the data of the work [1137]. The Handbook adopted the values $S^\circ_{298.15}=9.97\pm0.08$ cal/g-atom·degree and $H^\circ_{298.15}-H^\circ_0=1377\pm10$ cal/ /g-atom·degree, calculated by means of the data from the works [1137, 3450].

TABLE 257

Adopted Values of the Thermodynamic Quantities of Calcium, Strontium, Barium and Their Oxides in the Solid and Liquid State

1 Вещество	2 Состояние	$H^\circ_{298,15}-H^\circ_0$	$S^\circ_{298,15}$	$C^\circ_{p\,298,15}$	5 Коэффициенты в уравнении для C°_p а			6 Интервал температуры	7 T_m или T_{tr}	7 ΔH_m или ΔH_{tr}
		3 кал/моль	4 кал/моль·град		a	$b\cdot10^3$	$c\cdot10^{-5}$	°K	°K	кал/моль 3
Ca 8	Крист.	1377	9,97	6,30	5,31	3,33	—	298,15—713	713	270
Ca	»	—	—	—	1,50	7,74	—2,5	713—1122	1122	2070
Ca	9 Жидк.	—	—	—	7,4	—	—	1122—3400	—	—
CaO	8 Крист.	1670	9,5	10,24	11,67	1,08	1,56	298,15—1800	—	—
CaO	»	—	—	—	12,83	0,41	—	1800—2860	2860	19000
CaO	9 Жидк.	—	—	—	16,00	—	—	2860—6000	—	—
Sr	Крист. 8	1550	12,7	6,50	5,71	2,66	—	298,15—862	862	200
Sr	»	—	—	—	8,0	—	—	862—1043	1043	2200
Sr	Жидк. 9	—	—	—	7,4	—	—	1043—3100	—	—
SrO	Крист 8	2040	13,0	10,64	12,34	1,12	1,806	298,15—1200	—	—
SrO	»	—	—	—	13,21	0,29	—	1200—2730	2730	16700
SrO	Жидк. 9	—	—	—	16,00	—	—	2730—6000	—	—
Ba	Крист. 8	1640	14,5	6,76	5,69	3,60	—	298,15—643	643	140
Ba	»	—	—	—	8,0	—	—	643—983	983	1830
Ba	Жидк. 9	—	—	—	7,5	—	—	983—3500	—	—
BaO	Крист 8	2380	16,8	10,82	12,74	1,04	1,984	298,15—1200	—	—
BaO	»	—	—	—	13,65	0,16	—	1200—2196	2196	13800
BaO	Жидк 9	—	—	—	16,00	—	—	2196—6000	—	—

a) $C^\circ_p = a + bT - cT^{-2}$ (cal/mole·degree).

1) Substance
2) state
3) cal/mole;
4) cal/mole·degree
5) coefficients in the equation for C°_p
6) temperature range
7) or
8) cryst.
9) liquid.

Data on the heat capacity and enthalpy of calcium at temperatures above 298°K were obtained in several investigations, but the presence of a polymorphous transformation in calcium at 713°K makes the selection of the most reliable data difficult. Kubaschewski [2492] carried out a critical analysis of the results of these works, including unpublished data by Jauch on the enthalpy of Ca within the range 298--1223°K, and recommended a linear equation for the heat capacity of calcium in the range 198-713°K, a heat of transformation $\Delta H_{713}=0{,}27\pm\pm 0{,}04$ kcal/g-atom, an equation for the heat capacity of γ-Ca (713--1122°K), the heat of melting $\Delta Hm_{1122}=2{,}07\pm0{,}08$ kcal/g-atom and a value for the heat capacity of molten calcium $C^{\circ}_{p}=7{,}4\pm0{,}2$ cal/g-atom·degree (1122-1223°K), which have been adopted in the present Handbook. The last value was also used for the calculations of the thermodynamic functions of liquid calcium at higher temperatures. The calculated values of the thermodynamic functions of calcium (Table 330 (II)) agree within ±0.03 cal/g-atom·degree with the calculation results of Stull and Sinke [3894], carried out up to 1700°K.

The values of the thermodynamic functions of calcium in the solid and liquid state, calculated for the temperatures 293.15-3400°K, are given in Table 330 (II). The magnitude of the errors in the calculated values of $\Phi^{\bullet}_{T}$ are given in Table 258.

CaO. Calcium oxide and also the oxides of the other alkaline earth elements (SrO and BaO) are known only in the form of cubic modifications (structure of the NaCl type).

The heat capacity of calcium oxide at low temperatures has been measured by Nernst and Schwers [3046] (28-90°K) and Parks and Kelley [3192] (87-293°K). Kelley [2364], based on these data, recommended $S^{\bullet}_{298.15}=9{,}5\pm0{,}2$ cal/mole·degree. The value of S_{28}, obtained by extrapolation of the heat capacity to below 28°K, is 0.04 cal/mole·degree. The

The heat capacity of strontium was measured by Roberts [3450] within the range 1.5-20°K and by Glascock [1758] at room temperatures $S^{\circ}_{298,15} = 12{,}7 \pm 0{,}3$ cal/g-atom·degree). Using these data and also the values of the heat capacity of calcium, the Handbook authors, using the method of Karapet'yants, estimated the heat capacity of strontium within the temperature range 20-298°K and found the values $(C^{\circ}_{p298} = 6{,}5 \pm 0{,}3$ cal/g-atom·degree* and $H^{\circ}_{298,15} - H^{\circ}_{0} = 1550 \pm 30$ cal/g-atom.

Data on the heat capacity and enthalpy of strontium at temperatures over 298°K are lacking. The values of the transformation temperature (862°K) and the melting temperature of strontium (1043°K) were taken from the data of Eastman et al [1440]; they are in good agreement with the values, recommended by Kubaschewski [2493]. Kubaschewski [2493] carried out an estimate of the heat of melting $\Delta H_{1043} = 2{,}2 \pm 0{,}15$ kcal/g-atom, and Stull and Sinke [3894] of the heat of transformation of strontium $\Delta H_{862} = 0{,}2$ kcal/g-atom. The estimate of the heat capacity of strontium within the range 198-862°K was carried out by means of an equation, derived on the basis of the values $C^{\circ}_{p298} = 6{,}5$ cal/g-atom·degree [1758] and $C^{\circ}_{p862} = 8{,}0$ cal/g-atom·degree (see Table 257). The heat capacity of the high-temperature modification of strontium has been estimated as being 8.0 cal/g-atom·degree, and the heat capacity of liquid strontium has been taken as 7.4 cal/g-atom·degree on the basis of the data of [3894]. The differences between the values of Φ°_{T}, given in Table 335 (II) and those calculated up to 1600°K by Stull and Sinke [3894] do not exceed 0.25 cal/g-atom·degree and are due to the more precise value of $S^{\circ}_{298.15}$ as a result of the publication of the data of Roberts [3450].

The values of the thermodynamic functions of strontium in the solid and liquid state, calculated for the temperatures 293.15-3100°K, are given in Table 335 (II). The magnitude of the error in the calculated value $H^\circ_{298.15}-H^\circ_0=1670\pm20$ cal/mole, given in Table 257, has been calculated on the basis of the data from the works [3046, 3192].

Kelley [2363] re-examined the numerous enthalpy measurements on calcium oxide at high temperatures and recommended for the heat capacity of CaO in the range 298-1800°K the equation given in Table 257. The results of the enthalpy measurements on CaO, carried out in 1951 by Lander [2554] (564-1176°K), agree with the values recommended by Kelley [2363] to within 1.0-1.3% (700-1100°K). The heat capacity of CaO in the range from 1800°K to the melting point $2860\pm25^\circ$ K [917] has been estimated by the Handbook authors by means of a linear equation, derived on the basis of the values $C^\circ_{p1800}=13{,}57$ cal/mole·degree [2364] and $C^\circ_{p2860}=14{,}00$ cal/mole·degree; the last value has been obtained in accordance with the rule, formulated in chapter 3 (see page 258). The heat of melting of calcium oxide $\Delta Hm_{2860}=19{,}0\pm3{,}0$ kcal/mole has been taken from the estimate of Kubaschewski and Evans [2494]. The heat capacity of liquid CaO has been estimated as 16.0 cal/mole·degree.

