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CONTRIBUTIONS TO THE DATA ON THEORETICAL METALLURGY

III. The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances

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III. The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances[1]

By K. K. KELLEY[2]

INTRODUCTION

This work is part of the program of study of the Pacific Experiment Station of the United States Bureau of Mines and is a natural consequence of two earlier publications which dealt with the entropies at 298.1° K. (*199*)[3] and the specific heats at high temperatures (*200*) of inorganic substances. These earlier papers contain the data necessary for writing the thermodynamic equations for the heat and free-energy changes accompanying polymorphic transformations and fusions for all inorganic substances whose heat capacities have been measured in the ranges of temperature where such changes of state occur. It is the purpose of this present work (1) to apply the previously compiled entropy values and specific-heat equations to vapor-pressure and other pertinent data in obtaining heat and free energy of vaporization equations for inorganic substances valid up to the normal boiling or sublimation points (760 mm pressure), (2) to supplement wherever possible the data on heats and entropies of transformations and fusions, (3) to supplement the data on entropies of gases, and (4) to supply tables of vapor pressures for inorganic substances at various temperatures up to and including the boiling or sublimation point. This work also contains a bibliography of vapor-pressure data, complete so far as possible up to April 1934.

METHODS USED IN HEAT AND FREE ENERGY OF VAPORIZATION CALCULATIONS

Most of the free-energy and heat of vaporization equations given in the next section are based on vapor-pressure data. However, the results for a number of the metals and carbon were obtained by the use of tables of free energies of gases computed from spectroscopically determined energy levels by R. Overstreet (*273*), working under the direction of Prof. W. F. Giauque of the chemistry department of the University of California at Berkeley. For a few substances, reliable, directly determined, heat of vaporization data exist, and these figures

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[1] Work on manuscript completed April 1934.

[2] Associate physical chemist, Metallurgical Division, U. S. Bureau of Mines.

[3] Italicized numbers in parentheses refer to citations in the bibliography at the end of this report. Page references represent those in the citation and not in this bulletin.

also are employed after correcting for gas imperfection. Calculations from vapor-pressure data will be described first. The reader is referred to the textbook of Lewis and Randall (*226*) for more detailed discussion of some of the methods employed.

The free-energy change in a chemical reaction may be written (*226*)

$$\Delta F^\circ = -RT\ln K. \tag{1}$$

Here ΔF° is the standard free-energy change at the absolute temperature T, R is the gas constant per mole, and $\ln K$ is the natural logarithm of the equilibrium constant. In the special case where the reaction consists in a solid or liquid vaporizing without decomposition, this equation becomes simply

$$\Delta F^\circ = -RT\ln f, \tag{2}$$

where f is the fugacity or "ideal" vapor pressure. The fugacity equals the vapor pressure when the vapor behaves as a perfect gas. In other cases it is smaller than the vapor pressure by an amount which increases as gas imperfection becomes more pronounced, that is, as the pressure is increased or the temperature lowered. Most of the substances to be considered in the next section have appreciable vapor pressures only at relatively high temperatures, and since the vapor-pressure values themselves ordinarily are not known above 1 atmosphere, ΔF° will be computed from

$$\Delta F^\circ = -RT\ln P. \tag{3}$$

Except for comparatively few substances this is a necessity because data of state do not exist nor are the critical temperatures and pressures known which would enable one to make corrections based on the assumption of some equation of state. It should be emphasized that in the great majority of cases where equation (3) is used in the present work *no appreciable error is introduced.* When critical point data are available for a substance the Berthelot equation of state (*276*) will be adopted from which may be obtained

$$F_{\text{ideal}} - F_{\text{actual}} = -\frac{9}{128} R \frac{T_c}{P_c} P\left(1 - \frac{6T_c^2}{T^2}\right). \tag{4}$$

In this equation $F_{\text{ideal}} - F_{\text{actual}}$ is the free-energy change involved in transferring, at constant temperature T, 1 mole of gas from its actual state with fugacity f to the ideal state where $f = P$, P_c is the critical pressure, and T_c is the critical temperature. Another relationship based on Berthelot's equation which will be useful is

$$S_{\text{ideal}} - S_{\text{actual}} = \frac{27}{32} R \frac{T_c^3}{T^3} \frac{P}{P_c}. \tag{5}$$

The symbols on the right are the same as in equation (4) and $S_{\text{ideal}} - S_{\text{actual}}$ is the entropy change due to transferring 1 mole of gas from the actual to ideal state.

Before proceeding farther, some discussion of specific-heat equations seems necessary. In previous papers relating to heat capacities at high temperatures (*200*, *237*) specific-heat equations of the form

$$C_p = a + bT - cT^{-2} \tag{6}$$

were adopted for solids. The T^{-2} term sometimes is unnecessary, as in the case of the lower-melting metals. The high-temperature specific-heat data for liquids are quite meager and usually do not warrant more than a constant term in the specific-heat equation for the temperature range studied. For gases, the form of equation necessary to represent the specific-heat measurements depends upon the temperature range under consideration and on the reliability of the data. Usually a constant specific heat or one increasing linearly with the temperature will suffice. More often no data are available for the heat capacity of the gas, and it is desirable, if possible, to make a reasonable guess of the magnitude of the specific heat of the gas or of the difference in specific heat between gas and liquid or gas and solid, as the case may be. When this is not possible it is customary to take the difference in specific heat between the two phases as zero. The specific heat of the gas minus the specific heat of the solid or liquid is to be expressed as a function of the temperature. Equation (7) is as general as any for this representation and will be used for illustration.

$$\Delta C_p = \Delta a + \Delta bT - \Delta cT^{-2}. \tag{7}$$

The integral, $\int \Delta C_p dT$, gives the heat of vaporization. Designating this heat as ΔH, there is obtained from equation (7)

$$\Delta H = \Delta H_0 + \Delta aT + \frac{\Delta b}{2}T^2 + \Delta cT^{-1}, \tag{8}$$

where ΔH_0 is the constant of integration. The free-energy change is related to equation (8) by means of

$$\frac{\partial \frac{\Delta F^\circ}{T}}{\partial T} = -\frac{\Delta H}{T^2} = -\frac{\Delta H_0}{T^2} - \frac{\Delta a}{T} - \frac{\Delta b}{2} - \Delta cT^{-3}. \tag{9}$$

On integration, this gives

$$\frac{\Delta F^\circ}{T} = \frac{\Delta H_0}{T} - \Delta a \ln T - \frac{\Delta b}{2}T + \frac{\Delta c}{2}T^{-2} + I,$$

or

$$\Delta F^\circ = \Delta H_0 - \Delta a\, T \ln T - \frac{\Delta b}{2}T^2 + \frac{\Delta c}{2}T^{-1} + IT, \tag{10}$$

where I is another integration constant. Combining equations (3) and (10) results in

$$-R\ln P + \Delta a \ln T + \frac{\Delta b}{2}T - \frac{\Delta c}{2}T^{-2} = \frac{\Delta H_0}{T} + I. \tag{11}$$

The group of terms on the left usually is designated as Σ, so that

$$\Sigma = \frac{\Delta H_0}{T} + I. \tag{12}$$

To obtain ΔH_0, Σ is computed for each experimental vapor-pressure result and plotted against the reciprocal of T. The resulting plot should be a straight line, of which ΔH_0 is the slope, and it is so calculated. Next, $\frac{\Delta H_0}{T}$ is computed for the temperature of each vapor-pressure point and subtracted from the corresponding Σ-value. The result is I, which should be constant for all points within limits which are set by the relative errors in the vapor-pressure data themselves, provided the specific-heat terms are known with accuracy. The mean value or weighted mean value of I is adopted. Insertion of the values for ΔH_0 and I in equations (8) and (10) completes the expressions for heat and free energy of vaporization.

To further illustrate these calculations the measurements of Fiock and Rodebush (*106*) of the vapor pressure of liquid sodium chloride are considered. The specific heat of sodium chloride gas has not been measured, but the value $C_p(g)=9$ is a reasonable assumption for the temperatures involved. For the liquid, $C_p(l)=15.9$ (*200*) and for the reaction $NaCl(l) \rightarrow NaCl(g)$, the difference in heat capacities is, therefore, $\Delta C_p=-6.9$. The corresponding expression for Σ is

$$\Sigma=-R\ ln\ P-6.9ln\ T=-4.575\log P-15.9\log T,$$

where *ln* refers to natural logarithms (base *e*), log to ordinary logarithms (base 10), and $R=1.9869$ calories per degree (*177, vol. 1, p. 18*). The first and second columns of table 1 give the experimental results of Fiock and Rodebush.

TABLE 1.—*Free energy of vaporization data for liquid sodium chloride*

T	P (at.)	$-4.575\times\log P$ (at.)	$-15.9\times\log T$	Σ	$\frac{52,800}{T}$	I
1,250	8.06×10^{-3}	9.581	−49.241	−39.660	42.240	−81.90
1,276	1.146×10^{-2}	8.879	−49.382	−40.503	41.379	−81.88
1,301	1.628×10^{-2}	8.182	−49.517	−41.335	40.584	−81.91
1,327	2.246×10^{-2}	7.542	−49.654	−42.112	39.789	−81.90
1,353	3.054×10^{-2}	6.932	−49.788	−42.856	39.024	−81.88
1,378	4.119×10^{-2}	6.337	−49.913	−43.576	38.316	−81.89
1,403	5.430×10^{-2}	5.778	−50.039	−44.251	37.634	−81.88
1,428	7.126×10^{-2}	5.248	−50.160	−44.912	36.975	−81.89

Columns 3 and 4 give the quantities used in computing the Σ-values, which are tabulated in column 5. These Σ-values, when plotted against the reciprocal of the absolute temperature, fall on a straight line whose slope, ΔH_0, is found to be 52,800. The constant I is obtained by means of equation (12). Column 6 shows values of $\frac{\Delta H_0}{T}$ which are subtracted from the Σ's to obtain the I's in column 7. If no error has been made and if the data are sound the values of I obtained should be virtually constant and show no trend with the temperature. This is seen to be the case in the present instance. The mean value of I is -81.89, and the extreme variation in this quantity (the difference between the largest and smallest values) is only 0.03 unit, which shows that the experimental data have a high relative accuracy. It also should be noted that the differences between the individual I values and the mean represent the ordinal displacements of the individual points on the Σ v. $\frac{1}{T}$ plot from the straight line and that the figure for the extreme variation in I is a measure of the accuracy of the data and calculations since all the results fall in a band of this width on the Σ-function plot, this band being drawn parallel to and including the straight line.

These results for the vaporization of liquid sodium chloride may be summarized as follows:

Liquid→Gas (NaCl)
$C_p(g) = 9$,
$C_p(l) = 15.9$,
$\Delta C_p = -6.9$,
$\Delta H = 52{,}800 - 6.9\,T$,
$\Delta F^\circ = 52{,}800 + 15.9\,T \log T - 81.89\,T$,
B. P. = 1,738°, $\Delta H_{1738} = 40{,}808$; $\Delta S_{1738} = 23.5$,
$\Delta H_{298.1} = 50{,}743$; $\Delta F^\circ_{298.1} = 40{,}117$.

The free energy of vaporization is zero at the boiling point, B. P.= 1,738°. At this temperature the heat of vaporization is found to be 40,808 calories per gram formula weight, which corresponds to an entropy of vaporization of 23.5 units. The results for the heat and free energy of vaporization at the standard temperature, 298.1°, are, of course, hypothetical but are tabulated since they are useful.

For substances whose heats of vaporization have been measured accurately at their boiling points, equations (8) and (10) may be employed directly. The heat of vaporization, corrected for the effect of gas imperfection by means of equations (4) and (5), and the boiling-point temperature are sufficient for determining ΔH_0 in equation (8). At the boiling point the free energy of formation of the actual gas is zero, so the free-energy change accompanying the formation of the ideal gas is given by equation (5). This result, the boiling-point temperature, and ΔH_0, when substituted in equation (10) enable one to calculate I. The final equations obtained will, of course, be subject to any error introduced by the assumption of the Berthelot equation of state. In cases where this procedure is employed in the present work the assumption of Berthelot's equation already has been justified by other workers so far as equation (5) is concerned.

The methods utilizing spectroscopic data in the calculation of vapor pressures will be described next. These methods have been discussed by Giauque (*118*) and the calculation of a vapor-pressure equation illustrated by him for iodine (*119*). It is necessary first to obtain the expression for the free energy of a gas from the spectroscopically determined energy levels, and it is customary to separate translation from all other means of energy absorption in the molecule. The Boltzmann distribution law is applied to the latter, namely,

$$\frac{A_t}{A} = e^{-\frac{\epsilon_t}{kT}}. \qquad (13)$$

In this expression $\frac{A_t}{A}$ is the ratio of the numbers of molecules in two energy states, A_t referring to the state of higher energy; e is the natural logarithmic base; ϵ_t is the difference in energy between the two states; k is the gas constant per molecule; and T is the absolute temperature. Suppose A refers to the lowest energy state (disregarding translation); then, for each higher-energy state, $\frac{A_t}{A}$ may be computed by means of equation (13). If 1 mole of gas (Avogadro's number of molecules, N) is considered, then

$$N = A + Ae^{-\frac{\epsilon_1}{kT}} + Ae^{-\frac{\epsilon_2}{kT}} + Ae^{-\frac{\epsilon_3}{kT}} + \ldots \qquad (14)$$

If there is a group of states with energies so nearly alike that differences in the Boltzmann factors are negligible, it is customary to class these states together and write for the corresponding portion of equation (14)

$$p_iAe^{-\frac{\epsilon_i}{kT}},$$

where p_i is the number of these states of nearly identical energy. It is sometimes convenient to speak of these particular states as if they constituted one state of energy ϵ_i, in which case p_i is termed the a priori probability of the state of energy ϵ_i. If p_0, p_1, p_2, etc., are the numbers of the constituents in the successive groups of states which are considered together, then equation (14) becomes in general,

$$N = p0A + p_1Ae^{-\frac{\epsilon_1}{kT}} + p_2Ae^{-\frac{\epsilon_2}{kT}} + p_3Ae^{-\frac{\epsilon_3}{kT}} + \dots \qquad (15)$$

Let the total energy per mole (excluding translation) be E°_z at a given temperature and let the energy of the substance per mole in the perfect gas state at 0°K. be E°_0. $E^\circ_z - E^\circ_0$ may be computed from equation (16) by multiplying each term by the corresponding energy and adding. Therefore,

$$E^\circ_z - E^\circ_0 = op_0A + \epsilon_1p_1Ae^{-\frac{\epsilon_1}{kT}} + \epsilon_2p_2Ae^{-\frac{\epsilon_2}{kT}} + \epsilon_3p_3Ae^{-\frac{\epsilon_3}{kT}} + \dots \qquad (16)$$

$$= \Sigma\epsilon_ip_iAe^{-\frac{\epsilon_i}{kT}}. \qquad (17)$$

Eliminating A by means of equation (15) results in

$$E^\circ_z - E^\circ_0 = N\frac{\Sigma\epsilon_ip_ie^{-\frac{\epsilon_i}{kT}}}{\Sigma p_ie^{-\frac{\epsilon_i}{kT}}}, \qquad (18)$$

for

$$A = \frac{N}{p_0 + p_1e^{-\frac{\epsilon_1}{kT}} + p_2e^{-\frac{\epsilon_2}{kT}} + \dots} = \frac{N}{\Sigma p_ie^{-\frac{\epsilon_i}{kT}}}. \qquad (19)$$

Defining Q as $\Sigma p_ie^{-\frac{\epsilon_i}{kT}}$, equation (18) becomes

$$E^\circ_z - E^\circ_0 = NkT^2\frac{d\ln Q}{dT} = RT^2\frac{d\ln Q}{dT}. \qquad (20)$$

Differentiating equations (18) and (20) with respect to T,

$$\frac{dE^\circ_z}{dT} = \frac{N}{kT^2}\left[\frac{\Sigma\epsilon_i^2p_ie^{-\frac{\epsilon_i}{kT}}}{\Sigma p_ie^{-\frac{\epsilon_i}{kT}}} - \left(\frac{\Sigma\epsilon_ip_ie^{-\frac{\epsilon_i}{kT}}}{\Sigma p_ie^{-\frac{\epsilon_i}{kT}}}\right)^2\right], \qquad (21)$$

and

$$\frac{dE^\circ_z}{dT} = -R\frac{d}{dT}\left(\frac{d\ln Q}{d\frac{1}{T}}\right). \qquad (22)$$

The entropy of the gas (excluding translational entropy) is defined by

$$d\,S^\circ_z = \frac{dE^\circ_z}{dT}d\ln T, \qquad (23)$$

or

$$S^\circ_z - S^\circ_{z,0} = \int_0^T \frac{dE^\circ_z}{dT}d\ln T. \qquad (24)$$

The indicated integration is performed as follows:

$$S^\circ_I - S^\circ_{I,0} = -R\int_0^T \frac{d}{dT}\left(\frac{d\ln Q}{\frac{1}{dT}}\right) d\ln T, \tag{25}$$

$$= R\left[\ln Q + T\frac{d\ln Q}{dT}\right]_0^T, \tag{26}$$

$$= R\left[\ln Q - \ln Q_0 + T\frac{d\ln Q}{dT}\right], \tag{27}$$

$$= R\left[\ln \Sigma p_i e^{-\frac{\epsilon_i}{kT}} - \ln p_0 + \frac{1}{kT}\frac{\Sigma \epsilon_i p_i e^{-\frac{\epsilon_i}{kT}}}{\Sigma p_i e^{-\frac{\epsilon_i}{kT}}}\right]. \tag{28}$$

But $S^\circ_{I,0} = R \ln p_0$, so

$$S^\circ_I = R\left[\ln Q + T\frac{d\ln Q}{dT}\right]. \tag{29}$$

The translational entropy, S°_{Tr}, of a gas in the ideal state is given by the Sackur equation (*199*),

$$S^\circ_{Tr} = \frac{3}{2}R \ln M + \frac{3}{2}R \ln T + R \ln V + \frac{5}{2}R + C, \tag{30}$$

in which M is the molecular weight, T the absolute temperature, V the molal volume in cubic centimeters, R the gas constant per mole (1.9869 calories per degree), and $C = R \ln\frac{2\pi k^{3/2}}{h^3 N^{5/2}} = -16.024$ calories per mole per degree (h being Planck's constant). Replacing V in terms of T and P by the perfect gas law gives

$$S^\circ_{Tr} = \frac{3}{2}R \ln M + \frac{5}{2}R \ln T - R \ln P + \frac{5}{2}R + C + R \ln R. \tag{31}$$

If P is expressed in atmospheres then $C + R \ln R = -7.267$ calories per mole per degree.

The total entropy, S°, is represented by the sum of equations (29) and (31) or

$$S^\circ = \frac{3}{2}R \ln M + \frac{5}{2}R \ln T - R \ln P + \frac{5}{2}R + C + R \ln R + R \ln Q + RT\frac{d\ln Q}{dT}. \tag{32}$$

Free energy F° for the ideal gas is related to heat content H° and entropy S° by

$$F^\circ = H^\circ - TS^\circ, \tag{33}$$

where

$$H^\circ = E^\circ + PV = E^\circ + RT. \tag{34}$$

Combining equation (32) with (33) and (34) results in

$$F^\circ = E^\circ + RT - \frac{3}{2}R\,T \ln M - \frac{5}{2}RT \ln T + RT \ln P - \frac{5}{2}RT$$
$$- CT - RT \ln R - RT \ln Q - RT^2\frac{d\ln Q}{dT}. \tag{35}$$

Quantity E°, however, is the sum of E°_0, the energy of translation, $\frac{3}{2}RT$, and the energies involved in all other means of heat absorption or

$$E^\circ = E^\circ_0 + \frac{3}{2}RT + RT^2\frac{d\ln Q}{dT}. \tag{36}$$

Eliminating E° between equations (35) and (36) and rearranging slightly gives

$$\frac{F^\circ - E^\circ_0}{T} = -\frac{3}{2}R\ln M - \frac{5}{2}R\ln T + R\ln P - C - R\ln R - R\ln Q, \tag{37}$$

which is the desired expression for the free energy of the gas.

To illustrate the calculation of $\frac{F^\circ - E^\circ_0}{T}$, the data for copper given in table 2 are used. The energy levels designated are all that need be considered up to temperatures which considerably exceed the boiling point.

TABLE 2.—*Spectroscopic data for copper*

Type of state	p	Energy level (wave numbers)	Energy per molecule (ergs)
$1^2S_{1/2}$	2	0.00	0.0000
$2^2D_{5/2}$	6	11,202.8	2.1989×10^{-12}
$2^2D_{3/2}$	4	13,245.4	2.5998×10^{-12}
$2^2P_{1/2}$	2	30,535.2	5.9934×10^{-12}
$2^2P_{3/2}$	4	30,783.6	6.0422×10^{-12}

The first and third columns of this table are taken from the International Critical Tables (*177, vol. 5, p. 398*). The energies in ergs (fourth column) are obtained from the wave-number values and the relationship

$$\epsilon = h\,c\,\nu, \tag{38}$$

where ϵ is the energy per molecule in ergs, h is Planck's constant (6.547×10^{-27} erg-sec.), c is the velocity of light (2.99796×10^{10} cm per sec.), and ν is the wave number (cm^{-1}).

Next Q must be calculated for each temperature. For illustration, the temperatures 298.1° and 3,000° K. may be considered, the computations being summarized in table 3.

TABLE 3.—*Data for obtaining $Q_{298.1}$ and Q_{3000} for copper*

Type of state	p	$\frac{\epsilon}{k\cdot298.1}$	$\frac{\epsilon}{k\cdot3000}$	$e^{-\frac{\epsilon}{k\cdot298.1}}$	$e^{-\frac{\epsilon}{k\cdot3000}}$
$1^2S_{1/2}$	2	0.00	0.00	1.00	1.00
$2^2D_{5/2}$	6	53.807	5.3466	4.300×10^{-24}	4.765×10^{-3}
$2^2D_{3/2}$	4	63.617	6.3214	2.356×10^{-28}	1.798×10^{-3}
$2^2P_{1/2}$	2	146.66	14.572	2.028×10^{-64}	4.694×10^{-7}
$2^2P_{3/2}$	4	147.85	14.692	6.169×10^{-65}	4.163×10^{-7}
				$Q_{298.1}=2.0000$	$Q_{3000}=2.0358$

The third and fourth columns of table 3 show the values of $\frac{\epsilon}{kT}$ for the temperatures 298.1° and 3,000° K. (The value of k is 1.3709×10^{-16} ergs per degree per molecule.) In the fifth and sixth columns are given values of $e^{-\frac{\epsilon}{kT}}$ for 298.1 and 3,000° K., respectively. At 298.1° K. the numbers of copper atoms in levels higher than the zero level are entirely negligible, so $Q_{298.1}=\Sigma p_t e^{-\frac{\epsilon_t}{k \cdot 298.1}}=2.0000$. At 3,000° K., $Q_{3000}=2.0358$, and the three lower levels only need be considered since the accuracy with which the associated fundamental constants are known places a limit on the number of figures which are significant.

After evaluating Q, equation (37) may be solved for $\frac{F^\circ - E^\circ_0}{T}$. At 298.1° and 3,000° K. there are found for copper, $\frac{F^\circ - E^\circ_0}{298.1} = -34.786$ and $\frac{F^\circ - E^\circ_0}{3{,}000} = -46.290$. In this manner the $\frac{F^\circ - E^\circ_0}{T}$ values in column 2 of table 4 were obtained. Overstreet (*273*) has computed such values for a number of elementary gases in the temperature range 298.1 to 3,000° K.

TABLE 4.—*Free energy of vaporization data for copper*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_c - E^\circ_c}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−34.786	−3.90	−30.89	272.53	241.64
400	−36.247	−5.15	−31.10	203.10	172.00
500	−37.355	−6.20	−31.16	162.48	131.32
600	−38.261	−7.10	−31.16	135.40	104.24
700	−39.026	−7.90	−31.13	116.06	84.93
800	−39.689	−8.62	−31.07	101.55	70.48
900	−40.274	−9.26	−31.01	90.27	59.26
1,000	−40.797	−9.85	−30.95	81.24	50.29
1,100	−41.271	−10.40	−30.87	73.85	42.98
1,200	−41.703	−10.90	−30.80	67.70	36.90
1,300	−42.100	−11.39	−30.71	62.49	31.78
1,400	−42.469	−11.89	−30.58	58.03	27.45
1,500	−42.812	−12.47	−30.34	54.16	23.82
1,600	−43.133	−13.00	−30.13	50.78	20.65
1,700	−43.434	−13.50	−29.94	47.79	17.85
1,800	−43.718	−13.97	−29.75	45.13	15.38
1,900	−43.988	−14.40	−29.59	42.76	13.17
2,000	−44.242	−14.82	−29.42	40.62	11.20
2,500	−45.360	−16.61	−28.75	32.50	3.75
3,000	−46.290	−18.06	−28.23	27.08	−1.15

The next step involves the calculation of $\frac{F_c^\circ - E^\circ_{c,0}}{T}$ values for the solid and liquid states. (Subscript c is used to denote condensed state.) This is done by means of the relationships

$$H^\circ_c - E^\circ_{c,0} = \int_0^T C_p dT + \Sigma \Delta H_t, \tag{39}$$

$$S^\circ_c = \int_0^T \frac{C_p dT}{T} + \sum \frac{\Delta H_t}{T_t}, \tag{40}$$

and

$$F^\circ_c - E^\circ_{c,0} = H^\circ_c - E^\circ_{c,0} - TS^\circ_c. \tag{41}$$

Here $H^\circ_c - E_{c,}{}^\circ_0$ is the heat required to raise the temperature of 1 gram-atom of the metal from absolute zero to temperature T, S°_c is the entropy of 1 gram-atom at temperature T, $F^\circ_c - E^\circ_{c,0}$ is the free-energy change encountered in raising the temperature of 1 gram-atom from absolute zero to T, C_p is the true or instantaneous specific heat per gram-atom at constant pressure, $\Sigma \Delta H_t$ is the total heat absorbed by changes of state, and $\Sigma \frac{\Delta H_t}{T_t}$ the total of the entropy increments accompanying changes of state. In the case of copper each of the last two quantities consists of a single term, the heat and entropy of fusion, respectively, when the temperature is above the melting point. At temperatures below the melting point these quantities are zero in this instance. The quantities, $H^\circ_c - E^\circ_{c,0}$ and S°_c, are evaluated for any temperature by a combination of graphic and algebraic integration, the former being applied below 298.1° K. and the latter above this temperature where simple equations may be used to represent heat capacities. Column 3 of table 4 gives the calculated values of $\frac{F^\circ_c - E^\circ_{c,0}}{T}$ for copper. The data employed are $S^\circ_{c,298.1} = 7.92$ (*199*), $H^\circ_{c,298.1} - E^\circ_{c,0}$, computed from low-temperature specific-heat measurements to be 1,199 calories per gram-atom, the specific-heat equations for solid and liquid copper at high temperatures (*200*), $C_p(s) = 5.44 + 1.462 \times 10^{-3} T$ and $C_p(l) = 7.50$, and the heat of fusion at 1,357° K. (the melting point), 3,110 calories per gram-atom (*200*).

The difference between columns 2 and 3, which is shown in column 4, is

$$\frac{F^\circ - E^\circ_0}{T} - \frac{F^\circ_c - E^\circ_{c,0}}{T} = \frac{F^\circ - F^\circ_c}{T} - \frac{E^\circ - E^\circ_{c,0}}{T} = \frac{\Delta F^\circ}{T} - \frac{\Delta E^\circ_0}{T}.$$

Quantity ΔE°_0 is the difference in energy between the hypothetical ideal gas and crystalline copper at O°K. and ΔF° is the free energy of vaporization. To obtain ΔE°_0 at least one additional, relevant datum is necessary, and the procedure at this point will vary, depending on the information available. In the case of copper, Harteck (*144*) has measured the vapor pressure in the range 1,419 to 1,463° K. His figures enable one to calculate a smoothed value of $-R \ln P = \frac{\Delta F^\circ}{T} = 26.68$ at 1,420° K. Interpolation from column 4 of table 4 gives $\frac{\Delta F^\circ}{T} - \frac{\Delta E^\circ_0}{T} = -30.53$ at this temperature. Therefore, $\frac{\Delta E^\circ_0}{1,420} = 57.21$ or $\Delta E^\circ_0 = 81,240$ calories per gram-atom. Adding $\frac{81,240}{T}$ to the corresponding value in column 4 results in column 6, which gives $\frac{\Delta F^\circ}{T}$ at each temperature.

Vapor pressures may be computed from the values in column 6, and the equation, $-R \ln p = \frac{\Delta F^\circ}{T}$. However, it is desirable to write free energy equations for the vaporization of solid and liquid. The procedure for this process is subject to some variation, depending on the known facts regarding the particular substance concerned. In the present case, the entropies of crystalline and gaseous copper are known accurately at 298.1° K., namely, 7.92 and 39.75 calories per gram-atom per degree. The value for the solid is taken from the previously published entropy compilation (*199*), and the value for the gas is calculated from the Sackur equation with $R \ln 2$ added, since $p=2$ for the lowest energy state, and no other states are effective at 298.1° K. The difference between these two figures, 31.83, is the entropy of vaporization at 298.1° K. The specific-heat equations for gaseous and crystalline copper are set down and the difference, ΔC_p, obtained. From the latter the forms of the heat and free energy of vaporization are known and, since $\Delta F^\circ = \Delta H - T\Delta S$, constant I in the free-energy equation is obtainable from the entropy of vaporization as follows. (The specific heat of the gas is taken as 4.97 calories per gram-atom, although it is apparent that the actual specific heat has risen above this figure at 3,000° K. The difference, however, is not large enough to cause serious error in this case.)

Solid → Gas (Cu)

$$C_p(g) = 4.97,$$
$$C_p(s) = 5.44 + 1.462 \times 10^{-3}T,$$
$$\Delta C_p = -0.47 - 1.462 \times 10^{-3}T,$$
$$\Sigma = -R \ln P - 0.47 \ln T - 0.731\ T = -R \ln P - 1.08 \log T - 0.731 \times 10^{-3}T,$$
$$\Delta H = \Delta H_0 - 0.47\ T - 0.731 \times 10^{-3}T^2,$$
$$\Delta F^\circ = \Delta H_0 + 1.08\ T \log T + 0.731 \times 10^{-3}T^2 + IT,$$
$$\frac{\Delta H - \Delta F^\circ}{T} = \Delta S = -0.47 - 1.08 \log T - 1.462 \times 10^{-3}T - I.$$

Whence, putting $T=298.1°$ and $\Delta S=31.83$ in the latter equation, I is found to be -35.41.

Next Σ is calculated for each value of $\frac{\Delta F^\circ}{T}$ for crystalline copper. A summary of these computations is reproduced in the first five columns of table 5.

TABLE 5.—*Σ-function calculations for crystalline copper*

T	$\frac{\Delta F^\circ}{T}$ or $-R \ln P$	$-1.08 \log T$	$-0.731 \times 10^{-3}T$	Σ	$\frac{\Delta H_0}{T}$	ΔH_0
298.1	241.64	−2.672	−0.218	238.75	274.16	81,727
400	172.00	−2.810	−.292	168.90	204.31	81,724
500	131.32	−2.915	−.366	128.04	163.45	81,726
600	104.24	−3.000	−.439	100.80	136.21	81,728
700	84.93	−3.073	−.512	81.35	116.76	81,732
800	70.48	−3.135	−.585	66.76	102.17	81,736
900	59.26	−3.191	−.658	55.41	90.82	81,738
1,000	50.29	−3.240	−.731	46.32	81.73	81,730
1,100	42.98	−3.285	−.804	38.89	74.30	81,730
1,200	36.90	−3.326	−.877	32.70	68.11	81,732
1,300	31.78	−3.363	−.950	27.47	62.87	81,731

From equation (12), $\Sigma - I = \frac{\Delta H_0}{T}$; so knowing Σ and I, $\frac{\Delta H_0}{T}$ may be obtained at each temperature, and if the calculations are correct ΔH_0 should be constant within reasonable limits. Columns 6 and 7 of table 5 give the $\frac{\Delta H_0}{T}$ and ΔH_0 values so calculated. The difference between the largest and smallest ΔH_0 values is less than 0.02 percent and the mean $\Delta H_0 = 81{,}730$ is adopted. The heat and free energy of vaporization equations for solid copper are thus completed and

$$\Delta H = 81{,}730 - 0.47\ T - 0.731 \times 10^{-3}T^2,$$
$$\Delta F^\circ = 81{,}730 + 1.08\ T \log T + 0.731 \times 10^{-3}T^2 - 35.41\ T.$$

The calculations for liquid copper follow.