The values of the thermodynamic functions of calcium oxide in the solid and liquid state, calculated for the temperatures 293.15-6000°K, are given in Table 333 (II). The magnitude of the error in the calculated values of Φ°_T is given in Table 258.

Sr. Strontium has three polymorphous modifications, a cubic face-centered (α-Sr, structure of the Cu type), a hexagonal dense packed (β-Sr, structure of the Mg type) and a cubic body-centered (γ-Sr, structure of the Na type). The temperatures of the equilibrium transformations of strontium are 608 and 862°K. In view of the absence of experimental data on the heat capacity and enthalpy of strontium at temperatures above 298°K, only the polymorphous transformation at 862°K whose heat has been estimated by Stull and Sinke [3894] was taken into account in the calculation of the thermodynamic functions of strontium.

values of Φ^{*}_{T} is given in Table 258.

SrO. Anderson [550] measured the heat capacity of strontium oxide within the range 58-298°K and calculated the value $S^{\circ}_{298,15}=13,0\pm0,2$ cal/mole·degree. Extrapolation of the heat capacity to below 56.2°K gives the value $S_{56,2}=1,17$ cal/mole·degree. The value $H^{\circ}_{298,15}-H^{\circ}_{0}$ calculated on the basis of Anderson's data [550] is 2040 ± 20 cal/mole. The enthalpy of SrO within the range 406-1266°K was studied by Lander [2554]. The equation recommended by him for the heat capacity of SrO (see Table 257) is used up to 1200°K. The heat capacity of strontium oxide within the range from 1200°K to the melting point 2730±20° K [917] has been estimated by means of a linear equation, derived on the basis of the values $C^{\circ}_{p1200}=13,56$ cal/mole·degree [2554] and $C^{\circ}_{p2730}=14,0$ cal/mole·degree. The heat of melting of strontium oxide, according to an estimate by Kubaschewski and Evans [2494] is 16.7 ± 2.0 kcal/mole. The heat capacity of liquid SrO has been taken as 16.0 cal/mole·degree.

The values of the thermodynamic functions of strontium oxide in the solid and liquid state, calculated for the temperatures 293.15-6000°K, are given in Table 338 (II). The magnitude of the errors in the calculated values of Φ^{*}_{T} is given in Table 258.

Ba. Barium is known in the form of the cubic body-centered modification (α-Ba, structure type of Na) is stable up to 643°K and the high-temperature modification β-Ba, whose structure has not yet been determined.

The existing literature data on the heat capacity of barium apply to the lowest temperatures (Roberts [3450], 1.5-20°K) and to room temperature (Mendeleyev, see [2819], $C^{\circ}_{p}=6,87$ cal/g-atom·degree, 273-373°K). Calculation of the heat capacity of barium within the range of 20-298°K by the method of Karapet'yants, using the above data and the values of the heat capacity of potassium, gives the values $S^{\circ}_{298.15}$ =

= 14.5 ± 0.5 cal/g-atom·degree and $H^\circ_{298.15}-H^\circ_0=1640\pm50$ cal/g-atom.* Measurements of the enthalpy of the high-temperature modification of barium and of liquid barium have been carried out in the unpublished work of Jauch (see [2492, 2493], 723-1123°K). On the basis of these data, Kubaschewski [2493] recommended for the heat of transformation of barium the value $\Delta H_{643}=0,14\pm0,08$ kcal/g-atom and for the heat of melting of barium, $-\Delta H_{983}=1,83\pm0,07$ kcal/g-atom. The values of the heat capacity of the β-modification of barium obtained by Kubaschewski [2492] on the basis of the data of Jauch ($C^\circ_p=-1,36+19,2\cdot10^{-3}\,T$, 673—983° K) and of liquid barium ($C^\circ_p=11,5\pm0,3$ cal/g-atom·degree) are improbably high. Hence values were adopted in the Handbook, as in the summary of Stull and Sinke [3894] for the heat capacity of barium, which had been obtained by means of an approximate estimate, namely: a linear equation for the heat capacity of α-Ba (298—643° K) (see Table 257), the value $C^\circ_p=8,0$ cal/g-atom·degree (643-983°K) for β-Ba and the value $C^\circ_p=7,5$ cal/g-atom·degree for liquid barium.

The values of the thermodynamic functions of barium in the solid and liquid state, calculated for the temperatures 293.15-3500°K, are given in Table 340 (II). The magnitude of the errors in the calculated values of Φ^*_T is indicated in Table 258.

The differences between the values of the thermodynamic functions of solid and liquid barium, given in Table 340 (II) and those calculated up to 1900°K by Stull and Sinke [3894] attain approximately 1 cal/g-atom·degree and are due to the considerable improvement of the value $S^\circ_{298.15}$ as a result of the work of Roberts [3450].

BaO. The heat capacity of barium oxide within the range 56-299°K has been measured by Anderson [550] who recommended the value $S^\circ_{298.15}=16,8\pm0,3$ cal/mole·degree. The value $S^\circ_{56.2}$, obtained by extrapolation of the heat capacity below 56.2°K, is 2.56 cal/mole·degree. The value

$H^\circ_{298.15} - H^\circ_0 = 2380 \pm 30$ cal/mole has been calculated on the basis of the data of Anderson [550]. Lander [2554] (391-1299°K) studied the enthalpy of two samples of barium oxide, one of which contained 27% SrO, and the other had been obtained by thermal decomposition of BaO_2 containing an impurity of 1% SiO_2. On the basis of the data thus obtained, Lander [2554] recommended for the specific heat of pure BaO an equation which is used in the Handbook within the range 298-1200°K (see Table 257). For the heat capacity of barium oxide in the range from 1200°K to the melting point 2196 ± 10°K [917], a linear equation has been established on the basis of the values $C^\circ_{p1200} = 13.84$ cal/mole·degree [2554] and $C_{p2196} = 14.0$ cal/mole·degree. The heat of melting of BaO, adopted on the basis of the estimate made by Kubaschewski and Evans [2494], is 13.8 ± 2.0 kcal/mole. The heat capacity of liquid barium oxide has been estimated as 16.0 cal/mole·degree.

TABLE 258

Uncertainties (in cal/mole·degree) in the Values of Φ^*_T for Calcium, Strontium, Barium and Their Oxides in the Solid and Liquid State

T°, K	298	1000	1500	2000	3000
Ca	±0,08	±0,15	±0,2	±0,3	±0,6
CaO	±0,2	±0,25	±0,3	±0,4	±0,8
Sr	±0,3	±0,8	±1,2	±1,5	±2,0
SrO	±0,2	±0,3	±0,4	±0,5	±1,0
Ba	±0,5	±1,0	±1,4	±1,7	±2,2
BaO	±0,3	±0,4	±0,5	±0,7	±1,3

The values of the thermodynamic functions of barium oxide in the solid and liquid state, calculated for the temperatures 293.15-6000°K, are given in Table 343 (II). The magnitude of the possible error in the calculated values of Φ^*_T is indicated in Table 258.

§110. THERMOCHEMICAL QUANTITIES

The standard state of calcium is Ca (cryst.).

Ca. (gas). Table 259 gives a summary of the literature data on the pressure of saturated calcium vapor and also the heats of sublimation of calcium calculated by the Handbook authors on the basis of these data.