Liquid→Gas (Cu)

$$C_p(g)=4.97,$$
$$C_p(l)=7.50,$$
$$\Delta C_p=-2.53,$$
$$\Sigma=-R\ ln\ P-2.53\ ln\ T=-R\ ln\ P-5.83\log T,$$
$$\Delta H=\Delta H_0-2.53\ T,$$
$$\Delta F^{\circ}=\Delta H_0+5.83\ T\log T+I\ T.$$

At the melting point, 1,357° K., the equations for solid copper yield $\Delta H_{1357}=79{,}746$ and $\Delta H^{\circ}_{1357}=39{,}616$. For this temperature the free energies of vaporization of solid and liquid copper are equal, and the heats of vaporization differ by the heat of fusion, 3,110 calories per gram-atom. So for the vaporization of the liquid, $\Delta H_{1357}=79{,}746-3{,}110=76{,}636$ and $\Delta F^{\circ}_{1357}=39{,}616$. Substituting these values for ΔH and ΔF° at 1,357° K. in the last two equations above and solving for ΔH_0 and I there are found $\Delta H_0=80{,}070$ and $I=-48.08$. It will now be shown that these values are the same as those given by the spectroscopically determined figures. First the Σ value is calculated at each temperature in the liquid range as summarized in table 6. Then since $\Sigma-\frac{\Delta H_0}{T}=I$ (equation (12)), it follows that if the ΔH_0 value just obtained is used at each temperature to obtain values of $\frac{\Delta H_0}{T}$, the latter on subtraction from the corresponding Σ's should give a constant result, −48.08, within reasonable limits. The I values are shown in column 6 of table 6, the extreme variation being less than 0.1 percent.

TABLE 6.—*Σ-function calculations for liquid copper*

T	$\frac{\Delta F^{\circ}}{T}$ or $-R\ ln\ P$	$-5.83\log T$	Σ	$\frac{-80{,}070}{T}$	I
1,400	27.45	−18.34	9.11	−57.19	−48.08
1,500	23.82	−18.52	5.30	−53.38	−48.08
1,600	20.65	−18.68	1.97	−50.04	−48.07
1,700	17.85	−18.83	−.98	−47.10	−48.08
1,800	15.38	−18.98	−3.60	−44.48	−48.08
1,900	13.17	−19.12	−5.95	−42.14	−48.09
2,000	11.20	−19.24	−8.04	−40.04	−48.08
2,500	3.75	−19.81	−16.06	−32.03	−48.09
3,000	−1.15	−20.27	−21.42	−26.69	−48.11

Therefore, for the vaporization of liquid copper,

$$\Delta H=80{,}070-2.53\ T,$$

and

$$\Delta F^{\circ}=80{,}070+5.83\ T\log T-48.08\ T.$$

It may be well to emphasize at this point that the error in the spectroscopic part of these calculations is entirely negligible so that the accuracy is limited only by the errors in the specific-heat equations and in Harteck's vapor-pressure measurements. So far as crystalline copper is concerned the vapor pressure may be obtained at any temperature above 298.1° K., with no appreciably greater relative error than that in the measured value employed to obtain ΔE°_0, because the specific heats are known with relatively high accuracy in this case.

As an indication of the reliability of the equations for the liquid it is interesting to note that at 2,490° K. the calculated vapor pressure is 108 mm, while Sherman (*358*) reports a recent experimental value 105 mm, obtained by Fischer and Grieger at this temperature. Considering the high temperature involved the agreement is remarkable.

It is hoped that this typical example will serve to clarify this type of calculation. Numerous, slight variations in method may be advantageous under certain circumstances. Attention will be called to some of these in the next section, where the results of a number of similar calculations are given.

HEAT AND FREE ENERGY OF VAPORIZATION EQUATIONS

In this section heat and free energy of vaporization equations are derived for all the elements and inorganic compounds for which the necessary data are available. This survey is limited to substances which give a *component of the same chemical* constitution in the vapor as that of the solid or liquid. For example, decomposition reactions, such as the break-down of salt hydrates and carbonates, are omitted, since the gaseous phase in equilibrium with the solid (in these cases water and carbon dioxide) contains no measurable number of molecules having the composition of the solid, and the resulting pressures are not true vapor pressures in the sense this term is used here.

One of the main difficulties encountered in this work is the lack of information concerning gas densities. One or several molecular species may be present in the gaseous phase in appreciable amounts at a given temperature. In certain instances the different molecular species and their partial pressures are known, so that separate equations may be given for each variety of gas molecule. Or it may be known that only *one species* is present in appreciable amounts in a certain temperature range, in which case equations for that species are given which are based upon experimental results obtained in the specific range of temperature. Often such information is not available, and the molecular species must be chosen by means of analogy with similar substances, a rough knowledge of the magnitude of the entropy of vaporization, and consideration of the temperature range in which the substance has an appreciable vapor pressure.

In a few cases where conditions are complex and available information insufficient heat and free-energy equations are not given, but vapor-pressure relationships are derived. This procedure also has been followed for some substances for which the available experimental measurements are too crude or too scarce to warrant free-energy calculations. Consequently, such vapor-pressure equations may not be transformed into free-energy equations. *However, the* free-energy relationships tabulated here generally may be changed to forms more convenient for vapor-pressure calculations by means of the equation $\Delta F^\circ = -R\,T \ln P$. The exceptional cases, the majority of which are substances having high vapor pressures at low temperatures, are clearly indicated so that no confusion will result.

The specific-heat equations and other thermal data employed are taken from two earlier compilations of the author (*199, 200*) whenever possible. Where no measured values are available the specific heats or differences in specific heats used are merely assumptions based on analogy and may involve considerable uncertainty. Sometimes it has been necessary to ignore specific heats entirely. When assumptions have been made, if it is so desired, the heat and free-energy equations may be considered as empirical relationships which fit the experimental data and the corresponding ΔC_p or C_p equations no more than functions which are written down in forms analogous with those that would obtain if the specific heats were known.

Many values for heat and entropy accompanying changes of state, which have never been directly measured, have been extracted from the derived heat and free energy of vaporization equations. These figures may be used to supplement those previously given (*199*, *200*).

All thermodynamic data are expressed in 15° gram-calories per gram formula weight of gas and all temperatures in degrees absolute (Kelvin). The symbols *s*, *l*, and *g* refer to the solid, liquid, and gaseous states, respectively, the first being restricted to cases where only one crystalline modification is known to exist in the temperature range under consideration. The letters α, β, γ, and δ are used to designate different crystalline forms of the same substance for which the transformation points occur above ordinary temperatures, α being the stable variety at ordinary temperatures, and β, γ, and δ being stable in temperature ranges progressively higher. The symbols S_{I}, S_{II}, and S_{III} have been used here in an analogous manner to denote different crystalline forms of the same substance when transitions occur below ordinary temperatures, S_{I} being the highest temperature form and S_{II} and S_{III} forms stable in progressively lower temperature ranges. Since the last set of symbols has been used only for the condensed gases no confusion can arise in the meaning or assignment of these letters. In a few cases other designations corresponding to common usage have been employed.

ALUMINUM

Element.—The boiling point of aluminum at 1 atmosphere pressure was measured by Greenwood (*131*) and by Von Wartenberg (*425*). Their results show a considerable disagreement, being, respectively, 2,073° and 2,473°. A comparison of Greenwood's boiling-point determinations with those of other investigators makes it appear likely that his figure for aluminum is low by 255°. Consequently, the rounded value, 2,330°, is used in conjunction with Overstreet's (*273*) free-energy table for the gas to calculate the heat and free energy of vaporization by the methods illustrated in the previous section. At this temperature, $\frac{F^\circ - E^\circ_0}{T} = -44.53$ and $\frac{F^\circ_c - E^\circ_{c,0}}{T} = -15.81$. Therefore $\frac{\Delta E^\circ}{T} - \frac{\Delta E^\circ_0}{T} = -28.72$. However, at the boiling point $\Delta F^\circ = 0$, so it follows that $\Delta E^\circ_0 = 66{,}920$ calories per gram-atom. In table 7 the values of $\frac{\Delta F^\circ}{T}$ are summarized. The second column of this table is taken from the work of Overstreet.

TABLE 7.—*Free energy of vaporization data for aluminum*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_s - E^\circ_{s,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−33.766	−3.13	−30.64	224.49	193.85
400	−35.375	−4.28	−31.10	167.30	136.20
500	−36.579	−5.27	−31.31	133.84	102.53
600	−37.548	−6.14	−31.41	111.53	80.12
700	−38.360	−6.92	−31.44	95.60	64.16
800	−39.059	−7.64	−31.42	83.65	52.23
900	−39.671	−8.29	−31.38	74.36	42.98
1,000	−40.217	−9.09	−31.13	66.92	35.79
1,100	−40.708	−9.88	−30.83	60.84	30.01
1,200	−41.155	−10.60	−30.56	55.77	25.21
1,300	−41.566	−11.25	−30.32	51.48	21.16
1,400	−41.946	−11.85	−30.10	47.80	17.70
1,500	−42.299	−12.39	−29.91	44.61	14.70
1,600	−42.627	−12.90	−29.73	41.82	12.09
2,000	−43.762	−14.64	−29.12	33.46	4.34
2,100	−44.009	−15.01	−29.00	31.87	2.87
2,200	−44.245	−15.37	−28.87	30.42	1.55
2,300	−44.470	−15.71	−28.76	29.10	.34
2,400	−44.681	−16.04	−28.64	27.88	−.76

From the last column of table 7 the following heat and free energy of vaporization equations may be obtained:

Solid→Gas (Al)

$C_p(g) = 5.00,$
$C_p(s) = 4.80 + 3.22 \times 10^{-3}T,$
$\Delta C_p = 0.20 - 3.22 \times 10^{-3}T,$
$\Delta H = 67{,}580 + 0.20T - 1.61 \times 10^{-3}T^2,$
$\Delta F^\circ = 67{,}580 - 0.46T \log T + 1.61 \times 10^{-3}T^2 - 32.20\ T,$
$\Delta H_{298.1} = 67{,}497;\ \Delta F^\circ_{298.1} = 57{,}785,$
$\Delta S_{298.1} = 32.58;\ S_{298.1}(g) = 39.33.$

Liquid→Gas (Al)

$C_p(g) = 5.00,$
$C_p(l) = 7.00,$
$\Delta C_p = -2.00,$
$\Delta H = 65{,}680 - 2.00\ T,$
$\Delta F^\circ = 65{,}680 + 4.61T \log T - 43.72\ T,$
B. P. = 2330°; $\Delta H = 61{,}022;\ \Delta S = 26.2,$
$\Delta H_{298.1} = 65{,}084;\ \Delta F^\circ_{298.1} = 56{,}047.$

The specific heat of aluminum gas is taken as 5.00 instead of the classical value, $\frac{3}{2}R = 4.97$, to account for the rise in specific heat due to the occupation at high temperatures of energy levels higher than the zero level. The figure 5.00 is a mean value for the range 298.1 to 3,000°.

The accuracy of these calculations is limited largely by the figure for the boiling-point temperature used for obtaining ΔE°_0, since the error in ΔH_0 may be shown to have the same magnitude as the error in ΔE°_0.

Oxide.—Ruff and Konschak (*327*) (2,633–2,893°) and Ruff and Schmidt (*335*) (2,103–2,503°) have measured the vapor pressure of Al_2O_3. Due to the difficulties in research at such high temperatures their results are very discordant, and the data do not warrant free-energy calculations. However, the results of the former authors may be used to obtain an approximate expression for the vapor pressure of the liquid.

Liquid→Gas (Al_2O_3).

$$\log P(at.) = -\frac{27,320}{T} + 8.415.$$

This equation extrapolates to 1 atmosphere pressure at 3,250°.

Bromide.—Liquid aluminum bromide, Al_2Br_6, was studied by Fischer, Rahlfs, and Benze (*109*) (391–523°). A Σ-function plot of their results, based on the assumption that $C_p = 34$ for the gas, was made. The data in this case are very concordant and permit no choice in the manner of drawing the straight line. With $\Delta H_0 = 24,160$, the extreme variation in the I values is only 0.2 unit, and the mean value of I is -202.52. The results for the vaporization of the liquid follow:

Liquid→Gas (Al_2Br_6)

$C_p(g) = 34.0,$
$C_p(l) = 59.0,$
$\Delta C_p = -25.0,$
$\Delta H = 24,160 - 25.0T,$
$\Delta F^\circ = 24,160 + 57.6T \log T - 200.52T,$
B. P. = 529.5°; $\Delta H_{529.5} = 10,920$; $\Delta S_{529.5} = 20.6,$
$\Delta H_{298.1} = 16,710$; $\Delta F^\circ_{298.1} = 6,276.$

Similar results for the vaporization of the solid may be obtained from those for the liquid since the heat of fusion at the melting point, 370.6°, is known.

Solid→Gas (Al_2Br_6)

$C_p(g) = 34.0,$
$C_p(s) = 37.48 + 37.32 \times 10^{-3}T,$
$\Delta C_p = -3.48 - 37.32 \times 10^{-3}T,$
$\Delta H = 24,170 - 3.48T - 18.66 \times 10^{-3}T^2,$
$\Delta F^\circ = 24,170 + 8.01T \log T + 18.66 \times 10^{-3}T^2 - 82.07T,$
$\Delta H_{298.1} = 21,475$; $\Delta F^\circ_{298.1} = 7,271.$

Chloride.—Vapor-pressure measurements of aluminum chloride have been made by Fischer, Rahlfs, and Benze (*109*) (395–450°), Friedel and Crafts (*112*) (441–486°), Maier (*232*) (342–454°), Smits, Meyering, and Kamerans (*374*, *375*) (401–491°), and Treadwell and Terebesi (*421*) (389–476°). The Σ-function values were calculated on the assumption of $C_p = 34.0$ for 1 mole of Al_2Cl_6 gas. On the solid, Fischer, Rahlfs, and Benze, Smits, Meyering and Kamerans, and Treadwell and Terebesi are in substantial agreement. Maier obtained somewhat higher pressures and Friedel and Crafts somewhat lower. However, the straight line of the Σ v. $\frac{1}{T}$ plot drawn to fit the three sets of data in agreement is a fair representation of the mean of the remaining two sets. Accordingly, the following results are obtained for the vaporization of the solid.

Solid→Gas (Al_2Cl_6)

$C_p(g) = 34.0,$
$C_p(s) = 26.50 + 56.00 \times 10^{-3}T,$
$\Delta C_p = 7.50 - 56.00 \times 10^{-3}T,$
$\Delta H = 29,100 + 7.50T - 28.00 \times 10^{-3}T^2,$
$\Delta F^\circ = 29,100 - 17.27T \log T + 28.00 \times 10^{-3}T^2 - 31.01T,$
S.P. = 453.3°; $\Delta H_{453.3} = 26,747$; $\Delta S_{453.3} = 59.1,$
$\Delta H_{298.1} = 28,848$; $\Delta F^\circ_{298.1} = 9,605.$

The value for the entropy of sublimination, $\Delta S_{453.3} = 59.1$, would appear abnormally high, except for the fact that the measured heat of fusion at a slightly higher temperature (465.6°) is also high (16,960 calories per gram formula weight of Al_2Cl_6).

Three of the previously mentioned sets of data extend into the liquid range, since this substance melts at 465.6° under its own vapor pressure. For the liquid, the value of ΔH_0 may be obtained from the heat of fusion and the ΔH equation for the solid. This procedure was followed and I calculated from the Σ-function values and $\frac{\Delta H_0}{T}$ in the usual manner. The extreme variation is the values of I calculated from Smits, Meyering, and Benze's data is only 0.02 unit. In other words, the slopes of the Σ-function plots for solid and liquid confirm the measured value of heat of fusion. The calculations for liquid aluminum chloride are summarized below.

Liquid→Gas (Al_2Cl_6)

$C_p(g) = 34.0,$
$C_p(l) = 62.4,$
$\Delta C_p = -28.4,$
$\Delta H = 22{,}785 - 28.4T,$
$\Delta F^\circ = 22{,}785 + 65.4T \log T - 225.03T,$
$\Delta H_{298.1} = 14{,}319;\ \Delta F^\circ_{298.1} = 3{,}944.$

The equations for the liquid are valid up to 490°. One would hesitate to extrapolate them much beyond this temperature, since the pressure is over 3 atmospheres.

Iodide.—Fischer, Rahlfs, and Benze (*109*) (494–645°) also made vapor-pressure measurements of liquid aluminum iodide. The gas phase in this case is composed largely of Al_2I_6 molecules, but some dissociation into the AlI_3 species may occur in the temperature range covered by the measurements. The above authors estimate a dissociation of 24 percent at the boiling point. There are no data available for determining the partial pressures of these two molecular species over a range of temperature, consequently it is necessary at present to consider the total vapor pressure as being due to Al_2I_6 molecules.

The Σ v. $\frac{1}{T}$ plot, however, does not indicate any marked change of percentage dissociation with the temperature, and furthermore the entropy of vaporization calculated on the assumption of no dissociation is normal. Therefore, although it is not possible to state definitely the extent of dissociation, the value 24 percent at the boiling point appears to be too high. The results for the vaporization of the liquid follow.

Liquid→Gas (Al_2I_6)

$C_p(g) = 34.0,$
$C_p(l) = 57.6,$
$\Delta C_p = -23.6,$
$\Delta H = 30{,}900 - 23.6\ T,$
$\Delta F^\circ = 30{,}900 + 54.4\ T \log T - 200.25\ T,$
B. P. = 658.6°; $\Delta H_{658.6} = 15{,}357;\ \Delta S_{658.6} = 23.3,$
$\Delta H_{298.1} = 23{,}865;\ \Delta F^\circ_{298.1} = 11{,}331.$

The extreme variation in the individual I values is 0.46 unit, but if two values are discarded the variation is 0.28 unit.

No vapor-pressure figures are available for solid aluminum iodide, but heat and free energy of vaporization equations may be obtained from the results for the liquid and the heat of fusion.

Solid→Gas (Al_2I_6)

$C_p(g)=34.0,$
$C_p(s)=33.76+45.32\times10^{-3}T,$
$\Delta C_p=0.24-45.32\times10^{-3}T,$
$\Delta H=32{,}680+0.24\ T-22.66\times10^{-3}T^2,$
$\Delta F^\circ=32{,}680-0.55\ T\log T+22.66\times10^{-3}T^2-68.07\ T,$
$\Delta H_{298.1}=30{,}738;\ \Delta F^\circ_{298.1}=13{,}996.$

ANTIMONY

Element.—The vapor pressure of liquid antimony was studied by Greenwood (*131*) (1,713°), Leitgebel (*223*) (1,908°), Ruff and Bergdahl (*316*) (1,348–1,598°), and Winkler (*441*) (1,238°). The results obtained show great disagreement, the normal boiling-point figures having a spread of some 300°. To settle this question, Maier and Anderson (*236*) have made some boiling-point determinations in helium at pressures between 5 and 30 mm. Their results indicate that Greenwood's boiling point (760 mm) is about right, and so the equations to be given are based on the data of Maier and Anderson, and Greenwood. There appears to be considerable confusion concerning the molecular species present in the gaseous phase (*243, vol. 9, p. 365*). Polyatomic molecules are to be expected, but the particular species and the variation of partial pressures with temperature and pressure are not known. For the present purpose it is assumed that at the temperatures involved the gas is largely monatomic.

Liquid→Gas (Sb)

$C_p(g)=4.97,$
$C_p(l)=7.15,$
$\Delta C_p=-2.18,$
$\Delta H=50{,}400-2.18\ T,$
$\Delta F^\circ=50{,}400+5.02\ T\log T-45.65\ T,$
B. P. = 1,713°; $\Delta H_{1713}=46{,}666;\ \Delta S_{1713}=27.2,$
$\Delta H_{298.1}=49{,}750;\ \Delta F^\circ_{298.1}=40{,}495.$

The heat and free-energy equations for the vaporization of solid antimony may be obtained from the above results, the melting-point temperature, and the heat of fusion.

Solid→Gas (Sb)

$C_p(g)=4.97,$
$C_p(s)=5.51+1.78\times10^{-3}\ T,$
$\Delta C_p=-0.54-1.78\times10^{-3}T,$
$\Delta H=54{,}420-0.54\ T-0.89\times10^{-3}T^2,$
$\Delta F^\circ=54{,}420+1.24\ T\log T+0.89\times10^{-3}T^2-39.73\ T,$
$\Delta H_{298.1}=54{,}180;\ \Delta F^\circ_{298.1}=43{,}570;\ S_{298.1}\ (g)=46.1.$

The entropy of the gas at 298.1° calculated from the Sackur equation without correction for the multiplicity in the lowest energy state is 40.31. However, if antimony and bismuth are analogous so far as the type of energy level is concerned, this figure should be increased by $R\ ln\ 4=2.75$, which gives 43.06 for monatomic antimony. The value obtained from the heat and free-energy equations and the entropy of the solid is seen to be three units higher. This is probably due almost entirely to the assumption of monatomic gas made in treating the vapor-pressure results.

Oxide.—Hincke (*163*) (450–900°) has measured vapor pressures of three forms of antimony trioxide—cubic, orthorhombic, and liquid. His results for the two crystalline forms are satisfactory; but those for the liquid are subject, at the higher temperatures, to error caused by the slagging of his containers, with consequent lowering of the mole fraction of antimony trioxide present. The gas is known to consist of Sb_4O_6 molecules, and since there are no satisfactory means of approximating the specific heat of a gas of this type, ΔC_p is taken as zero. The difference in free energy at 298.1° between the cubic and orthorhombic forms, which was obtained by Roberts and Fenwick (*307*), was used as a guide in deriving the equations for the orthorhombic variety.

Solid (cubic)→Gas (Sb_4O_6)
$\Delta H = 47{,}600,$
$\Delta F^\circ = 47{,}600 - 42.88\ T,$
$\Delta F^\circ_{298.1} = 34{,}817.$

Solid (orthorhombic)→Gas (Sb_4O_6)
$\Delta H = 44{,}820,$
$\Delta F^\circ = 44{,}820 - 39.58\ T,$
$\Delta F^\circ_{298.1} = 33{,}021.$

Liquid→Gas (Sb_4O_6)
$\Delta H = 17{,}820,$
$\Delta F^\circ = 17{,}830 - 10.50\ T,$
$\text{B.P.} = 1{,}698^\circ;\ \Delta S_{1698} = 10.5,$
$\Delta F^\circ_{298.1} = 14{,}700.$

From these equations it is seen that the transition point between cubic and orthorhombic antimony trioxide is at 842°, and the heat of transformation is 2,780 calories per formula weight of Sb_4O_6. An abnormally low entropy of vaporization is obtained for the liquid, but this is also shown by some measurements of Maier (*235*). The computed heat of fusion of the orthorhombic form, 26,990 calories per gram-formula weight at the melting point, 928°, appears high.

Trichloride.—Liquid antimony trichloride was studied by Anschütz and Evans (7) (376–387°), Braune and Tiedje (*39*) (373–428°), and Maier (*232*) (323–500°). The pressures measured by Maier are very concordant and somewhat higher than those of the other investigators. A Σ vs. $\frac{1}{T}$ plot for his results (assuming $C_p = 18$ calories per mole of $SbCl_3$ gas) gives an extreme variation in I of 0.52 unit, but if one point is omitted the variation becomes 0.29 unit.

Liquid→Gas ($SbCl_3$)
$C_p(g) = 18.0,$
$C_p(l) = 32.0,$
$\Delta C_p = -14.0,$
$\Delta H = 17{,}250 - 14.0\ T,$
$\Delta F^\circ = 17{,}250 + 32.2\ T \log T - 121.74\ T,$
$\text{B. P.} = 492^\circ;\ \Delta H_{492} = 10{,}362;\ \Delta S_{492} = 21.05$
$\Delta H_{298.1} = 13{,}077;\ \Delta F^\circ_{298.1} = 4{,}710.$

The results for the liquid are used in calculating those for the solid. The additional data required are the melting point (346°) and the heat of fusion (3,030 calories per gram formula weight). The latter datum was obtained by Tolloczko (*409*, *410*).

Solid→Gas ($SbCl_3$)

$C_p(g)=18.0,$
$C_p(s)=10.3+51.1\times10^{-3}T,$
$\Delta C_p=7.7-51.1\times10^{-3}T,$
$\Delta H=15{,}830+7.7\,T-25.6\times10^{-3}T^2,$
$\Delta F^\circ=15{,}830-17.73\,T\log T+25.6\times10^{-3}T^2+0.30\,T,$
$\Delta H_{298.1}=15{,}855;\ \Delta F^\circ_{298.1}=5{,}111.$

Pentachloride.—Anschütz and Evans (*7*) (341–352°) and Braune and Tiedje (*39*) (324–431°) have made vapor-pressure measurements of liquid $SbCl_5$. This substance undergoes decomposition, which becomes marked around 350°. Consequently, since at best the calculations for this substance are only approximations, ΔC_p will be neglected.

Liquid→Gas ($SbCl_5$)

$\Delta H=11{,}570,$
$\Delta F^\circ=11{,}570-26.0\,T,$
$\Delta F^\circ_{298.1}=3{,}819.$

The boiling point extrapolated from the free-energy equation, 445°, does not have much significance because of the decomposition. The entropy of vaporization, 26.0 units, is also undoubtedly in error due to decomposition effects. However, the vapor-pressure relationship corresponding to the free energy of vaporization equation represents the actual experimental pressure data well. Information is not available for calculations for the solid.

ARGON

Element.—Vapor-pressure measurements of argon were made by Crommelin (*71*) (68–84°), Born (*37*) (65–90°), Holst and Hamburger (*171*) (83–90°), Ramsay and Travers (*296*) (77–156°), and Olszewski (*266*) (86°). In making the calculations an average was taken of the results of Born, Holst and Hamburger, and Ramsay and Travers. No correction was made for gas imperfection, and ΔC_p was taken as zero.

Solid→Gas (A)

$\Delta H=1{,}880,$
$\Delta F^\circ=1{,}880-21.67\,T.$

Liquid→Gas (A)

$\Delta H=1{,}590,$
$\Delta F^\circ=1{,}590-18.21\,T,$
B. P.$=87.3;\ \Delta S_{87.3}=18.21.$

Heat of vaporization and entropy values derived from the above equations are subject to the errors involved in neglecting gas imperfection, ΔC_p, etc. However, these effects nearly cancel in the calculation of free energy. The average I values computed separately for the three sets of data considered have a spread of 0.15 unit for the solid and 0.05 unit for the liquid. The melting point is 83.8°, and 290 calories per gram-atom is obtained for the heat of fusion.

ARSENIC

Element.—The following investigators have studied the vapor pressure of arsenic: Gibson (*125*) (742–842°), Horiba (*172*) (723–1,126°), Preuner and Brockmöller (*291*) (673–873°), Ruff and Bergdahl (*316*) (732–838°), and Ruff and Mugdan (*333*) (777–906°). Preuner and Brockmöller have studied the reactions $As_4=2As_2$ and $As_2=2As$ in the gas phase. At 800° their results show that the partial pressures of As_2 and As are negligible in comparison with that of As_4, or at this temperature the difference between the total vapor pressure and the As_4 partial pressure is well within the limits of error in the measured total vapor-pressure values. Consequently, up to temperatures in this region the gas may be treated as though it were composed solely of As_4 molecules. In this case, if ΔC_p is neglected the following results are obtained for the gray or rhombic form of arsenic:

Solid→Gas (As_4)
$\Delta H = 31{,}000$,
$\Delta F^\circ = 31{,}000 - 35.12\ T$,
S. P. = 883°; $\Delta S_{883} = 35.1$,
$\Delta F^\circ_{298.1} = 20{,}531$.

Trioxide.—Vapor-pressure measurements of arsenic trioxide have been made by Niederschulte (*260*) (514–580°), Rushton and Daniels (*340*) (do not present actual data but give equations), Smellie (*366*) (333–423°), Smits and Beljaars (*368*) (537–616°), Stelzner (*380*) (426–438°), and Welch and Duschak (*436*) (373–573°). The solid exhibits two crystalline modifications, the orthorhombic, stable below 506°, and the monoclinic, stable between 506° and the melting point, 586°. The gas has the composition As_4O_6 and, as in the case of the corresponding antimony compound, ΔC_p is ignored. Rushton and Daniels, and Smits and Beljaars obtained much lower pressure results for the orthorhombic form than did Smellie and Welch and Duschak. In fact, the results of these two last-mentioned investigators are about a mean of the figures for the orthorhombic and monoclinic forms obtained by others. For the present purpose the data of Rushton and Daniels, and Smits and Beljaars on the orthorrhombic form are averaged. This is done by assigning the same ΔH_0 to both sets and taking the mean of the average I values for the two sets, which are −49.63 and −49.33, respectively. The equations for the monoclinic and liquid forms are based largely on the results of Smits and Beljaars.

Orthorhombic→Gas (As_4O_6)
$\Delta H = 30{,}520$,
$\Delta F^\circ = 30{,}520 - 49.48\ T$.
$\Delta F^\circ_{298.1} = 15{,}770$.
Monoclinic→Gas (As_4O_6)
$\Delta H = 22{,}300$,
$\Delta F^\circ = 22{,}300 - 33.24\ T$.
$\Delta F^\circ_{298.1} = 12{,}391$.
Liquid→Gas (As_4O_6)
$\Delta H = 14{,}300$,
$\Delta F^\circ = 14{,}300 - 19.58\ T$,
B. P. = 730.3°; $\Delta S_{730.3} = 19.6$,
$\Delta F^\circ_{298.1} = 8{,}463$.

From these equations it follows that the transition point of the orthorhombic → monoclinic transformation is at 506°, the heat and entropy of transformation being 8,220 calories per formula weight and 16.2 calories per degree per formula weight, respectively. The monoclinic form melts at 586° with a heat of fusion of 8,000 calores and an entropy of fusion of 13.7 calores per degree per formula weight.

Trichloride.—Baxter, Bezzenberger, and Wilson (*19*) (273–372°) and Maier (*232*) (282–397°) have measured the vapor pressure of liquid arsenic trichloride. Their results do not agree, although the values from each investigation are consistent among themselves. In obtaining the following equations the results of Maier were adopted, since Baxter, Bezzenberger, and Wilson assumed a perfect gas in obtaining their results below 323°, and their figures above 323° are probably in error due to the mutual solubility of arsenic trichloride and sulphuric acid, as was discussed by Maier.

Liquid→Gas ($AsCl_3$)

$C_p(g)=20.3,$
$C_p(l)=31.9,$
$\Delta C_p=-11.6,$
$\Delta H=12{,}150-11.6\,T,$
$\Delta F^\circ=12{,}150+26.7\,T\log T-100.11\,T,$
B. P.$=395°$; $\Delta H_{395}=7{,}567$; $\Delta S_{395}=19.2,$
$\Delta H_{298.1}=8{,}692$; $\Delta F^\circ_{298.1}=2{,}009$

Pentafluoride.—Ruff, Braida, Bretschneider, Menzel, and Plant (*337*) (156–200°) have reported vapor-pressure data on solid and liquid arsenic pentafluoride, AsF_5. Since the temperatures involved are considerably below ordinary temperatures and nothing is known regarding the specific heat of this substance, ΔC_p is taken as zero to obtain the following results.

Solid→Gas (AsF_5)

$\Delta H=7{,}780,$
$\Delta F^\circ=7{,}780-37.15\,T.$

Liquid→Gas (AsF_5)

$\Delta H=4{,}980,$
$\Delta F^\circ=4{,}980-22.60\,T,$
B. P.$=220.3°$; $\Delta S_{220.3}=22.6.$

Other relevant thermal data corresponding to these equations are the melting point, 192.4°, the heat of fusion, 2,800 calories, and the entropy of fusion, 14.55 calories per degree.

BARIUM

Element.—The vapor pressure of liquid barium was investigated by Hartmann and Schneider (*146*) (1,333–1,411°) and Ruff and Hartmann (*322*) (1,203–1,403°). Their data are not in agreement but apparently the results of Hartmann and Schneider may be taken as superseding the older ones of Ruff and Hartmann. A Σ v. $\frac{1}{T}$ plot of the figures of Hartmann and Schneider gives $\Delta H_0=40{,}500$ and $I=-40.32$, the extreme variation in I being 0.39. Data are not available for obtaining equations for solid barium.

Liquid→Gas (Ba)

$C_p(g)=4.97,$
$C_p(l)=7.50,$
$\Delta C_p=-2.53,$
$\Delta H=40{,}500-2.53\,T,$
$\Delta F^\circ=40{,}500+5.83\,T\log T-40.32\,T,$
B. P.$=1911°$; $\Delta H_{1911}=35{,}665$; $\Delta S_{1911}=18.7,$
$\Delta H_{298.1}=39{,}746$; $\Delta F^\circ_{298.1}=32{,}781.$

Oxide.—Vapor-pressure measurements of barium oxide were made by Claasen and Veenemans (*64*) (1,200–1,500°) and Thompson and Armstrong (*407*) (1,550–1,680°). The data do not warrant free-energy calculations, so a log P equation only is given. This equation is that given by Claasen and Veenemans with mm changed to atmospheres.

Solid→Gas (BaO)

$$\log P(at.) = -\frac{19{,}700}{T} + 5.99.$$

BERYLLIUM

Bromide.—Rahlfs and Fischer (*294*) (624–695°) have measured the vapor pressure of solid beryllium bromide. They state that the gas is composed of Be_2Br_4 and $BeBr_2$ molecules, the dissociation being around 50 percent at the sublimation point. Under these conditions and with the present meager information no free-energy calculations are possible. However, an equation is given for the total vapor pressure.

Solid→Gas ($Be_2Br_4 + BeBr_2$)

$$\log P(at.) = -\frac{6{,}540}{T} + 8.754,$$
$$\text{S. P.} = 747°.$$

Chloride.— Rahlfs and Fischer (*294*) (613–733°) also studied solid and liquid beryllium chloride. The same state of affairs concerning dissociation exists here as in the case of the bromide, and only equations for the total vapor pressure are given.