The results of the measurements, carried out by Pilling [3248] by the method of evaporation from a surface are insufficiently reliable owing to the inaccuracy of the measurement method used by him and the contamination of the sample (97.2% Ca, 1.6% Mg and 1.2% $CaCl_2$). The data of Ruff and Hartmann [3554] obtained by the spring balance method (variant of the method of boiling point determination) are erroneous (for criticism of Ruff's method of determination of the saturation vapor pressure of metals see the review by Eucken [1496]). The vapor pressures of calcium, measured by Rudberg [3547] by the effusion method, are almost 10 times lower than the data of other authors which can be accounted for by the imperfection of the apparatus and method used for the temperature measurement in this work.

The most reliable measurements of the vapor pressure of calcium were carried out by Priselkov and Nesmeyanov [337], Douglas [1384] and Tomlin [3999] by means of different variants of the effusion method. The results of these measurements are in good agreement and give the value ΔHs_0(Ca, cryst.) = 42.1 kcal/g-atom. The measurement results of Hartmann and Schneider [1967] obtained by the method of boiling point determination also agree with these data. The curve of the vapor pressure over solid calcium, presented in the recently published work by Smith and Smith [3785] is too steep and results in a heat of sublimation $\Delta Hs_0=42.9$ kcal/g-atom, which is greater than the values obtained on the basis of the data of other investigators.

TABLE 259

Results of the Calculation of the Heat of Sublimation of Calcium

A Авторы	B Год	C Метод	Интервал температуры, °K D	Число измерений E	ΔHs_0, ккал/г-атом F
a Пиллинг [3248]	1921	i испарения с поверхности	776–973	6	41,8
b Руфф, Хартманн [3554]	1924	k кипения	1233—1380	7	40,9 ±1,8
c Хартманн, Шнейдер [1967] . .	1929	»	1254—1546	11	41,97±0,25
d Рудберг [3547]	1934	l Кнудсена	774—897	8	45,97±0,16
e Приселков, Несмеянов [337] .	1954	»	748—943	11	42,05±0,15
f Дуглас [1384]	1954	»	807—918	13	42,17±0,22
g Томлин [3999]	1954	»	801—877	6	42,08±0,13
h Смит, Смит [3785]	1959	»	730—965	—	42,9

A) Authors
B) year
C) method
D) temperature range, °K
E) number of measurements
F) ΔH_{S_0}, kcal/g-atom.

a) Pilling [3248]
b) Ruff, Hartmann [3554]
c) Hartmann, Schneider [1967]
d) Rudberg
e) Priselkov, Nesmeyanov [337]
f) Douglas [1384]
g) Tomlin [3999]
h) Smith, Smith [3785]
i) evaporation from a surface
k) boiling
l) Knudsen.

The Handbook adopted the value

$$\Delta Hs_0\,(\mathrm{Ca, cryst.}) = \Delta H^\circ f_0\,(\mathrm{Ca, gas}) = 42{,}1 \pm 0{,}2 \text{ kcal/g-atom},$$

which is the mean of the values calculated by means of the data of Priselkov and An. Nesmeyanov [337], Douglas [1384] and Tomlin [3999]. This value practically coincides with the value recommended by Stull and Sinke [3894].

<u>Ca^+ (gas)</u>. The value of the ionization energy of the calcium atom adopted in the Handbook, 49,304.8 cm^{-1} or

$$I\,(\mathrm{Ca}) = 140{,}975 \text{ kcal/g-atom},$$

has been taken from the work of Moore [2941]. The error in this value does not exceed 1 cal/g-atom. To the adopted value corresponds

$$\Delta H^\circ f_0\,(\mathrm{Ca^+, газ}) = 183{,}075 \pm 0{,}2 \text{ kcal/g-atom}.$$

CaO (cryst.). Bichowsky and Rossini [813] have reviewed critically the numerous literature data on the heats of dissolution of calcium oxide and metallic calcium in hydrochloric acid. Based on these data, they calculated the heat of formation of calcium oxide $\Delta H^\circ f_{291} = -151{,}7$ kcal/mole. Later on Rossini et al [3508] reduced this value to standard temperature and, taking into account several recent works, recommended the value $\Delta H^\circ f_{298.15} = -151{,}9$ kcal/mole.

Siemonsen [3720] measured the heat of combustion of metallic calcium in chlorine and found $\Delta H_{293} = -187{,}8$ kcal/mole (the scatter of the individual measurements exceeded 2 kcal/mole). On the basis of this value and also several thermal effects of other reactions [3508] it is possible to establish a cycle which does not contain the heat of dissolution of calcium in hydrochloric acid. The heat of formation of CaO calculated in this way is $\Delta H^\circ f_{298.15} = -149{,}7$ kcal/mole.

Attempts to obtain a fairly accurate value for the heat of formation of calcium oxide by the method of combustion of metallic calcium in oxygen remained without success for a long time [3013, 1901]. In 1956 Huber and Holley [2141] carried out a new determination of the heat of combustion of calcium in oxygen. A carefully analyzed sample of calcium with high purity (99.37% Ca, main impurities 0.07% CaO and 0.52 % CaH_2). It was found by a special analysis that formation of CaO_2 did not take place.

The heat of formation of calcium oxide,

$$\Delta H^\circ f_{298.15}(\mathrm{CaO, cryst.}) = -151{,}79 \pm 0{,}21 \text{ kcal/mole},$$

found in the work of Huber and Holley [2141] has been adopted in the Handbook.

The value obtained from the thermochemical cycle which includes the heat of solution of calcium in water, is very close to the adopted value. The agreement with the value, calculated on the basis of the heat of formation of calcium chloride, is less good which is a consequence of the relatively low accuracy of the heat of formation of $CaCl_2$ used in the calculation.

The heat of dissociation of calcium carbonate which can be calculated on the basis of the numerous studies of this reaction, gives only the difference between the heats of formation of calcium oxide and calcium carbonate. Because both these values are calculated from thermochemical cycles which include the heat of solution of calcium in hydrochloric acid (the least accurate member of the cycle), this calculation cannot give an independent value for the heat of formation of calcium oxide.

CaO (gas). The vapor pressure of calcium oxide has been measured by Ruff and Schmidt [3564] and Claassen and Veenemans [1116]. The results obtained by Ruff and Schmidt are erroneous, mainly because of the reduction of the calcium oxide by the graphite (or carbide) walls of the crucible. Claassen and Veenemans measured the rate of evaporation of calcium oxide and other alkaline earth metal oxides from platinum foil, coated with a layer of calcium oxide with a thickness of 100-200 microns. It was assumed that the temperature of the platinum was the same as that of the calcium oxide coating. However, Blevett, Liebhafsky and Hennelly [842] showed that owing to the difference in the emission coefficients of platinum and the alkaline earth metal oxides and also because of the low thermal conductivity of these oxides this assumption may result in considerable errors in the measured temperatures. The results of the seven tests (1617-1728°K) carried out by Claassen and Veenemans [1116] can be represented by the equation

$$\lg p(\text{atm}) = -\frac{27\,400}{T} + 7{,}25^{1}.$$

The composition of the products from the evaporation of calcium oxide are given further on. The partial pressures of Ca, O_2 and O, formed as a result of the dissociation of the calcium oxide in the condensed state, were calculated on the basis of the thermodynamic properties of these substances as adopted in the Handbook. It was assumed that $V_{Ca} = V_O + 2V_{O_2}$, where V is the evaporation rate. The partial pressure of CaO, the total vapor pressure over the calcium oxide Σp (in atm) and the proportion of Ca in the vapor, calculated by means of the data of Claassen and Veenemans [116] are given below:

T, °K	p_{Ca}	p_{O_2}	p_O	p_{CaO}	Σp	$\frac{p_{Ca}}{p_{Ca}+p_{CaO}}$, %
1600	$7{,}76 \cdot 10^{-11}$	$7{,}26 \cdot 10^{-12}$	$3{,}88 \cdot 10^{-11}$	$4{,}11 \cdot 10^{-11}$	$1{,}648 \cdot 10^{-10}$	65,4
1750	$2{,}27 \cdot 10^{-9}$	$2{,}30 \cdot 10^{-10}$	$1{,}11 \cdot 10^{-9}$	$1{,}21 \cdot 10^{-9}$	$4{,}82 \cdot 10^{-9}$	65,2

It might be of interest to mention that the proportion of calcium in the vapor is practically independent of the temperature. The increase in temperature, which promotes the dissociation, is compensated in this case by the increase in pressure, which has the opposite effect.

Calculation of the heat of sublimation of calcium oxide on the basis of the data obtained by Claassen and Veenemans [1116], allowance being made for the formation of atomic calcium in the vapor (the method of calculation is described in the work [296]) led to the value $\Delta Hs_0 = 140$ kcal/mole.* The uncertainty in this value, estimated on the basis of the scatter of individual experimental points, is ±4 kcal/mole. To this value of the heat of sublimation corresponds a dissociation energy $D_0(CaO) = 112 \pm 4$ kcal/mole.

Drummond and Barrow [1409], using the data of Claassen and Veenemans [1116], calculated the heat of sublimation of calcium oxide as 137.5 kcal]mole. The difference between this value and those found in the present Handbook, is explained by the fact that the authors of the work [1409] did not allow for the dissociation of the calcium oxide and that they used a wrong equation, representing the experimental data for their calculation [1116] and obviously taken from the work of Kelley [2355] (see footnote, page 1768).

Pelchowitch [3213], using a mass spectrometer, investigated the composition of the products of the evaporation of calcium oxide from heated platinum foil. The main evaporation product under these conditions at 1550-1800°K proved to be atomic calcium. The dependence of the current of CaO^+ ions on temperature found by Pelchowitch corresponds to the heat of sublimation of calcium oxide $\Delta Hs_0=174$ kcal/mole, or $\Delta Hs_{1713}=169$ kcal/mole, which sharply contradicts the value calculated above on the basis of the data of Claassen and Veenemans [1116]. It may be assumed, as in the case of SrO, that calculation of the heat of sublimation of calcium oxide on the basis of the results of measurements of the intensity of the CaO^+ ion current leads to incorrect results. In fact, it was found in the work [3213] during an investigation of the evaporation of barium oxide, that a considerable proportion of the barium oxide (40-50%) dissociates during ionization under the influence of the electron beam. As the molecule CaO is much less stable than BaO, it may be expected that the dissociation of CaO as a result of the ionizing effect of the electron gun will be even more considerable and thus, the ion current CaO^+ measured by Pelchowitch [3213] cannot serve directly as a measure of the CaO concentration in the vapor. In these cases it is necessary for the transition from the ion current to the partial pressures to allow for the degree of dissociation during the ionization, which cannot be done at the present time. It should be pointed out that Pelchowitch himself [3213] did not calculate the heat of sublimation of calcium oxide on the basis of the data obtained by him, and that he reported in this work only the angle of slope of the curve which expresses the logarithm of the CaO^+ ion current as a function of temperature.

The numerical value of the dissociation energy of calcium oxide can also be calculated on the basis of a study of the dissociation equilibrium of this molecule in flames.* Huldt and Lagerqvist [2148, 2149] investigated the dissociation equilibrium of calcium oxide in acetylene-air flames (2240-2430°K) and found $D_0(CaO)=120$ kcal/mole. However, later on the same authors [2150] corrected this value and recommended 112.7 kcal/mole.** In the works of Veyts and Gurvich [122, 125, 121], the dissociation equilibrium of calcium oxide was studied in carbon monoxide-oxygen, acetylene-air, acetylene-oxygen and hydrogen-oxygen flames over a temperature range of 2370 to 3210°K. One of the sources of error in the values of the dissociation energy of CaO, determined by the method of studying the equilibrium in flames, is the indeterminacy of the probability of the electronic transition connected with the Ca line (4227 A), which also accounts for the differences between the dissociation energies of calcium oxide of 115 [125] and 117.0 kcal/mole [121], recommended on the basis of the same experimental data. At the present time, however, the probability of this transition has been determined very accurately [327]. Recalculation of the data, obtained in the last work of Huldt and Lagerqvist [2150] and in the works of Veyts and Gurvich [125, 121] with allowance being made for the transition probability found in the work [327] leads to values of $D_0(CaO)$ of 113.2 and 114.9 ± 4 kcal/mole, respectively. The value obtained on the basis of the data, given in the works [122, 125, 121] is the more reliable because in these works the investigations were carried out in several types of flames over a wider range of temperatures and, besides the partial pressure of the atomic calcium had been measured by two independent methods.

The agreement between the dissociation energies obtained on the basis of measurements of the vapor pressure of calcium oxide and studies of the dissociation of calcium oxide in flames, may be considered to be completely satisfactory. Because the results of the vapor pressure measurements on calcium oxide, carried out by Claassen and Veenemans [1116] exhibit a large scatter and their accuracy is reduced in consequence of the marked dissociation of the calcium oxide in the vapor, the value $D_0(CaO)$ obtained in the investigations of the flame equilibria, is more reliable. The dissociation energy of calcium oxide, obtained by Veyts and Gurvich [125, 121] has been adopted in the Handbook

$$D_0(CaO) = 115 \pm 4 \text{ kcal/mole},$$

To this value corresponds

$$\Delta H^\circ f_0(CaO, \text{gas}) = -13{,}913 \pm 4{,}0 \text{ kcal/mole},$$
$$\Delta Hs_0(CaO, \text{cryst.}) = 137{,}133 \pm 4{,}0 \text{ kcal/mole}.$$

The standard state of strontium is Sr (cryst.).

Sr. (gas). The pressure of saturated strontium vapor has been investigated by the method of boiling point determination by Ruff and Hartmann [3554] (1217-1411°K) and Hartmann and Schneider [1967] (1199--1379°K) and by the effusion method by Priselkov and Nesmeyanov [337] 673-873°K). The calculations of the heat of sublimation of strontium on the basis of these data gives values of 38.0 ± 2, 39.46 ± 0.05 and 38.6 ± 0.3 kcal/g-atom, respectively. The data of Ruff and Hartmann [3554], as in the case of calcium (see page 1765), are erroneous and were not used for this reason. The causes of the considerable differences between the data of Hartmann and Schneider [1967] and Priselkov and Nesmeyanov [337] are not clear. The better correspondence between the heats of sublimation of strontium at 0°K, calculated by means of the second and third laws of thermodynamics from the data of Hartmann and Schneider, makes it possible to regard them as slightly more reliable. The value

$$\Delta Hs_0(\mathrm{Sr, cryst.}) = \Delta H^\circ f_0(\mathrm{Sr, gas}) = 39{,}2 \pm 0{,}8 \text{ kcal/g-atom}$$

which has been adopted in the Handbook, is the weighted average of the values calculated from the data of Hartmann and Schneider [1967] and those of Priselkov and Nesmeyanov [337]. The uncertainty in this value is due mainly to the inaccuracy of the thermodynamic functions of solid and liquid strontium (see Table 258).

Sr$^+$ (gas). The ionization potential of the strontium atom is 45,925.6 cm^{-1}, or

$$I(\mathrm{Sr}) = 131{,}313 \text{ kcal/g-atom},$$

which has been adopted in the work of Moore [2941]; the uncertainty in this value is about 1 cal/g-atom. To this value corresponds

$$\Delta H^\circ f_0(\mathrm{Sr^+, gas}) = 170{,}513 \pm 0{,}8 \text{ kcal/g-atom.}$$

SrO (cryst.). The data on the heats of solution of strontium in hydrochloric acid and of strontium oxide in water and in hydrochloric acid were examined by Bichowsky and Rossini [813] and the value $\Delta H^\circ f_{291} = -140{,}8$ kcal/mole was recommended for the heat of formation of strontium oxide. Rossini et al [3508] later recalculated this value to standard conditions and recommended $\Delta H^\circ f_{298{,}16} = -141{,}1$ kcal/mole.