Solid→Gas ($Be_2Cl_4 + BeCl_2$)

$$\log P(at.) = -\frac{6{,}450}{T} + 8.553.$$

Liquid→Gas ($Be_2Cl_4 + BeCl_2$)

$$\log P(at.) = -\frac{5{,}990}{T} + 7.875,$$
$$\text{B. P.} = 761°.$$

This substance melts at 678°.

Iodide.—Solid beryllium iodide also was studied by Rahlfs and Fischer (*294*) (578–703°). Here again and for the same reasons a total vapor-pressure equation only is included.

Solid→Gas ($Be_2I_4 + BeI_2$)

$$\log P(at.) = -\frac{5{,}990}{T} + 7.882,$$
$$\text{S. P.} = 760°.$$

This substance sublimes at 760°, which is also approximately the melting point.

BISMUTH

Element.—Barus (*16*) (1,425–1,506°), Greenwood (*131, 132, 133*) (1,473–2,333°), Leitgebel (*223*) (1,833°), and Ruff and Bergdahl (*316*) (1,483–1,763°) have measured vapor pressures of liquid bismuth. These results show wide disagreement, and there is also considerable uncertainty concerning the molecular species present in the gas. To settle the question of the course of the vapor-pressure curve Maier and Anderson (*236*) have made some boiling-point determinations under reduced pressure and have obtained concordant results covering the range 2 to 35 mm. Their data extrapolate nicely into the normal boiling-point determination of Greenwood. In view of the uncertainty regarding the complexity of the gas only an empirical vapor-pressure equation, based on the data of Maier and Anderson and of Greenwood, is given.

Liquid→Gas (Bi_x)

$$\log P(at.) = -\frac{16{,}700}{T} - 1.32 \log T + 14.140,$$

B. P. = 1,693°.

Bromide.—Evnevich and Sukhodskii (*101*) (614–767°) have made a very concordant set of vapor-pressure measurements of liquid bismuth bromide. A Σ-function plot of their data, assuming $\Delta C_p = -14$ per mole of $BiBr_2$, is a straight line with an extreme variation in I of 0.07 unit.

Liquid→Gas ($BiBr_3$)

$\Delta C_p = -14,$
$\Delta H = 28{,}300 - 14\ T,$
$\Delta F° = 28{,}300 + 32.2\ T \log T - 130.84\ T,$
B. P. = 734°; $\Delta H_{734} = 18{,}024$; $\Delta S_{734} = 24.6,$
$\Delta H_{298.1} = 24{,}127$; $\Delta F°_{298.1} = 13{,}048.$

Chloride.—Vapor-pressure measurements of bismuth chloride were made by Evnevich and Sukhodskii (*101*) (612–746°) and Maier (*232*) (367–742°). The two sets of data are in good agreement, except for two values below 4 cm given by Maier. The extreme variation in I for both sets of results (excluding two of Maier's points) is 0.29 unit.

Liquid→Gas ($BiCl_3$)

$\Delta C_p = -14,$
$\Delta H = 27{,}350 - 14\ T,$
$\Delta F° = 27{,}350 + 32.2\ T \log T - 130.20\ T,$
B. P. = 714°; $\Delta H_{714} = 17{,}354$; $\Delta S_{714} = 24.3,$
$\Delta H_{298.1} = 23.177$; $\Delta F°_{298.1} = 12{,}288.$

BORON

Bromide.—Stock and Kusz (*384*) (223–363°) have measured the vapor pressure of boron bromide. BBr_3, in the liquid state. They also give one result for the solid. The data have a high relative accuracy, the extreme variation in I being 0.21. The necessary data are lacking for obtaining equations for the solid.

Liquid→Gas (BBr_3)

$\Delta C_p = -14,$
$\Delta H = 12{,}400 - 14\ T,$
$\Delta F° = 12{,}400 + 32.2\ T \log T - 116.51\ T,$
B. P. = 364.4°; $\Delta H_{364.4} = 7{,}298$; $\Delta S_{364.4} = 20.0,$
$\Delta H_{298.1} = 8{,}227$; $\Delta F°_{298.1} = 1{,}419.$

Chloride.—Boron chloride, BCl_3, was studied by Regnault (*300*) (245–355°) and Stock and Priess (*391*) (193–286°). The two sets of measurements are in only fair agreement, and the later work of Stock and Priess is utilized. Their data above 213° show an extreme variation in I of 0.10 unit. Four lower-temperature determinations show a larger variation.

Liquid→Gas (BCl_3)

$\Delta C_p = -14,$
$\Delta H = 9{,}680 - 14\ T,$
$\Delta F° = 9{,}680 + 32.2\ T \log T - 112.97\ T,$
B. P. = 285.6°; $\Delta H_{285.6} = 5{,}682$; $\Delta S_{285.6} = 19.9,$
$\Delta H_{298.1} = 5{,}507$; $\Delta F°_{298.1} = -245.$

Fluoride.—Measurements of the vapor pressure of boron fluoride, BF_3, were made by Booth and Carter (*36*) (223–261°), Pohland and Harlos (*288*) (127–170°), and Ruff, Braida, Bretschneider, Menzel, and Plant (*337*) (123–169°). The data of Booth and Carter are above 13 atmospheres and are not useful for the present purpose. The measurements of the other investigators are in agreement.

In this case it is possible to derive equations for both the solid and liquid states. On account of the low temperatures involved ΔC_p is ignored.

Solid→Gas (BF_3)
$\Delta H = 5{,}100,$
$\Delta F^\circ = 5{,}100 - 30.14\ T.$
Liquid→Gas (BF_3)
$\Delta H = 4{,}620,$
$\Delta F^\circ = 4{,}620 - 26.83\ T,$
B. P. = 172.2°; $\Delta S_{172.2} = 26.8.$

These equations show the heat of fusion to be 480 calories per gram formula weight at the melting point, 145°. The entropy of vaporization, 26.8, seems abnormally high in comparison with the results for the bromide and chloride.

Hydrides.—Boron forms a whole series of hydrides somewhat analogous to the hydrocarbons. Vapor-pressure measurements have been made of a number of these compounds by Stock and his coworkers.

The compound B_2H_6 was studied by Stock and Frederici (*382*) (143–183°) and Stock and Kusz (*383*) (125–181°). The later work of Stock and Kusz is adopted, since the two sets of measurements show considerable disagreement. ΔC_p is assumed zero, since the temperatures involved are so low. The melting point of this compound is 107.6°.

Liquid→Gas (B_2H_6)
$\Delta H = 3{,}685,$
$\Delta F^\circ = 3{,}685 - 20.39\ T,$
B. P. = 180.7°; $\Delta S_{180.7} = 20.4.$

Stock and Kusz (*383*) (160–291°), Stock and Massenez (*386*) (279–289°), and Stock and Pohland (*388*) (154–214°) have measured the vapor pressure of the substance B_4H_{10}. The measurements for the liquid state are in good agreement, but those for the solid are scattered. Consequently, equations are given for the liquid range only.

Liquid→Gas (B_4H_{10})
$\Delta H = 6{,}470,$
$\Delta F^\circ = 6{,}470 - 22.39\ T,$
B. P. = 289°; $\Delta S_{289} = 22.4,$
$\Delta F^\circ_{298.1} = -204.$

This substance melts at 153.3°.

Stock and Kusz (*383*) (232–288°) also have made measurements of the vapor pressure of B_5H_9. This substance melts at 226.2°.

Liquid→Gas (B_5H_9)
$\Delta H = 7{,}700,$
$\Delta F^\circ = 7{,}700 - 23.26\ T,$
B. P. = 331°; $\Delta S_{331} = 23.3,$
$\Delta F^\circ_{298.1} = 766.$

The compound, B_5H_{11}, was studied by Stock and Pohland (*388*) (220–273°).

Liquid→Gas (B_5H_{11})
$\Delta H = 8{,}500$,
$\Delta F^\circ = 8{,}500 - 25.01\ T$,
B. P. = 340°; $\Delta S_{340} = 25.0$,
$\Delta F^\circ_{298.1} = 1{,}045$.

The entropy of vaporization figure, 25.0, is probably too high.

Stock and Kusz (*383*) report one vapor-pressure measurement of the hydride B_6H_{10}, 7.2 mm at 273.1°. Stock and Massenez (*386*) (233–297°) have measured the vapor pressure of B_6H_{12}. Calculations show that their data give an impossibly low entropy of vaporization, consequently equations for this substance are omitted.

The hydride, $B_{10}H_{14}$, also was studied by Stock and Pohland (*389*) (328–429°). Their measurements include both the solid and liquid ranges, as this substance melts at 372.8°. When heated to moderate temperatures this substance decomposes, the decomposition being very marked around 440°.

Solid→Gas ($B_{10}H_{14}$)
$\Delta H = 19{,}400$,
$\Delta F^\circ = 19{,}400 - 44.88\ T$,
$\Delta F^\circ_{298.1} = 6{,}021$.
Liquid→Gas ($B_{10}H_{14}$)
$\Delta H = 11{,}600$,
$\Delta F^\circ = 11{,}600 - 23.96\ T$,
$\Delta F^\circ_{298.1} = 4{,}458$.

These equations indicate a heat of fusion of 7,800 calories at 372.8° and a corresponding entropy of fusion of 20.9 calories per degree.

Derivatives of boron hydrides.—Stock, Kusz, and Priess (*401*) (193–268°) have made vapor-pressure measurements of the compound B_2H_5Br. The melting point of this substance is 169°.

Liquid→Gas (B_2H_5Br)
$\Delta H = 6{,}230$,
$\Delta F^\circ = 6{,}230 - 21.54\ T$,
B. P. = 289°; $\Delta S_{289} = 21.5$,
$\Delta F^\circ_{298.1} = -191$.

The derivative, $B_3N_3H_6$, was studied by Stock and Pohland (*387*) (197–273°). This substance melts at 215°, but equations for the liquid only are included since the data for the solid are erratic.

Liquid→Gas ($B_3N_3H_6$)
$\Delta H = 7{,}670$,
$\Delta F^\circ = 7{,}670 - 23.71\ T$,
B. P. = 323.5°; $\Delta S_{323.5} = 23.7$,
$\Delta F^\circ_{298.1} = 602$.

BROMINE

Element.—Many investigators have studied the vapor pressure of bromine—Cuthbertson and Cuthbertson (77) (193–266°), Henglein, Von Rosenberg, and Muchlinski (*151*) (177–241°), Isnardi (*178*) (252–273°), Jolly and Briscoe (*190*) (284–324°), Ramsay and Young (*298*) (255–329°), Roozeboom (*313*) (273–333°), Scheffer and Voogd (*347*) (253–362°), and Wright (*443*) (289–294°). Bromine melts at 265.9°, so that there are six sets of data on the liquid to be considered. The Σ-function plot shows all the data on the liquid to be in good agreement with the values of ΔH_0 and I, 10, 100, and −77.50, respectively. The I values of the individual sets lie between −77.45 and −77.56.

Liquid→Gas (Br_2)

$C_p(g)=9.0,$
$C_p(l)=17.1,$
$\Delta C_p=-8.1,$
$\Delta H=10{,}100-8.1\ T,$
$\Delta F^\circ=10{,}100+18.65\ T\log T-77.50\ T,$
B. P.$=331.1°$; $\Delta H_{331.1}=7{,}418$; $\Delta S_{331.1}=22.4,$
$\Delta H_{298.1}=7{,}685$; $\Delta F^\circ_{298.1}=754.$

The data for the solid are in agreement for a considerable range of temperatures below the melting point but are quite widely scattered at lower temperatures. The following equations for the solid are based on those for the liquid and the directly measured heat of fusion, 2,580 calories per gram formula weight.

Solid→Gas (Br_2)

$C_p(g)=9.0,$
$C_p(s)=14.0,$
$\Delta C_p=-5.0,$
$\Delta H=11{,}860-5.0\ T,$
$\Delta F^\circ=11{,}860+11.5\ T\log T-66.78\ T,$
$\Delta H_{298.1}=10{,}370$; $\Delta F^\circ_{298.1}=436.$

These equations for the solid are in agreement with all the data of Scheffer and Voogd and with the other data in the temperature range in which the data themselves agree.

Fluoride.—Bromine pentafluoride, BrF_5, was studied by Ruff and Menzel (*332*) (185–297°). This substance melts at 211.8°, so that measurements exist for both the solid and liquid states. In deriving the equations ΔC_p is ignored.

Solid→Gas (BrF_5)

$\Delta H=8{,}825,$
$\Delta F^\circ=8{,}825-30.23\ T,$
$\Delta F^\circ_{298.1}=-187.$

Liquid→Gas (BrF_5)

$\Delta H=7{,}470,$
$\Delta F^\circ=7{,}470-23.83\ T,$
B. P.$=313.5°$; $\Delta S_{313.5}=23.8,$
$\Delta F^\circ_{298.1}=366.$

From these equations the heat of fusion is 1,355 calories per formula weight at 211.8°.

CADMIUM

Element.—Vapor-pressure measurements of cadmium were made by Barus (*16*) (717–1,054°), Braune (*38*) (618–846°), Burmeister and Jellinek (*54*) (956°), Egerton (*95*) (401–482°), Egerton and Raleigh (*97*) (523–577°), Folger and Rodebush (*110*) (594–868°), Hansen (*142*) (1,022°), Heycock and Lamplough (*161*) (1,039°), Jenkins (*186*) (773–1,109°), Kordez and Raaz (*212*) (1,037°), and Ruff and Bergdahl (*316*) (823–1,055°). For the liquid state the data are in agreement, except those of Barus and Ruff and Bergdahl. Braune, and Rodebush and Dixon, especially, agree remarkably well, and the equations to be given are based largely on these two works. In this case, the values of I in the free-energy equations were obtained directly from the entropies of the gas and solid at 298.1° and the high-temperature specific heats. The entropy of the gas at 298.1°, calculated from the Sackur equation, is 40.07. The I values obtained are -31.75 for the solid and -40.15 for the liquid. These figures in conjunction with the Σ-function values result in the following equations:

Liquid→Gas (Cd)

$C_p(g)=4.97$,
$C_p(l)=7.13$,
$\Delta C_p=-2.16$,
$\Delta H=26{,}110-2.16\ T$,
$\Delta F^\circ=26{,}110+4.97\ T\log T-40.15\ T$,
B. P. $=1{,}038$; $\Delta H_{1038}=23{,}868$; $\Delta S_{1038}=23.0$,
$\Delta H_{298.1}=25{,}466$; $\Delta F^\circ_{298.1}=17{,}807$.

Solid→Gas (Cd)

$C_p(g)=4.97$,
$C_p(s)=5.46+2.466\times10^{-3}T$,
$\Delta C_p=-0.49-2.466\times10^{-3}T$,
$\Delta H=27{,}010-0.49\ T-1.233\times10^{3}T^2$,
$\Delta F^\circ=27{,}010+1.13\ T\log T+1.233\times10^{3}T^2-31.75\ T$,
$\Delta H_{298.1}=26{,}754$; $\Delta F^\circ_{298.1}=18{,}489$; $S_{298.1}(g)=40.07$.

Oxide.—Feiser (*103*) (1,273–1,498°) and Hincke (*164*) (1,140–1,311°) have measured the vapor pressure of cadmium oxide, CdO. At these temperatures $C_p=9$ has been assumed for the specific heat of the gas. If one determination is omitted, Hincke's data show a variation in I of only 0.54 unit, which, considering the temperatures involved, indicates high relative accuracy. Feiser's results have been given no weight, for while they are in fair agreement with those of Hincke, his experimental method, involving rates of evaporation, is not one of high accuracy.

Solid→Gas (CdO)

$C_p(g)=9.0$,
$C_p(s)=9.65+2.08\times10^{-3}T$,
$\Delta C_p=-0.65-2.08\times10^{-3}T$,
$\Delta H=58{,}500-0.65T-1.04\times10^{-3}T^2$,
$\Delta F^\circ=58{,}500+1.50\ T\log T+1.04\times10^{-3}T^2-38.73\ T$,
S. P. $=1{,}832^\circ$; $\Delta H_{1832}=53{,}820$; $\Delta S_{1832}=29.4$,
$\Delta H_{298.1}=58{,}214$; $\Delta F^\circ_{298.1}=48{,}153$; $\Delta S_{298.1}=33.8$,
$S_{298.1}(g)=46.9$.

Bromide.—Greiner and Jellinek (*134*) report a vapor pressure of 200 mm at 1,025° for liquid cadmium bromide. This is the only available figure for this substance.