The heat of combustion of metallic strontium in chlorine (-210 kcal/mole), measured by Siemonsen [3720], enables the construction of another thermodynamic cycle to be achieved, in which the heat of solution of metallic strontium in hydrochloric acid does not appear. This calculation, in which several other data from the work [3508] are included, gives a value of about -153 kcal/mole, which differs greatly from that calculated by Rossini et al [3508]. The results of the measurements of the heat of combustion of strontium in chlorine carried out by Siemonsen [3720] are not accurate (the experimental values vary within the limits of 202 and 217 kcal/mole); hence, preference has been given in the Handbook to the heat of formation of strontium oxide.

$$\Delta H^\circ f_{298,15}(\mathrm{SrO,\ cryst.}) = -141{,}1 \pm 2{,}0 \ \mathrm{kcal/mole},$$

calculated on the basis of the thermochemical cycle including the heat of dissolution of metallic strontium.

SrO (gas). Claassen and Veenemans [1116] investigated the rate of evaporation of strontium oxide from heated platinum foil. The vapor pressure of strontium oxide, obtained by these authors within the temperature range of 1495-1635°K (under the assumption that strontium oxide is the only product of evaporation) can be described by the equation $\lg p\,(\mathrm{atm}) = -\frac{30\,700}{T} + 10{,}47$.* The calculation of the heat of sublimation of SrO, carried out by the authors of the Handbook, allowance being made for the formation of Sr atoms in the vapor (the method of calculation is described in the work [2961], gave the value $\Delta Hs_0 = 128$ kcal/mole. The calculated Sr content of the vapor, according to the data of the work [1116], decreases with increase in temperature and amounts to 61% at 1500°K and 29.2% at 1650°K.

Moore, Allison and Struthers [2944] carried out a detailed investigation on the rate of evaporation of strontium oxide from a platinum strip. In contrast to the preceding work, the quantity of strontium oxide, evaporated from the strip and condensed on the collector, was determined not only by gravimetric analysis but also by a polarographic method and the method of radioactive tracers. In individual studies it was found that under the conditions of the work [2944], reduction of the strontium oxide does not take place. The results of 19 tests (1290--1650°K) carried out in the work [2944], taking into account the data of Claassen and Veenemans [1116], can be represented by the equation

$\lg M = -\frac{23\,660}{T} + 10{,}468,$ where M is the rate of evaporation of SrO (in $\mathrm{g \cdot cm^{-2} \cdot h^{-1}}$). Assuming that the sole evaporation product is SrO, the authors of the work [2944] found for the heat of sublimation $\Delta Hs_0 = 126 \pm 0.8$ kcal/mole. An approximate calculation of the formation of atomic strontium (on the assumption that SrO dissociates to an extent of 40%) led the authors of the work [2944] to the value 126.6 kcal/mole.

The results of the calculation of the composition of the dissociation products of strontium oxide in the condensed state on the basis of the thermodynamic properties of the corresponding substances as adopted in the Handbook, are given below. The partial pressures of SrO, the total vapor pressure over solid strontium oxide Σp (in atmospheres) and the content of atomic strontium (in %) were calculated on the basis of the data of Moore et al [2944]:

T, °K	p_{Sr}	p_{O_2}	p_O	p_{SrO}	Σp	$\frac{p_{Sr}}{p_{Sr} + p_{SrO}}$, %
1300	$1{,}33 \cdot 10^{-13}$	$2{,}18 \cdot 10^{-14}$	$2{,}60 \cdot 10^{-14}$	$2{,}67 \cdot 10^{-13}$	$4{,}48 \cdot 10^{-13}$	33,3
1500	$5{,}78 \cdot 10^{-11}$	$8{,}95 \cdot 10^{-12}$	$1{,}21 \cdot 10^{-11}$	$5{,}52 \cdot 10^{-11}$	$1{,}34 \cdot 10^{-10}$	51,2
1650	$2{,}06 \cdot 10^{-9}$	$3{,}09 \cdot 10^{-10}$	$4{,}44 \cdot 10^{-10}$	$1{,}12 \cdot 10^{-9}$	$3{,}93 \cdot 10^{-9}$	64,8

The heat of sublimation of SrO, calculated by means of the data of the work [2944], allowance being made for the formation of Sr atoms in the vapor, is $\Delta Hs_0 = 128$ kcal/mole* which agrees with the results of the calculations on the basis of the data of Claassen and Veenemans [1116]. The uncertainty in this error is estimated to be ± 4 kcal/mole. To this heat of sublimation corresponds $D_0(\mathrm{SrO}) = 110.8 \pm 5$ kcal/mole. It should be pointed out that the above given calculations were carried out on the assumption that the condensation coefficient of strontium oxide is equal to unity. It was found in the work of Morgulis, Gavrilyuk and Kulik [302] that the condensation coefficient of strontium oxide on tungsten, depending on the degree to which it is coated with strontium oxide, varies from 0.1 (pure tungsten) to 0.4-0.5 (approximately 30 molecular layers of strontium oxide). Because the method of evaporation from a covered surface had been used in the works [1116, 2944], a value of the evaporation coefficient of less than unity would have resulted in lower values of the calculated partial pressures of strontium oxide as compared with the true value.

The mass-spectrometric investigations of the evaporation of strontium oxide from a surface [3213] and from an effusion cell [3305] which will be examined further on, led to coincident results which obviously attests to the fact that the evaporation coefficient of strontium oxide cannot be much less than unity. If it be assumed that the evaporation coefficient of strontium oxide is 0.5, the heat of sublimation should be 2 kcal/mole less and the value of D_0(SrO) must be reduced by the same amount.

Pelchowitch [3213] investigated the mass spectrum of the evaporation products of strontium oxide from a heated platinum strip (1400--1750°K). He found that the main evaporation product under these conditions is atomic strontium (the ratio of the ionic current of Sr^+ and SrO^+ was always greater than 50). An investigation of the dependence of the logarithm of the Sr^+ ion current on temperature showed that, as in the case of the evaporation of BaO, the experimental points can be accommodated not by one, but two line curves with an inflection point at 1600°K. By virtue of its relatively low intensity, the SrO^+ current can be studied only at temperatures over 1600°K. The slope angle of the straight line $\lg I(SrO^+)-1/T$ corresponds to a heat of sublimation of strontium oxide of 160 kcal/mole (or 154 kcal/mole at 0°K).

Porter, Chupka and Inghram [3305] carried out an investigation of the mass spectrum of the products of evaporation of strontium oxide from an effusion cell, made of aluminum oxide. The main evaporation product proved to be strontium: at a temperature of 2100°K, the ratio of the Sr^+ and SrO^+ ion currents was 300:36:1. The calibration of the apparatus by the method of evaporating a certain quantity of silver, used by the authors of [3305] made it possible to find the partial pressure $p_{SrO} = 3{,}6 \cdot 10^{-8}$ atmospheres at 2100°K. Calculation of the heat of sublimation of SrO on the basis of the above given value p_{SrO} leads to a value of $\Delta Hs_0 = 151$ kcal/mole.* The calculation of the composition of the dissociation products of solid strontium oxide under conditions of evaporation from an effusion cell [296], carried out on the basis of the thermodynamic data adopted in the present Handbook, gave the following values at 2100°K: $p_{Sr} = 4{,}24 \cdot 10^{-6}$, $p_{O_2} = 5{,}52 \cdot 10^{-7}$ and $p_O = 1{,}03 \cdot 10^{-6}$ atmospheres. If we assume [3153] that the ionization cross sections of strontium and strontium oxide are equal, then, on the basis of the calculated value $p_{Sr} = 4{,}24 \cdot 10^{-6}$ atmospheres and the ratio of the ion currents of strontium and strontium oxide, found by Porter et al [3305], we can calculate the value $p_{SrO} = 1{,}4 \cdot 10^{-8}$ at. To this value corresponds a heat of sublimation of strontium oxide $\Delta Hs_0 = 154{,}6$ kcal/mole.