Chloride.—Vapor-pressure measurements of liquid cadmium chloride were made by Greiner and Jellinek (*134*) (1,025°) and Maier (*232*) (1,001–1,286°). With the exception of Maier's lowest temperature point these data are in good agreement, giving an extreme variation in I of 0.34 unit. Data are not available for obtaining equations for the solid.

Liquid→Gas ($CdCl_2$)

$\Delta C_p=-10$,
$\Delta H=42{,}260-10\ T$,
$\Delta F^\circ=42{,}260+23.0\ T\log T-105.23\ T$,
B. P. $=1{,}240^\circ$; $\Delta H_{1240}=29{,}860$; $\Delta S_{1240}=24.1$,
$\Delta H_{298.1}=39{,}279$; $\Delta F^\circ_{298.1}=27{,}856$.

Iodide.—Measurements of solid and liquid cadmium iodide were made by Schmidt and Walter (*352*) (616–723°). The data are not good enough to warrant taking account of ΔC_p, but approximate equations for both solid and liquid are given.

Solid→Gas (CdI_2)

$\Delta H = 29{,}060,$
$\Delta F^\circ = 29{,}060 - 29.32\ T$
$\Delta F^\circ_{298.1} = 20{,}320.$

Liquid→Gas (CdI_2)

$\Delta H = 25{,}400,$
$\Delta F^\circ = 25{,}400 - 23.77\ T,$
B. P. $= 1{,}069^\circ$; $\Delta S_{1069} = 23.8,$
$\Delta F^\circ_{298.1} = 18{,}314.$

From these equations the heat of fusion at the melting point (660°) is computed to be 3,660 calories per gram formula weight.

CALCIUM

Element.—Vapor-pressure measurements of liquid calcium were made by Hartmann and Schneider (*146*) (1,254–1,546°) and Ruff and Hartmann (*322*) (1,233–1,380°), while Pilling (*286*) (776–973°) has studied the β or high-temperature form of the solid. Overstreet (*273*) has computed free-energy values for calcium gas up to 3,000° from spectroscopic data. Since the heat of fusion of calcium has not been measured, Pilling's data for the solid will be used to calculate ΔE_0°. (In obtaining the equations for the liquid a value of heat of fusion, 2,380 calories per gram-atom, at the melting point, 1,124°, has been assumed arbitrarily. This value corresponds to an entropy of fusion of 2.1 units, which is a little lower than the average value for the metals, 2.3. Consequently, the equations for the liquid are less accurate than those for the solid forms by an unknown amount which depends upon the error in this assumption. However, vapor pressures computed from the free-energy equation for the liquid agree with the experimental values of Hartmann and Schneider.) At 830° a smoothed value of $\frac{\Delta F^\circ}{T} = -R\ ln\ P = 24.98$ is obtained, and at the same temperature an interpolation from Overstreet's figures gives $\frac{F^\circ - E_0^\circ}{T} = -37.12$ for he gas, while the corresponding value for the β-form is $\frac{F_c^\circ - E_{c,0}^\circ}{T} = -10.93$. Combination of these figures results in $\frac{\Delta E_0^\circ}{T} = 51.17$ at 830° or $\Delta E_0^\circ = 42{,}470$ calories per gram-atom. Table 8, of which the first two columns are due to Overstreet, summarizes the calculations of $\frac{\Delta F^\circ}{T}$ at various temperatures.

TABLE 8.—*Free energy of vaporization data for calcium*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_s - E^\circ_{s,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−32.033	−5.33	−26.70	142.47	115.77
400	−33.493	−6.76	−26.73	106.18	79.45
600	−35.507	−8.96	−26.55	70.78	44.23
700	−36.273	−9.88	−26.39	60.67	34.28
800	−36.936	−10.70	−26.24	53.09	26.85
900	−37.521	−11.45	−26.07	47.19	21.12
1,000	−38.045	−12.13	−25.91	42.47	16.56
1,100	−38.518	−12.76	−25.76	38.61	12.85
1,200	−38.950	−13.47	−25.48	35.39	9.91
1,300	−39.348	−14.17	−25.18	32.67	7.49
1,400	−39.716	−14.80	−24.92	30.34	5.42
1,500	−40.059	−15.38	−24.68	28.31	3.63
1,600	−40.379	−15.92	−24.46	26.54	2.08
1,700	−40.681	−16.44	−24.24	24.98	.74
1,800	−40.964	−16.92	−24.04	23.59	−.45
1,900	−41.233	−17.36	−23.87	22.35	−1.52
2,000	−41.488	−17.79	−23.70	21.24	−2.46

In deriving equations from the data in table 8 it was found expedient to use the value for the entropy of calcium gas at 298.1°. This may be obtained from the Sackur equation and is 37.00 calories per degree per gram-atom. No correction in this figure is necessary, since $p=1$ for the lowest energy state, and no other states are effective at 298.1°. The entropy of vaporization of α-calcium at 298.1°, 27.05, is obtained from the above figure for the gas and 9.95 for the entropy of the α-form. Constant I is obtainable directly from the entropy of vaporization and the specific-heat equations. Applying the value of I to the Σ-function results computed from the data in the last column of table 8, the quantity ΔH_0 is obtained at each of the three temperatures pertaining to the α-form. The ΔH_0 values so calculated have a spread of only 5 calories. The following equations are for the α-form, which is stable up to 673°.

Alpha→Gas (Ca)

$C_p(g)=4.97,$

$C_p(\alpha)=5.31+3.33\times10^{-3}T,$

$\Delta C_p=-0.34-3.33\times10^{-3}T,$

$\Delta H=42{,}820-0.34\,T-1.665\times10^{-3}T^2,$

$\Delta F^\circ=42{,}820+0.78\,T\log T+1.665\times10^{-3}T^2-30.31\,T,$

$\Delta H_{298.1}=42{,}571;\ \Delta F^\circ_{298.1}=34{,}508;\ \Delta S_{298.1}=27.05,$

$S_{298.1}=37.00.$

The calculations for the β and liquid forms were made in a similar manner; first I was obtained, and then values of ΔH_0 were computed from Σ-function data. In the case of the β form the values of ΔH_0 has an extreme variation of 7 calories, while for the liquid the spread was 50 calories.

Beta→Gas (Ca)

$C_p(g)=4.97,$

$C_p(\beta)=6.29+1.40\times10^{-3}T,$

$\Delta C_p=-1.32-1.40\times10^{-3}T,$

$\Delta H=42{,}940-1.32\,T-0.70\times10^{-3}T^2.$

$\Delta F^\circ=42{,}940+3.04\,T\log T+0.70\times10^{-3}T^2-36.20\,T,$

$\Delta H_{298.1}=42{,}485;\ \Delta F^\circ_{298.1}=34{,}453.$

Liquid → Gas (Ca)

$C_p(g) = 4.97,$
$C_p(l) = 7.50,$
$\Delta C_p = -2.53,$
$\Delta H = 41{,}030 - 2.53\ T,$
$\Delta F^\circ = 41{,}030 + 5.83\ T \log T - 42.23\ T,$
B. P. = 1,760°; $\Delta H_{1760} = 36{,}577$; $\Delta S_{1760} = 20.78,$
$\Delta H_{298.1} = 40{,}276$; $\Delta F^\circ_{298.1} = 32{,}741.$

Oxide.—Claasen and Veenemans (*64*) (1,600–1,750°) and Ruff and Schmidt (*335*) (2,190–2,910°) have measured the vapor pressure of calcium oxide. The results of Ruff and Schmidt are very erratic, and Claasen and Veenemans do not present their actual data but report a vapor-pressure equation. This equation after converting millimeters to atmospheres is adopted here, but heat and free-energy equations are omitted because of the uncertainties involved.

Solid → Gas (CaO)

$$\log P(at.) = -\frac{27{,}400}{T} + 6.89.$$

CARBON

Element.—A number of investigators have obtained experimental vapor-pressure data for carbon—Alterthum and Koref (*4*) (2,000–3,500°), Herbst (*156, 157*) (3,800–4,200°), Kohn (*210*) (4,015–4,705°), Kohn and Guckel (*211*) (3,980–4,705°), Marshall and Norton (*239*) (4,200–4,705°), Ryschkewitsch (*343*) (3,015–3,670°), Thiel and Ritter (*405*) (1,960–3,150°), and Wertenstein and Jedrzejewski (*437*) (2,800–3,500°). Overstreet (*273*) has computed free-energy values for monatomic and diatomic carbon gas up to 5,000° and has calculated the partial pressures of these species, in equilibrium with the solid, at various temperatures.

Several difficulties are encountered with carbon, including (1) the large proportion of diatomic molecules present, (2) the high temperatures involved, which make extrapolation of specific heats uncertain, and (3) uncertainty as to the form of the carbon. So far as the vapor-pressure measurements are concerned there is only one investigation, that of Wertenstein and Jedrzejewski, where data have been presented in such form that the partial pressures of the monatomic and diatomic species may be determined. These authors have arrived at vapor-pressure results by studying the rate of evaporation of carbon from filaments (Langmuir's method). Their data are much lower than those obtained by observations of craters. However, they are in agreement, at least in order of magnitude, with the data of Alterthum and Koref, who also used the filament method. Furthermore, there is reason to believe that the results from the crater observations are high. Consequently, if free energy of vaporization equations are to be derived, there is no other choice than to base them on the work of Wertenstein and Jedrzejewski. These authors do not give their actual data but report a vapor-pressure equation and one showing the rate of evaporation as a function of the temperature.

The theoretical relationship for the rate of evaporation per second per unit area is

$$m = P\sqrt{\frac{M}{2\pi RT}}\ (411),$$

where m is the rate of evaporation per second per square centimeter, P the vapor pressure, M the molecular weight of the gas, R the gas constant per mole, and T the absolute temperature. If P is expressed in millimeters and m in grams, this equation becomes

$$m(g)=58.32\times10^{-3}P(\mathrm{mm})\sqrt{\frac{M}{T}}.$$

If P_c and P_{c_2} denote the partial pressures of the monatomic and diatomic carbon, respectively, and m_c and m_{c_2} the corresponding evaporation rates, then

$$m_c=58.32\times10^{-3}P_c\sqrt{\frac{12}{T}},$$

and

$$m_{c_2}=58.32\times10^{-3}P_{c_2}\sqrt{\frac{24}{T}}.$$

The latter two equations and those for $m=m_{c_1}+m_{c_2}$ and $P=P_c+P_{c_2}$ given by Wertenstein and Jedrzejewski may be solved for the quantities P_c, P_{c_2}, m_c, and m_{c_2} at any temperature. The values of P_c were computed at 2,800° and 3,500°, the extremes of the range of applicability of Wertenstein and Jedrzejewski's total vapor-pressure equation. From these quantities, $\frac{\Delta F^\circ}{T}$ values were computed, and the latter in conjunction with Overstreet's table of $\frac{F^\circ-E^\circ_0}{T}$ for the gas and the corresponding $\frac{F^\circ_c-E^\circ_{c,0}}{T}$ for the solid makes possible the calculation of $\Delta E^\circ_0=197{,}000$ calories per gram-atom for the monatomic gas. The ΔE°_0 for the diatomic gas may be obtained from this value, and the figure given by Birge (*28*) for the energy of dissociation of diatomic carbon gas, 161,400 calories per mole. $\Delta E^\circ_0=232{,}600$ calories is found for the diatomic gas. These ΔE°_0 results are the same as those obtained by Overstreet. Tables 9 and 10 summarize the calculations of $\frac{\Delta F^\circ}{T}$ for the formation of monatomic and diatomic gases from the solid. In computing the $\frac{F^\circ_c-E^\circ_{c,0}}{T}$ values for the solid the specific-heat equation of β-graphite was used up to 1,500°. A plot was made of these values and the resulting curve extrapolated to 5,000°. This extrapolation is admittedly quite uncertain.

TABLE 9.—*Free energy of vaporization data for carbon (monatomic gas)*

T	$\frac{F^\circ-E^\circ_0}{T}$	$\frac{F^\circ_c-E^\circ_{c,0}}{T}$	$\frac{\Delta F^\circ-\Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−32.537	−0.45	−32.09	660.85	628.76
500	−35.213	−1.08	−34.13	394.00	359.87
1,000	−38.736	−2.71	−36.03	197.00	160.97
1,500	−40.777	−4.13	−36.65	131.33	94.68
2,000	−42.221	−5.38	−36.84	98.50	61.66
2,500	−43.340	−6.45	−36.89	78.80	41.91
3,000	−44.258	−7.38	−36.88	65.67	28.79
3,500	−45.038	−8.19	−36.85	56.29	19.44
4,000	−45.718	−8.92	−36.80	49.25	12.45
4,500	−46.321	−9.58	−36.74	43.78	7.04
5,000	−46.864	−10.20	−36.64	39.40	2.74

TABLE 10.—*Free energy of vaporization data for carbon (diatomic gas)*

T	$\frac{F^\circ-E^\circ_0}{T}$	$\frac{F^\circ_s-E^\circ_{0.s}}{T}$	$\frac{\Delta F^\circ-\Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
2,000	−54.934	−10.76	−44.17	116.30	72.13
2,500	−56.739	−12.90	−43.84	93.04	49.20
3,000	−58.238	−14.76	−43.48	77.53	34.05
3,500	−59.522	−16.38	−43.14	66.46	23.32
4,000	−60.645	−17.84	−42.80	58.15	15.35
4,500	−61.626	−19.16	−42.47	51.69	9.22
5,000	−62.521	−20.40	−42.12	46.52	4.40

In handling these data empirical free-energy equations of the form $\Delta F^\circ = A + BT \log T + CT$, were derived for the formation of C and C_2 gases. It was found possible to fit the data with a maximum deviation of less than 0.3 percent. The following are the derived equations. Wertenstein and Jedrzejewski's equation for the total vapor pressure also is included.

Solid→ Gas (C)

$\Delta H = 199{,}350 - 1.009\ T,$
$\Delta F^\circ = 199{,}350 + 2.324\ T \log T - 45.73\ T,$
$P_c = 1$ at. at 5,379°; $\Delta H_{5379} = 193{,}923$; $\Delta S_{5379} = 36.0,$
$\Delta H_{298.1} = 199{,}049$; $\Delta F^\circ_{298.1} = 187{,}432.$

Solid→ Gas (C_2)

$\Delta H = 239{,}600 - 4.52\ T,$
$\Delta F^\circ = 239{,}600 + 10.40\ T \log T - 82.00\ T,$
$P_{c2} = 1$ at. at 5,566°; $\Delta H_{5566} = 214{,}442$; $\Delta S_{5566} = 38.5,$
$\Delta H_{298.1} = 238{,}253$; $\Delta F^\circ_{298.1} = 222{,}827.$

Solid→ Gas ($C + C_2$) (total pressure),

$$\log P(at.) = -\frac{47{,}000}{T} - 0.75 \log T + 11.99,$$

S. P. = 5,100°.

The combined equations for C and C_2 gases would put the boiling point at 5,265° instead of 5,100°, as given by Wertenstein and Jedrzejewski's equation. This is due in part to taking the mean value of ΔE_0° for the extreme temperatures covered by their investigation. The difference in the computed ΔE_0° values amounts to some 3,000 calories. Moreover, the equations for the formation of monatomic gas do not give the correct entropy of this gas at 298.1, which means the ΔH equation is in error, since the ΔF° equation was made to fit the data. For this reason, additional equations are given which are somewhat better but applicable only below 2,000°. These equations were obtained in the usual manner.

Solid→ Gas (C)

$C_p(g) = 5.12,$
$C_p(s) = 2.67 + 2.617 \times 10^{-3} T - 1.169 \times 10^{5} T^{-2},$
$\Delta C_p = 2.45 - 2.617 \times 10^{-3} T + 1.169 \times 10^{5} T^{-2},$
$\Delta H = 197{,}720 + 2.45\ T - 1.308 \times 10^{-3} T^2 - 1.169 \times 10^{5} T^{-1},$
$\Delta F^\circ = 197{,}720 - 5.64\ T \log T + 1.308 \times 10^{-3} T^2 - 0.5845 \times 10^{5} T^{-1} - 21.23\ T,$
$\Delta H_{298.1} = 197{,}942$; $\Delta F^\circ_{298.1} = 187{,}151,$
$\Delta S_{298.1} = 36.20$; $S_{298.1}(g) = 37.50.$

Solid→ Gas (C_2)

$C_p(g) = 8.00,$
$C_p(s) = 5.34 + 5.234 \times 10^{-3} T - 2.338 \times 10^{5} T^{-2},$
$\Delta C_p = 2.66 - 5.234 \times 10^{-3} T + 2.338 \times 10^{5} T^{-2},$
$\Delta H = 235{,}820 + 2.66\ T - 2.617 \times 10^{-3} T^2 - 2.338 \times 10^{5} T^{-1},$
$\Delta F^\circ = 235{,}820 - 6.13\ T \log T + 2.617 \times 10^{-3} T^2 - 1.169 \times 10^{5} T^{-1} - 30.75\ T,$
$\Delta H_{298.1} = 235{,}596$; $\Delta F^\circ_{298.1} = 221{,}972,$
$\Delta S_{298.1} = 45.70$; $S_{298.1}(g) = 48.30.$

Monoxide.—Vapor-pressure measurements of carbon monoxide were made by Baly and Donnan (*15*) (68-90°), Clusius and Tesko (*66*) (60-80°), Crommelin, Bijleveld, and Brown (*74*) (56-133°), Clayton and Giauque (*65*) (60-83°), Olszewski (*267*) (62-134°), and Verschoyle (*422*) (73-89°). This substance exhibits two crystalline modifications, S_I stable above 61.55° and S_{II} stable below 61.55°. The melting point is 68.09° and the boiling point 81.61°. These figures, as well as the accompanying latent heats, were determined by Clayton and Giauque. Their measured heat of vaporization, after correction to the ideal state, and the heats of transition and fusion may be used to obtain heat and free energy of vaporization equations. The specific heat of the liquid is practically constant at 14.44 calories per gram formula weight and the heat capacities of the solid forms may be represented by the equations, $C_p(S_I)=5.05+0.11\ T$ and $C_p(S_{II})=-1.25+0.24\ T$.

Liquid→Gas (CO)

$C_p(g)=6.95,$
$C_p(l)=14.44,$
$\Delta C_p=-7.49,$
$\Delta H=2{,}080-7.49\ T,$
$\Delta F^\circ=2{,}080+17.25\ T\log T-58.36\ T.$

S_I→Gas (CO)

$C_p(g)=6.95,$
$C_p(S_I)=5.05+0.11\ T,$
$\Delta C_p=1.90-0.11\ T,$
$\Delta H=1{,}896+1.90\ T-0.055\ T^2,$
$\Delta F^\circ=1{,}896-4.37\ T\log T+0.055\ T^2-19.78\ T.$

S_{II}→Gas (CO)

$C_p(g)=6.95,$
$C_p(S_{II})=-1.25+0.24\ T,$
$\Delta C_p=8.20-0.24\ T,$
$\Delta H=1{,}905+8.20\ T-0.12\ T^2,$
$\Delta F^\circ=1{,}905-18.88\ T\log T+0.12\ T^2+2.04\ T.$

Vapor-pressure equations obtained from the above free-energy relationships for the liquid and S_I forms cannot be expected to represent the experimental determinations since the equations involve corrections to the ideal state. The following vapor-pressure equations, however, reproduce the experimental data closely and should be used for actual vapor-pressure calculations.

Liquid→Gas (CO)

$$\log P\ (at.)=-\frac{460.8}{T}-3.77\log T+12.853,$$

B. P.=81.61°.

S_I→Gas (CO)

$$\log P\ (at.)=-\frac{424.0}{T}+0.955\log T-0.0120\ T+4.483.$$

Three vapor-pressure measurements have been made on the low-temperature solid modification, S_{II}. Since the vapor pressure is below 2 cm at all temperatures where this form exists there can be but little difference between the actual and ideal gases, consequently the vapor-pressure expression derivable from the free-energy equation is satisfactory for this form.

Dioxide.—The vapor pressure of carbon dioxide was studied by Amagat (*5*) (273–304°), Bridgeman (*42*) (273°), Falck (*102*) (135–191°), Henning (*152*) (191–195°), Henning and Stock (*155*) (163–193°), Jenkins and Pye (*185*) (213–303°), Meyers and Van Dusen (*246, 247*) (93–304°), Olszewski (*265*) (66–83°), Onnes and Weber (*269*) (90–106°), Regnault (*300*) (247–316°), Von Siemens (*360*) (118–196°), Stock, Henning, and Kusz (*400*) (63–196°), Villard (*423*) (194–293°), Weber (*434*) (105–138°), and Zeleny and Smith (*453*) (139–266°). The data other than those of Zeleny and Smith are in good agreement in the temperature range of interest for the present purpose.

In deriving the heat and free-energy equations, the measurements of Henning and Stock and their coworkers were adopted. No correction was made for gas imperfection, and consequently the heat equation is somewhat in error. The free-energy equation, however, is substantially correct. The specific heat of solid carbon dioxide above 80° may be represented by $C_p(s)=6.22+0.0355\ T$ and the classical value $C_p(g)=4R=7.95$ is assumed for the gas.

Solid→Gas (CO_2)

$C_p(g)=7.95,$
$C_p(s)=6.22+0.0355\ T,$
$\Delta C_p=1.73-0.0355\ T,$
$\Delta H=6{,}440+1.73\ T-0.0178\ T^2,$
$\Delta F°=6{,}440-3.98\ T\log T+0.0178\ T^2-27.45\ T,$
S. P.$=194.6°$; $\Delta H_{194.6}=6{,}103$; $\Delta S_{194.6}=31.36.$

The heat and entropy of vaporization values at the sublimation point, 194.6°, are somewhat different from those previously reported (*199*). However, the entropy of CO_2 gas calculated from the existing low-temperature thermal data is probably too high by 1.3 units, as compared to the most recent spectroscopic studies. The change in the entropy of vaporization figure diminishes this discrepancy by 0.6 unit.

Carbonyl sulphide.—Stock and Kusz (*386*) (138–223°) and Ilosvay (*174*) (273–358°) have measured the vapor pressure of liquid carbonyl sulphide, COS. The data of Stock and Kusz are very consistent. Ilosvay's results are for pressures above 12 atmospheres and cannot be used for the present purpose. Since no information is available and the temperatures involved are low, ΔC_p is taken as zero.

Liquid→Gas (COS)

$\Delta H=4{,}920,$
$\Delta F°=4{,}920-22.07\ T,$
B. P.$=223°$; $\Delta S_{223}=22.1.$

Bisulphide.—A number of investigators have studied the vapor pressure of carbon bisulphide—Henning and Stock (*155*) (248–284°), Mali (*238*) (294–319°), Regnault (*300*) (257–410°), Rex (*301*) (273–303°), Von Siemens (*360*) (194–319°), Stock, Henning, and Kusz (*400*) (255–298°), and Wüllner and Grotrian (*446*) (293–358°). These data are very concordant, as the values of I for the different investigations all lie in a range of 0.06 unit.

Liquid→Gas (CS_2)
$C_p(g) = 12.2$,
$C_p(l) = 18.4$,
$\Delta C_p = -6.2$,
$\Delta H = 8{,}530 - 6.2\ T$,
$\Delta F^\circ = 8{,}530 + 14.3\ T \log T - 62.52\ T$,
B. P. $= 319.35°$; $\Delta H_{319.35} = 6{,}550$; $\Delta S_{319.35} = 20.51$,
$\Delta H_{298.1} = 6{,}682$; $\Delta F^\circ_{298.1} = 441$.

Subsulphide.—Stock and Praetorius (*390*) (293–363°) have measured the vapor pressure of liquid carbon subsulphide, C_3S_2. This substance polymerizes when heated to 373°. The calculated boiling point to be given is an extrapolated value assuming no polymerization. ΔC_p is ignored.

Liquid→Gas (C_3S_2)
$\Delta H = 10{,}500$,
$\Delta F^\circ = 10{,}500 - 23.45\ T$,
(B. P. $= 448°$) ($\Delta S_{448} = 23.4$),
$\Delta F^\circ_{298.1} = 3{,}510$.

Stock and Praetorius give 273.6° for the melting point of this substance.

Selenosulphide.—Carbon selenosulphide, CSeS, was studied by Stock and Willfroth (*395*) (273–357°). This substance melts at 188°. $\Delta C_p = -10$ has been assumed.

Liquid→Gas (CSeS)
$\Delta C_p = -10$,
$\Delta H = 10{,}885 - 10\ T$,
$\Delta F^\circ = 10{,}885 + 23.0\ T \log T - 89.17\ T$,
B. P. $= 358.5°$; $\Delta H_{358.5} = 7{,}300$; $\Delta S_{358.5} = 20.4$,
$\Delta H_{298.1} = 7{,}904$; $\Delta F^\circ_{298.1} = 1{,}268$.

Carbonyl chloride.—Measurements of the vapor pressure of carbonyl chloride (phosgene), $COCl_2$, were made by Atkinson, Heycock, and Pope (*13*) (90–373°), Germann and Taylor (*116*) (273–443°), and Paterno and Mazzuchelli (*277*) (250–298°). The results of Germann and Taylor and Paterno and Mazzuchelli are in good agreement. This substance boils just below room temperature, and so ΔC_p is ignored.

Liquid→Gas ($COCl_2$)
$\Delta H = 5{,}990$,
$\Delta F^\circ = 5{,}990 - 21.31\ T$,
B. P. $= 281.1°$; $\Delta S_{298.1} = 21.3$,
$\Delta F^\circ_{298.1} = -363$.

Methane.—Methane is included here for, while it is a substance which falls outside the category of this compilation, it nevertheless has considerable importance metallurgically. Vapor-pressure measurements of this substance were made by Henning and Stock (*155*) (80–109°), Karwat (*194*) (76–88°), and Stock, Henning, and Kusz (*400*) (91–123°). The specific heat of liquid methane may be taken as constant, 12.95 calories, and that of the solid down to 50° is approximated by $C_p(s) = 4.85 + 0.060\ T$. Using the low-temperature thermal data previously adopted for methane (*199*), which agree with the entropy calculated from spectroscopic data, the following equations result:

Liquid→Gas (CH_4)

$C_p(g) = 7.95,$
$C_p(l) = 12.95,$
$\Delta C_p = -5.00,$
$\Delta H = 2{,}598 - 5.00\,T,$
$\Delta F^\circ = 2{,}598 + 11.5\,T \log T - 46.81\,T,$
B. P. = 111.7°; $\Delta H_{111.7} = 2{,}040$; $\Delta S_{111.7} = 18.26.$

Solid→Gas (CH_4)

$C_p(g) = 7.95,$
$C_p(s) = 4.85 + 0.060\,T,$
$\Delta C_p = 3.10 - 0.060\,T,$
$\Delta H = 2{,}334 + 3.10\,T - 0.030\,T^2,$
$\Delta F^\circ = 2{,}334 - 7.13\,T \log T + 0.030\,T^2 - 10.21\,T,$
M. P. = 90.6°.

Vapor-pressure equations derived from the above results do not fit the experimental data well, and so the following expressions are included for use in more accurate calculations of this property.

Liquid→Gas (CH_4)

$$\log P(at.) = -\frac{559.6}{T} - 2.514 \log T + 10.157.$$

Solid→Gas (CH_4)

$$\log P(at.) = -\frac{501.9}{T} + 1.55 \log T - 0.0066\,T + 2.157.$$

Tetrachloride.—Measurements of the vapor pressure of carbon tetrachloride were made by Drucker, Jiméno, and Kangro (*91*) (251–270°), Grimm (*135*) (348–350°), Hertz and Rathmann (*159*) (298–349°), Mali (*238*) (294–338°), Mündel (*256*) (202–223°), Regnault (*300*) (242–462°), Rex (*301*) (273–303°), Schreinmakers (*353*) (306–349°), Wertheimer (*438*) (273–556°), and Young (*450*, *452*) (253–556°). The agreement between these sets of data is good, the average I values of the individual sets lying in a range of 0.30 unit.

Liquid→Gas (CCl_4)

$C_p(g) = 21.5,$
$C_p(l) = 32.0,$
$\Delta C_p = -10.5,$
$\Delta H = 10{,}960 - 10.5\,T,$
$\Delta F^\circ = 10{,}960 + 24.2\,T \log T - 92.87\,T,$
B. P. = 350°; $\Delta H_{350} = 7{,}283$; $\Delta S_{350} = 20.8,$
$\Delta H_{298.1} = 7{,}830$; $\Delta F^\circ_{298.1} = 1{,}125.$

Tetrafluoride.—Menzel and Mohry (*244*) (80–146°) have measured the vapor pressure of carbon tetrafluoride. This substance melts at 89.5°, but only one measurement is given for the solid. Consequently, calculations are restricted to the liquid state. ΔC_p has been ignored.

Liquid→Gas (CF_4)

$\Delta H = 3{,}110,$
$\Delta F^\circ = 3{,}110 - 21.42\,T,$
B. P. = 145.2°; $\Delta S_{145.2} = 21.4.$

Cyanogen.—Perry and Bardwell (*281*) (179–266°) have measured the vapor pressure of solid and liquid cyanogen $(CN)_2$. Their data are very concordant. Neglecting ΔC_p, the following equations result:

Liquid→Gas [$(CN)_2$]
$\Delta H = 5{,}710,$
$\Delta F^\circ = 5{,}710 - 22.66\ T,$
B. P. = 252°; $\Delta S_{252} = 22.7,$
$\Delta F^\circ_{298.1} = -1{,}045.$

Solid→Gas [$(CN)_2$]
$\Delta H = 7{,}770,$
$\Delta F^\circ = 7{,}770 - 31.05\ T,$
$\Delta F^\circ_{298.1} = -1{,}486.$

At the melting point, 246°, the calculated heat of fusion is 2,060 calories per formula weight, corresponding to an entropy of fusion of 8.4 units.

Cyanogen bromide.—Baxter, Bezzenberger, and Wilson (*19*) (255–308°) have studied the vapor pressure of solid cyanogen bromide, CNBr. This substance melts at 325°. ΔC_p has been taken as zero.

Solid→Gas (CNBr)
$\Delta H = 11{,}010,$
$\Delta F^\circ = 11{,}010 - 33.28\ T,$
$\Delta F^\circ_{298.1} = 1{,}089.$

Cyanogen chloride.—Solid and liquid cyanogen chloride, CNCl, were studied by Regnault (*300*) (240–344°). Neglecting ΔC_p, the following equations result:

Solid→Gas (CNCl)
$\Delta H = 8{,}540,$
$\Delta F^\circ = 8{,}540 - 30.39\ T,$
$\Delta F^\circ_{298.1} = -519.$

Liquid→Gas (CNCl)
$\Delta H = 6{,}300,$
$\Delta F^\circ = 6{,}300 - 22.04\ T,$
B. P. = 286°; $\Delta S_{286} = 22.0,$
$\Delta F^\circ_{298.1} = -270.$

The heat of fusion is 2,240 calories per gram formula weight at the melting point 268°, and the entropy of fusion is 8.35 units.

Cyanogen fluoride.—Cosslett (*68*) (134–201°) has studied solid cyanogen fluoride. This substance sublimes at 1 atmosphere pressure.

Solid→Gas (CNF)
$\Delta H = 5{,}780,$
$\Delta F^\circ = 5{,}780 - 28.85\ T,$
S. P. = 200.3°; $\Delta S_{200.3} = 28.8.$

Cyanogen iodide.—Solid cyanogen iodide was investigated by Yost and Stone (*448*) (298–374°). The vapor pressure reaches 1 atmosphere at a temperature below the melting point.

Solid→Gas (CNI)
$\Delta H = 13{,}980,$
$\Delta F^\circ = 13{,}980 - 33.76\ T,$
S. P. = 414°; $\Delta S_{414} = 33.8,$
$\Delta F^\circ_{298.1} = 3{,}916.$

CESIUM

Element.—Vapor-pressure measurements of cesium were made by Füchtbauer and Bartels (*113*) (461–506°), Hackspill (*140*) (503–670°), Kröner (*216*) (522–629°), Langmuir and Kingdon (*220*) (297°), Ruff and Johannsen (*324*) (943°), and Scott (*357*) (321–387°). Overstreet

(*273*) has computed free-energy values for the gas, but these cannot be utilized in this case, since low-temperature heat-capacity data are lacking. A Σ-function plot shows all the data except those of Scott, who worked at very low pressures, to be in agreement. The equations for the solid are based on those for the liquid and thermal data

Liquid→Gas (Cs)
$C_p(g)=4.97,$
$C_p(l)=8.00,$
$\Delta C_p=-3.03,$
$\Delta H=19{,}240-3.03\ T,$
$\Delta F^\circ=19{,}240+6.98\ T\log T-40.80\ T,$
B. P. = 963°; $\Delta H_{963}=16{,}322$; $\Delta S_{963}=16.95,$
$\Delta H_{298.1}=18{,}337$; $\Delta F^\circ_{298.1}=12{,}227.$

Solid→Gas (Cs)
$C_p(g)=4.97,$
$C_p(s)=1.96+18.2\times10^{-3}T,$
$\Delta C_p=3.01-18.2\times10^{-3}T,$
$\Delta H=18{,}740+3.01\ T-9.1\times10^{-3}T^2,$
$\Delta F^\circ=18{,}740-6.93\ T\log T+9.1\times10^{-3}T^2-7.40\ T,$
$\Delta H_{298.1}=18{,}828$; $\Delta F^\circ_{298.1}=12{,}231$; $\Delta S_{298.1}=22.13.$

From the entropy of vaporization of the solid at 298.1°, 22.13, and the entropy of the gas, 41.95, the entropy of the solid at 298.1° is computed to be 19.8 units. This property of the solid has never been directly determined. No great accuracy is claimed for this calculated value, but it is not greatly different from the result, 19.0, which was obtained by other means (*199*) and was designated as being "probably low."