Thus, the results of the mass-spectrometric studies [3305, 3213] give the heat of sublimation and dissociation energy of strontium oxide of $\Delta Hs_0 = 153 \pm 3$ kcal/mole and $D_0(SrO) = 86$ kcal/mole, which differ markedly from those calculated on the basis of the results of the investigations on the vapor pressure by the method of evaporation from a surface [1116, 1294]: $\Delta Hs_0 = 128$ kcal/mole and $D_0(SrO) = 110{,}8$ kcal/mole. The difference between these values exceeds somewhat the usual uncertainties in the above described methods. Brewer and Searcy [95] showed that the cause of the difference may be the reducing conditions in the effusion cell** or the low evaporation coefficient of strontium oxide. However, Moore et al [1294] showed that a reduction of the strontium oxide had not taken place in their work. It is also difficult to imagine that during the evaporation of strontium oxide from an effusion chamber, made of alumina [3305] reducing conditions could play an important part (see section on BaO in the work [2170]. It is not possible to account for the difference by a low evaporation coefficient of strontium oxide, because higher pressures were found in studies carried out by the method of evaporation from a surface [1116, 2944].

It may be assumed that the cause of the marked difference in the results of the mass-spectrometric measurements and the results of the measurements by conventional methods consists in the fact that the authors of the mass-spectrometric measurements [3305] failed to allow for the dissociation of the strontium oxide during the ionization. In fact, during the investigations on barium oxide [3213, 2170], it was found that approximately half of the BaO^+ ions dissociate during the ionization. As the stability of the molecule SrO is much less than that of BaO, it may be expected that the SrO^+ ion will also be less stable than the BaO^+ ion. In this case, the dissociation of the SrO^+ should take place with greater intensity than the dissociation of BaO^+, and the heat of sublimation of SrO calculated on the basis of the SrO^+ ion current proves to be much too high.

The dissociation energy of strontium oxide can be found as a result of studies of flame equilibria. A detailed description of the experimental method and the method calculating the dissociation energies is given in the work [122]. The measurements, carried out by Huldt and Lagerqvist in an acetylene-air flame at temperatures of 2430°K [2148, 2149] and 2240-2430°K [2150], enabled the dissociation energies of strontium oxide, of 111.0 and 111.7 kcal/mole,* respectively, to be calculated.

Flames of acetylene with oxygen and air, hydrogen with oxygen and carbon monoxide with oxygen (2370-3210°K) were used in the works of Veyts and Gurvich [122, 125, 121]. The dissociation energies of strontium oxide obtained in these flames: 111.0, 111.0 and 111.8 kcal/mole (undertainty ±4 kcal/mole), agree fully with those obtained by Huldt and Lagerqvist. Recalculation of these values, allowing for the recently obtained more precise values of the transition probability of Sr [327] leads to $D_0(\mathrm{SrO}) = 113{,}2 \pm 4$ kcal/mole. The dissociation energy thus determined, agrees within the limits of error with the results of the investigations on the vapor pressure over strontium oxide.

The dissociation energy of strontium oxide

$$D_0(\mathrm{SrO}) = 112 \pm 2 \text{ kcal/mole},$$

which is the average of the value, found on the basis of the measurements of the vapor pressure of strontium oxide and that obtained in the investigation of the dissociation equilibrium in flames, has been adopted in the Handbook. To this value correspond

$$\Delta H^{\circ}f_0(\mathrm{SrO}, \text{gas}) = -13{,}813 \pm 2{,}1 \text{ kcal/mole},$$
$$\Delta Hs_0(\mathrm{SrO}, \text{cryst.}) = 126{,}740 \pm 2{,}9 \text{ kcal/mole}.$$

The standard state of barium is Ba (cryst.).

Ba (gas). The pressure of saturated barium vapor was measured by the method of boiling point determination by Ruff and Hartmann [3354] (1203-1403°K) and Hartmann and Schneider [1967] (1333-1411°K) and the effusion method by Rudberg and Lempert [3548] (798-1023°K) and by Zaitseva [194b] (914-996°K). Calculation of the heat of sublimation of barium on the basis of these data gives values of $38{,}8 \pm 2{,}4$, $42{,}9 \pm 0{,}2$, $46{,}9 \pm 0{,}4$ and $46{,}7 \pm 0{,}96$ kcal/g-atom, respectively. The data of Ruff and Hartmann [3554], as pointed out previously (see page 1765), are erroneous. The causes for the considerable difference between the data of Hartmann and Schneider [1967] and the results of the effusion measurements [3548, 194b] are not known.

The results of the effusion measurements are obviously more reliable. They agree well with each other. The value

$$\Delta Hs_0(\mathrm{Ba}, \text{cryst.}) = \Delta H^{\circ}f_0(\mathrm{Ba}, \text{газ}) = 46{,}8 \pm 2 \text{ kcal/g-atom},$$

calculated on the basis of the effusion measurements [3548, 194b] has adopted in the Handbook.

Ba$^+$ (gas). The ionization potential of the barium atom, equal to 42,032.4 cm^{-1}, or

$$I(\mathrm{Ba}) = 120{,}182 \text{ kcal/g-atom},$$

has been adopted from Moore [2941]; its uncertainty is about 1 cal/g-atom. To this value corresponds

$$\Delta H^\circ f_0 (\mathrm{Ba}^+, \text{gas}) = 166{,}982 \pm 2 \text{ kcal/g-atom}.$$

BaO (cryst.). The heat of formation of barium oxide has been calculated by Bichowsky and Rossini [813] on the basis of the literature data on the heats of solution of barium oxide in water and hydrochloric acid and of metallic barium in hydrochloric acid. The value $\Delta H^\circ f_{291} = -133$ kcal/mole recommended by Bichowsky and Rossini [813] was later recalculated by Rossini et al [3508] to the standard temperature of 25°C. The value recommended by Rossini et al [3508] for the heat of formation of crystalline barium oxide

$$\Delta H^\circ f_{298.15} (\mathrm{BaO}, \text{cryst.}) = -133{,}4 \pm 2 \text{ kcal/mole},$$

has been adopted in the Handbook.

The thermodynamic cycle, including the heat of formation of barium chloride, equal to -219.3 kcal/mole (determined by Siemonsen [3720] by direct combustion of metallic barium in chlorine) gives a heat of formation of barium oxide of about -147 kcal/mole. This value is less accurate than that adopted in the Handbook, mainly because of the low accuracy of the heat of combustion of barium in chlorine found by Siemonsen [3720] (the results of individual measurements of Siemonsen are within the range of -214 to -233 kcal/mole). Comparison of the heats of formation of $BaCl_2$, LiCl and $SrCl_2$ with the measurement results of other authors shows that a systematic error is obviously present in the measurements of Siemonsen.

BaO (gas). Barium oxide is the only alkaline earth metal oxide which evaporates in the form of BaO molecules practically without dissociation. This conclusion was obtained in numerous investigations carried out by the mass-spectrometric method (a bibliography is given in the works [466, 2170 and 3213]). The results of the mass-spectrometric works are confirmed by thermodynamic calculations: the partial pressure of atomic barium over barium oxide, calculated on the basis of the thermodynamic data, proved to be by three to four orders of magnitude less than the partial pressure of barium oxide, found in experimental investigations.

The first investigation on the vapor pressure of barium oxide was carried out by Thompson and Armstrong [3978] by the channel method. This work had certain deficiencies: the pressures obtained in it proved to be much too high. Inghram, Chupka and Porter [2170] advanced a hypothesis on the possibility of formation of Ba_2O_3 (gas) under the experimental conditions of Thompson and Armstrong.

The rate of evaporation of barium oxide from a metal strip, coated with barium oxide, has been measured by Claassen and Veenemans [1116] (1223-1475°K) and Hermann [2008 (1200-1555°K). Calculation of the heat of sublimation of BaO at 0°K on the basis of the data obtained by these authors leads to values of 102.8 ± 0.5 and 102.5 ± 2 kcal/ /mole and the corresponding values of D_0(BaO) of 136.1 ± 3 and 136.4 ± ± 3.5 kcal/mole. It is possible that certain errors were made in the temperature measurements in these works (see [842]) due to the low thermal conductivity of barium oxide and the indeterminacy of the emission coefficient of the surface coated with barium oxide.

Blevett, Liebhafsky and Hennelly [842] investigated the vapor pressure of barium oxide by the effusion method. The pressures found by them were in good agreement with the pressures measured by Claassen and Veenemans [1116] over the same temperature range by the method of evaporation from a surface which attests to the fact that the evaporation coefficient of barium oxide is close to unity.

Using a specially designed effusion chamber, the authors of the work [842] enlarged the temperature range considerably, carrying out measurements in the region 1526-1731°K. The pressures of barium oxide found in this series of experiments proved to be in excellent agreement with those obtained at lower temperatures and can be expressed by the general equation $\lg p(\text{atm}) = -\frac{19\,400}{T} + 5{,}75\ (1200-1800°\,K)$. Calculation of the heat of sublimation of barium oxide on the basis of the experimental data, obtained by Blevett, Liebhafsky and Hennelly [842], led to the value $\Delta Hs_0 = 100{,}7 \pm 0{,}6$ kcal/mole or $D_0(BaO) = 138{,}2 \pm 3$ kcal/mole.

Of the investigations on the vapor pressure of barium oxide, carried out by the mass-spectrometric method, the most important are the works of Pelchowitch [3213], Inghram, Chupka and Porter [2170] and Shchukarev and Semenov [466]. Pelchowitch [3213] measured the BaO^+ ion current which appears during the ionization of the evaporation products of barium oxide from the surface of a metal strip (platinum, nickel, tantalum). It was found that under the experimental conditions (temperatures of 1150-1400°K), tantalum is oxidized by barium oxide. Platinum and nickel did not enter into a reaction with the barium oxide under the same conditions. Pelchowitch measured the ion current as a function of temperature and found that during evaporation from platinum, the relation of the logarithm of the ion current and temperature can be expressed by two straight lines with a slope corresponding to the heats of sublimation of 114.4 kcal/mole (1150-1250°K) and 94.3 kcal/mole (1260-1400°K). Measurements of the electrical conductivity of barium oxide, carried out by Pelchowitch [3213] also demonstrated the existence of a point of inflection at 1260°K. The existence of a point of inflection at around 1260°K has not yet been explained. A phase transformation in this region with a heat of about 20 kcal/mole is impossible because the fusion temperature of barium oxide (2196°K) is considerably higher.

It should be pointed out that an inflection point was not observed during the evaporation of barium oxide from nickel. In addition to the BaO^+ ions, Pelchowitch [3213] observed considerable quantities of Ba^+ ions. At energies of the ionizing electrons of 30 to 80 ev, the ratio of the Ba^+ and BaO^+ ion currents was approximately equal to unity. However, at lower energies of the ionizing electrons, this ratio decreased rapidly which indicates the formation of Ba^+ ions in consequence of a dissociation of part of the BaO molecules during ionization.

Shchukarev and Semenov [466], like Pelchowitch [3213], investigated the rate of evaporation of barium oxide from a platinum strip, but the ionization of the vapor was carried out not by electrons but on the surface of a heated tungsten strip. The authors of the work [466] found a relation of the vapor pressure of barium oxide and temperature $\lg P(\text{atm}) = -\frac{19\,400}{T} + 5{,}81$ and calculated, on the basis of this relation, the heats of sublimation of barium oxide as $\Delta Hs_{1323} = 89$ kcal/mole (or $\Delta Hs_0 = 94$ kcal/mole). The more reliable value $\Delta Hs_0 = 102 \pm 1$ kcal/mole (and the corresponding value $D_0(BaO) = 137$ kcal/mole) can be calculated on the basis of the above given equation by means of the thermodynamic functions of barium oxide in the gaseous and condensed state, which were adopted in the present Handbook.

A detailed study of the composition and the vapor pressure of barium oxide by the mass spectrometric method was carried out by Inghram, Chupka and Porter [2170]. In contrast to the preceding mass-spectrometric investigations, the authors of the work [2170] used an effusion cell of alumina which enabled them to carry out the investigation under conditions closer to equilibrium. On the basis of the ion current as a function of temperature, the authors of the work [2170] found a value of the heat of sublimation of barium oxide $\Delta Hs_{1700}=102\pm8$ kcal/mole (or $\Delta Hs_0=109$ kcal/mole). The calibration of the apparatus carried out in the work [2170] by the method of evaporating a known quantity of silver made it possible to calculate the absolute vapor pressure of barium oxide at four temperatures from 1530 to 1758°K. To these values corresponds a heat of sublimation of barium oxide $\Delta Hs_0=104$ kcal/mole and $D_0(BaO)=135$ kcal/mole. The authors of the work [2170] assumed that the error in this value is ±4 kcal/mole. The authors of the work [2170] found in barium oxide vapor, in addition to BaO molecules, molecules of Ba_2O_2 (heat of evaporation $\Delta Hs_{1700}=105\pm10$ kcal/mole), Ba_2O (heat of dissociation into gaseous barium oxide and barium $\Delta H_{1700}=93\pm17$ kcal/mole) and Ba_2O_3.

Inghram, Chupka and Porter [2170], like Pelchowitch [3213], observed considerable quantities of Ba^+ ions in barium oxide vapor. The intensity of the Ba^+ ion current varied not only as a function of temperature but also of time. The authors of the work [2170] proposed that one part of the Ba^+ ions was formed on account of dissociation of BaO during ionization, and another on account of a reduction of the barium oxide by impurities. A reducing medium should not greatly affect the measured pressure of barium oxide because the evaporation was carried out from an effusion chamber with a small orifice and the equilibrium between the gaseous and solid barium oxide should not have been disturbed. However, the dissociation of the barium oxide during ionization could have markedly lowered the value of the partial pressure of barium oxide calculated by the authors of [2170]. The experimental data given in the works [2170, 3213] allow of the conclusion that about half the BaO molecules dissociate during ionization. Introduction of the corresponding correction gives a heat of sublimation of barium oxide $\Delta Hs_0 = 102$ kcal/mole.

Thus, the results of the vapor pressure measurements on barium oxide by the method of evaporation from a surface [1116, 2008], the effusion method [842] and the mass-spectrometric method [466, 2170] are in fairly good agreement. The most reliable measurement results are apparently those obtained by the effusion method [842].

The dissociation energy of barium oxide can be calculated on the basis of the results obtained in the studies of the dissociation equilibrium of BaO in flames (a description of the method and calculations is given in the work [122]). Huldt and Lagerqvist [2148, 2149, 2150] carried out an investigation in acetylene-air flames (2240-2430°K), and obtained for D_0(BaO) the values 126.8 and 128 kcal/mole. A recalculation of the data of the work [2150], based on the thermodynamic functions of barium, adopted in the present Handbook (see also [126]), led to the value $D_0(BaO) = 130{,}5$ kcal/mole. In an analogous work, carried out by James [2210], a value of 134.5 kcal/mole was obtained.*

In the works of Veyts and Gurvich [122, 125, 121] the investigation was carried out in acetylene-air and acetylene-oxygen and in oxygen-hydrogen flames (2450-3210°K). The dissociation energy of BaO, obtained in flame studies, depends on the probability of the transition corresponding to the barium line λ 5536Å. On the basis of the transition probability, found in the work of Ostrovskiy [327] and the results of the measurements, carried out in the works [122, 125, 121], the value $D_0(BaO) = 137 \pm 4$ kcal/mole was calculated. Recalculation of the data of Hyldt and Lagerqvist [2150], with allowance made for the new values of the transition probability, gives 129 kcal/mole.

It should be pointed out that because the evaporation of the barium oxide takes place in the form of BaO molecules without any marked decomposition or association, the results of the measurements carried out by the Knudsen method and the method of evaporation from a surface deserve special confidence. The value $D_0(BaO) = 137$ kcal/mole, found in the work [122] during a spectroscopic study of the dissociation equilibrium of BaO in flames is in excellent agreement with these measurement results.

To the value

$$D_0(BaO) = 137 \pm 2 \text{ kcal/mole},$$

which has been adopted in the Handbook, corresponds

$$\Delta H^\circ f_0(BaO, \text{gas}) = -31,213 \pm 3 \text{ kcal/mole},$$

$$\Delta Hs_0(BaO, \text{cryst.}) = 101,89 \pm 3,5 \text{ kcal/mole}.$$

TABLE 260

Adopted Values (in cal/mole) of the Thermodynamic Functions of Calcium, Strontium, Barium and Their Oxides

Вещество A	Состояние B	D_0, f или ΔHs_0 C	$\Delta H^\circ f_0$	$\Delta H^\circ f_{293,15}$	$\Delta H^\circ f_{298,15}$	$H^\circ_{293,15} - H^\circ_0$	$H^\circ_{298,15} - H^\circ_0$
Ca	Крист.	42 100^{а}	0	0	0	1346	1377
Ca	Газ	—	42 100	42 210	42 204	1456	1481
Ca^+	»	140 975^{б}	183 075	184 641	184 660	1456	1481
CaO	Крист.	137 133^{а}	—151 046	—151 793	—151 790	1619	1670
CaO	Газ	115 000	— 13 913	— 14 178	— 14 188	2101	2140
Sr	Крист.	39 200^{а}	0	0	0	1518	1550
Sr	Газ	—	39 200	39 138	39 131	1456	1481
Sr^+	»	131 313^{б}	170 513	171 907	171 925	1456	1481
SrO	Крист.	126 740^{а}	—140 553	—141 104	—141 100	1987	2040
SrO	Газ	112 000	— 13 813	— 14 230	— 14 240	2121	2161
Ba	Крист.	46 800^{а}	0	0	0	1606	1640
Ba	Газ	—	46 800	46 650	46 641	1456	1481
Ba^+	»	120 182^{б}	166 982	168 288	168 304	1456	1481
BaO	Крист.	101 800^{а}	—133 103	—133 403	—133 400	2326	2380
BaO	Газ	137 000	— 31 213	— 31 724	— 31 737	2115	2154

A) Substance; B) state; C) or. a) The heats of sublimation at 0°K are given; b) the ionization potentials of the corresponding neutral atoms are given.

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[Footnotes]

1743 The work of Garton and Codling [1655a] in which the absorption spectrum of the Ba atom had been again investigated, was published in 1960. Transitions to several states ^1P, $^3P_1$ and $^3D_1$ with the configuration $\ldots 5dnp$ and $n > 8$ were observed in this work. The energy of these states is of the order of about 40,800 to 45,600 cm^{-1} while the present Handbook gives them as equal to the energy of the ionization limit $\ldots 5d(^2D)\,nl'$, i.e., 47,390 cm^{-1}.

1747 It has been reported in the recently published work by Parkinson and Nicholls [3191] that the absorption spectrum in the shock tube showed bands of the system $A^1\Sigma \leftarrow X^1\Sigma$ of the molecule BaO. In the case of barium oxide the ground state $^1\Sigma$, evidently correlates with the state $Ba(^1D) + O(^3P)$.

1748 It should be pointed out that constants are given in the works of Lejeune [2589] and King [2401] which were obtained as a result of a study of the orange and green bands which, as shown later [2205, 2151] belong to the triatomic molecule CaOH.

1751 The absorption spectrum of BaO has been reported only in the work of Parkinson and Nicholls [3191]. The authors of the work [3191] observed bands of the system $A^1\Sigma - X^1\Sigma$ with $v' < 2$ and $v' < 8$ during excitation in the shock.

1761 The same value was obtained by comparison of the standard entropies of the alkali and alkaline earth elements. The earlier estimates of $S^\circ_{298.15}$ [2364, 3508 and 1093] give the values 12.5 ± 0.5; 10.0 and 13.3 cal/g-atom·degree, respectively.

1763 The earlier estimates of $S^\circ_{298.15}$ gave larger values: 15.1 [273], 16.0 [2364] and 16.2 ± 1.0 cal/g-atom·degree [2494].

1768 The monograph of Kelley [2355] gives the incorrect equation $\lg p\,(\text{atm}) = -\frac{27400}{T} + 6{,}89$, which accounts for the error in the recalculation of the data of the work [1116] from millimeters Hg to atmospheres.

1769 Claassen and Veenemans [1116], based on the temperature dependence of the vapor pressure of calcium oxide (without taking the dissociation into account), found $\Delta Hs_{1873} = 120$ kcal/mole (or $\Delta Hs_0 = 125$ kcal/mole). The difference between this

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and the value calculated in the present Handbook is due to the great scatter of the experimental points and the narrow temperature range, which affects the results of the calculations, carried out by the method used by Claassen and Veenemans, particularly strongly.

1771* A detailed description of this method and the technique of processing of the experimental data can be found in the work [122].

1771** Huldt and Lagerqvist [2150] assumed that the fundamental electronic state of the molecule CaO (and also of SrO) is the state ${}^3\Sigma$. As has been shown in the work [121], this assumption is erroneous. The value has been recalculated on the assumption that the electronic ground state is the state ${}^1\Sigma$.

1774 The incorrect equation

$$\lg p_{\text{atm}} = -\frac{30\,700}{T} + 10{,}24.$$

has been given in the work of Kelley [2355].

1775 Drummond and Barrow [1409], based on the data of the work [2944] calculated the heat of sublimation of strontium oxide as 125.7 kcal/mole. The lower value obtained by these authors is explained by the fact that they failed to allow for the dissociation of strontium oxide in their calculations.

1777* Porter, Chupka and Inghram [3305] found for the heat of sublimation the value $\Delta Hs_{298,16} = 155{,}1$ kcal/mole. The difference between this and the value calculated by the authors of the Handbook is explained primarily by the different electronic ground states of the molecule SrO, adopted in the calculation of the thermodynamic functions of SrO (gas).

1777** During the mass spectrometric recording of the quantity of strontium oxide in the vapor, reducing conditions result in higher values for the heat of sublimation. If the quantity of strontium oxide in the vapor is determined by the gravimetric, potentiometric or radioactive tracer method, reducing conditions result in lower calculated heats of sublimation.

1778 During the calculation of D_0(SrO), Huldt and Lagerqvist [2150] assumed that the electronic ground state of the molecule SrO (like that of CaO) is the state ${}^3\Sigma$. In the present Handbook it has been assumed that the ground state of this molecule is the ${}^1\Sigma$ state (see §107). Values of D_0(SrO), re-

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calculated for the ground state ${}^{4}\Sigma$ are given accordingly.

1785 The thesis of James [2210] is known from an abstract in Chemical Abstracts.