Bromide.—The vapor pressure of liquid cesium bromide was measured by Ruff and Mugdan (*333*) (1,250–1,580°) and Von Wartenberg and Schulz (*432*) (1,325–1,575°). The data of the latter authors were given the more weight in drawing the line in the Σ-function plot, which was made assuming $\Delta C_p=-7$. Data are not available for deriving equations for the solid.

Liquid→Gas (CsBr)
$\Delta C_p=-7.0,$
$\Delta H=47{,}000-7.0\ T,$
$\Delta F^\circ=47{,}000+16.1\ T\log T-81.34\ T,$
B. P. = 1,573°; $\Delta H_{1573}=35{,}990$; $\Delta S_{1573}=22.9,$
$\Delta H_{298.1}=44{,}913$; $\Delta F^\circ_{298.1}=34{,}629.$

Chloride.—Cesium chloride was studied by Fiock and Rodebush (*106*) (1,097–1,293°), Ruff and Mugdan (*333*) (1,259–1,568°) and Von Wartenberg and Schulz (*432*) (1,335–1,577°). The results of Fiock and Rodebush and of Von Wartenberg and Schulz are in very good agreement. Ruff and Mugdan's figures are in approximate agreement but do not exhibit the relative accuracy shown by the other two sets of data. Equations for the liquid only are derivable, and again $\Delta C_p=-7.0$ is assumed.

Liquid→Gas (CsCl)
$\Delta C_p=-7.0,$
$\Delta H=46{,}700-7.0\ T,$
$\Delta F^\circ=46{,}700+16.1\ T\log T-81.15\ T,$
B. P. = 1,573°; $\Delta H_{1573}=35{,}690$; $\Delta S_{1573}=22.7,$
$\Delta H_{298.1}=44{,}613$; $\Delta F^\circ_{298.1}=34{,}385.$

Fluoride.—Measurements of the vapor pressure of liquid cesium fluoride were made by Ruff, Schmidt, and Mugdan (*339*) (1,306–1.528°) and Von Wartenberg and Schulz (*432*) (1,228–1,524°). The data are consistent, except at the lower end of the temperature range covered.

Liquid→Gas (CsF)

$\Delta C_p = -7.0,$
$\Delta H = 45,000 - 7.0\ T,$
$\Delta F° = 45,000 + 16.1\ T \log T - 80.78\ T,$
B. P. $= 1,524°$; $\Delta H_{1524} = 34,332$; $\Delta S_{1524} = 22.5,$
$\Delta H_{298.1} = 42,913$; $\Delta F°_{298.1} = 32,795.$

Iodide.—The vapor pressure of liquid cesium iodide was measured by Ruff and Mugdan (*333*) (1,325–1,553°) and Von Wartenberg and Schulz (*432*) (1,296–1,553°). The data are much poorer than for the other cesium halides. Both investigations set the boiling point at 1,553°, and by analogy with the other halides the entropy of vaporization at the boiling point should be about 23.1. Using these facts as guides in drawing the Σ v. $\frac{1}{T}$ line, the following equations result:

Liquid→Gas (CsI)

$\Delta C_p = -7.0,$
$\Delta H = 46,800 - 7.0\ T,$
$\Delta F° = 46,800 + 16.1\ T \log T - 81.51\ T,$
B. P. $= 1,553°$; $\Delta H_{1553} = 35,929$; $\Delta S_{1553} = 23.1,$
$\Delta H_{298.1} = 44,713$; $\Delta F°_{298.1} = 34,378.$

CHLORINE

Element.—Vapor-pressure measurements of chlorine were made by Harteck (*145*) (162–243°), Henglein, Von Rosenberg, and Muchlinski (*151*) (119–195°), Johnson and McIntosh (*188*) (167–241°), Knietsch (*207*) (185–419°), Pellaton (*280*) (194–420°), and Trautz and Gerwig (*415*) (194–238°). Free-energy equations are derived, based on low-temperature thermal data. The correction to the perfect gas state amounts to 40 calories per mole (based on Berthelot's equation) on the heat of vaporization and 13 calories per mole on the free energy of vaporization at 238.4°, the boiling point. The specific heat of the liquid may be taken as constant, 16.0; and the average specific heat of the solid over the temperature range of importance is 13.0. These figures and the heat of fusion are utilized in obtaining the following results.

Liquid→Gas (Cl_2)

$C_p(g) = 8.0,$
$C_p(l) = 16.0,$
$\Delta C_p = -8.0,$
$\Delta H = 6,330 - 8.0\ T,$
$\Delta F° = 6,330 + 18.4\ T \log T - 70.23\ T.$

Solid→Gas (Cl_2)

$C_p(g) = 8.00,$
$C_p(s) = 13.0,$
$\Delta C_p = -5.0,$
$\Delta H = 7,430 - 5.0\ T,$
$\Delta F° = 7,430 + 11.5\ T \log T - 61.26\ T,$
M. P. $= 170.8°.$

For the calculation of actual vapor pressures the following relationships are given, which are based on the experimental vapor-pressure data:

Liquid→Gas (Cl_2)

$$\log P\ (at.) = -\frac{1499.5}{T} - 4.022 \log T + 15.854,$$

B. P. $= 238.4°.$

Solid→Gas (Cl_2)

$$\log P\,(at.) = -\frac{1607}{T} - 2.51 \log T + 12.986,$$

M. P. = 170.8°.

Monoxide.—Chlorine monoxide, Cl_2O, was studied by Goodeve (*127*) (173–288°). This substance melts at about 157°. In the absence of information, at these low temperatures ΔC_p is taken as zero.

Liquid→Gas (Cl_2O)

$\Delta H = 6{,}280,$
$\Delta F° = 6{,}280 - 22.83\ T,$
B. P. = 275.1°; $\Delta S_{275.1} = 22.8,$
$\Delta F°_{298.1} = -526.$

Dioxide.—King and Partington (*203*) (193–284°) have measured the vapor pressure of chlorine dioxide, ClO_2. Neglecting ΔC_p, the following results are obtained:

Liquid→Gas (ClO_2)

$\Delta H = 7{,}100,$
$\Delta F° = 7{,}100 - 25.00\ T,$
B. P. = 284.0°; $\Delta S_{284.0} = 25.0,$
$\Delta F°_{298.1} = -352.$

The value for the entropy of vaporization seems too high.

Heptoxide.—Measurements on liquid chlorine heptoxide, Cl_2O_7, were made by Goodeve and Powney (*128*) (244–303°). This substance melts at about 182°. ΔC_p has been neglected.

Liquid→Gas (Cl_2O_7)

$\Delta H = 8{,}480,$
$\Delta F° = 8{,}480 - 24.11\ T,$
B. P. = 352°; $\Delta S_{352} = 24.1,$
$\Delta F°_{298.1} = 1{,}293.$

Some decomposition of this substance probably occurs in the temperature range studied, which accounts for the magnitude of the entropy of vaporization.

Monofluoride.—Chlorine monofluoride, ClF, was studied by Ruff and Laass (*329*) (128–173°). The data are too erratic to warrant free-energy calculations, and only a vapor-pressure equation is included.

Liquid→Gas (ClF)

$$\log P\,(at.) = -\frac{1126}{T} + 6.529,$$

B. P. = 172°.

Trifluoride.—Ruff and Krug (*328*) (201–273°) have studied chlorine trifluoride, ClF_3. This substance melts at about 190°. ΔC_p has been neglected.

Liquid→Gas (ClF_3)

$\Delta H = 5{,}890,$
$\Delta F° = 5{,}890 - 20.71\ T,$
B. P. = 284.4°; $\Delta S_{284.4} = 20.7,$
$\Delta F°_{298.1} = -284.$

CHROMIUM

Element.—The only vapor-pressure measurement of chromium is that of Greenwood (*131*) (2,473°), who determined the boiling point at 760 mm pressure. Overstreet (*273*) has computed the free energy of the gas up to 3,000° from spectroscopic data. Examination of Greenwood's boiling-point data for the metals indicates that his boiling-point temperature for chromium should be raised to about 2,750°. At this temperature, then, $\frac{\Delta F^\circ}{T}=0$, and interpolation from Overstreet's table gives $\frac{F^\circ - E^\circ_0}{T} = -47.84$ for the gas. The quantity, $\frac{F^\circ_c - E^\circ_{c,0}}{T}$, is computed to be -15.54 at this temperature. These figures result in $\Delta E^\circ_0 = 88{,}825$. The calculations of $\frac{\Delta F^\circ}{T}$ at various temperatures are summarized in table 11.

TABLE 11.—*Free energy of vaporization data for chromium*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_c - E^\circ_{c,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−36.677	−2.33	−34.35	297.97	263.62
400	−38.137	−3.39	−34.75	222.06	187.31
500	−39.246	−4.32	−34.93	177.65	142.72
600	−40.151	−5.15	−35.00	148.04	113.04
700	−40.917	−5.89	−35.03	126.89	91.86
800	−41.580	−6.59	−34.99	111.03	76.04
900	−42.165	−7.23	−34.93	98.69	63.76
1,000	−42.689	−7.81	−34.88	88.82	53.94
1,100	−43.162	−8.36	−34.80	80.75	45.95
1,200	−43.595	−8.89	−34.71	74.02	39.31
1,300	−43.993	−9.39	−34.60	68.33	33.73
1,400	−44.362	−9.86	−34.50	63.45	28.95
1,500	−44.708	−10.31	−34.40	59.22	24.82
1,600	−45.030	−10.75	−34.28	55.52	21.24
1,700	−45.336	−11.17	−34.17	52.25	18.08
1,800	−45.623	−11.58	−34.04	49.35	15.31
1,900	−45.898	−12.06	−33.84	46.75	12.91
2,000	−46.160	−12.53	−33.63	44.41	10.78
2,500	−47.326	−14.64	−32.69	35.53	2.84
2,600	−47.538	−15.01	−32.53	34.16	1.63
2,700	−47.742	−15.37	−32.37	32.90	.53
2,800	−47.942	−15.71	−32.23	31.72	−.51

From these data the following equations may be derived by the usual methods. The specific heat of the gas has been taken as 5.04, 0.07 higher than the classical value, to account for energy absorption in electron transitions. This is a roughly computed average value between 298.1 and 3,000°.

Solid→Gas (Cr)

$C_p(g)=5.04,$
$C_p(s)=4.84+2.95\times10^{-3}T,$
$\Delta C_p=0.20-2.95\times10^{-3}T,$
$\Delta H=89{,}440+0.20\ T-1.48\times10^{-3}T^2,$
$\Delta F^\circ=89{,}440-0.46\ T\log T+1.48\times10^{-3}T^2-35.58\ T,$
$\Delta H_{298.1}=89{,}368;\ \Delta F^\circ_{298.1}=78{,}627;$
$\Delta S_{298.1}=36.03;\ S^\circ_{298.1}(g)=41.63.$

Liquid→Gas (Cr)

$C_p(g)=5.04,$
$C_p(l)=9.70,$
$\Delta C_p=-4.66,$
$\Delta H=89{,}450-4.66\ T,$
$\Delta F^\circ=89{,}450+10.73\ T\log T-69.38\ T,$
B. P. = 2,750°; $\Delta H_{2750}=76{,}635;\ \Delta S_{2750}=27.8,$
$\Delta H_{298.1}=88{,}061;\ \Delta F^\circ_{298.1}=76{,}683.$

Chloride.—Ephraim (*98*) (1,153–1,206°) and Jellinek and Koop (*183*) (973–1,273°) have studied the vapor pressure of chromic chloride, $CrCl_3$, and are in complete disagreement Work now in progress at the Pacific Experiment Station of the Bureau of Mines definitely shows that the vapor is not stoichiometrically chromic chloride. Consequently, no equations will be given for this substance until the entire system has been investigated.

Oxychloride.—The vapor pressure of liquid chromium oxychloride, CrO_2Cl_2, was measured by Moles and Gómez (*251*) (353–394°). $\Delta C_p = -18$ has been assumed for this substance.

Liquid→Gas (CrO_2Cl_2)
$\Delta C_p = -18,$
$\Delta H = 15{,}270 - 18\,T,$
$\Delta F^\circ = 15{,}270 + 41.5\,T \log T - 146.68\,T,$
B. P. = 390°; $\Delta H_{390} = 8{,}250$; $\Delta S_{390} = 21.2,$
$\Delta H_{298.1} = 9{,}904$; $\Delta F^\circ_{298.1} = 2{,}156.$

COBALT

Element.—Ruff and Keilig (*325*) have reported 30 mm for the vapor pressure of cobalt at 2,375°. This is the only available figure for this substance and consequently no free energy equation is derived.

Chloride.—Maier (*232*) (906–1,365°) has measured the vapor pressure of cobalt chloride, $CoCl_2$. His results are somewhat erratic in the lower part of the temperature range studied but are very consistent above 1,100°. In the following relationships $\Delta C_p = -10$ has been assumed.

Liquid→Gas ($CoCl_2$)
$\Delta C_p = -10,$
$\Delta H = 40{,}400 - 10\,T,$
$\Delta F^\circ = 40{,}400 + 23.0\,T \log T - 102.33\,T,$
B. P. = 1,323°; $\Delta H_{1323} = 27{,}170$; $\Delta S_{1323} = 20.5,$
$\Delta H_{298.1} = 37{,}419$; $\Delta F_{298.1} = 26{,}860.$

Carbonyl.—Mond, Hirtz, and Cowap (*252*) have reported 0.072 mm for the vapor pressure of $Co_2(CO)_8$ at 288.1°.

COLUMBIUM

Fluoride.—The only columbium compound whose vapor has been measured is the fluoride CbF_5, studied by Ruff and Schiller (*334*) (457–490°). The data are too erratic to warrant any but the simplest possible treatment.

Liquid→Gas (CbF_5)
$\Delta H = 11{,}070,$
$\Delta F^\circ = 11{,}070 - 22.22\,T,$
B. P. = 498°; $\Delta S_{498} = 22.2,$
$\Delta F^\circ_{298.1} = 4{,}446.$

COPPER

Element.—Greenwood (*131, 132, 133*) (2,253–2,583°), Harteck (*144*) (1,419–1,463°), Jones, Langmuir, and Mackay (*191*) (1,186–1,298°), Mack, Osterhof, and Kraner (*230*) (1,083°), Ruff and Bergdahl (*316*) (2,378–2,573°), Ruff and Konschak (*327*) (2,138–2,643°), and Von Wartenberg (*425*) (2,473°) have measured the vapor pressure of copper. Sherman (*358*) recently reported a value of 105.2 mm at 2,490° obtained by Fischer and Grieger, whose results have not been published. The data of Harteck are probably the most reliable and indicate that the higher temperature results of Greenwood, Von Wartenberg, and Ruff and his coworkers are in error. Harteck's data were used in obtaining $\Delta E^\circ_0 = 81{,}240$ for this substance, which already has been discussed as an example illustrating calculations from spectroscopic data, and it was shown that the free-energy equation obtained for the liquid is in agreement with the recent value of Fischer and Grieger at 2,490° reported by Sherman. It should be noted that Fischer and Grieger's result is in the temperature range covered by the investigators who are believed to be in error. The explanation of this discrepancy must be either that errors were made in temperature measurements or else gaseous impurities were present in the samples of copper used. For completeness, the table giving $\frac{\Delta F^\circ}{T}$ and the equations for copper are repeated.

TABLE 12.—*Free energy of vaporization data for copper*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_s - E^\circ_{s,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−34.786	−3.90	−30.89	272.53	241.64
400	−36.247	−5.15	−31.10	203.10	172.00
500	−37.355	−6.20	−31.16	162.48	131.32
600	−38.261	−7.10	−31.16	135.40	104.24
700	−39.026	−7.90	−31.13	116.06	84.93
800	−39.689	−8.62	−31.07	101.55	70.48
900	−40.274	−9.26	−31.01	90.27	59.26
1,000	−40.797	−9.85	−30.95	81.24	50.29
1,100	−41.271	−10.40	−30.87	73.85	42.98
1,200	−41.703	−10.90	−30.80	67.70	36.90
1,300	−42.100	−11.39	−30.71	62.49	31.78
1,400	−42.469	−11.89	−30.58	58.03	27.45
1,500	−42.812	−12.47	−30.34	54.16	23.82
1,600	−43.133	−13.00	−30.13	50.78	20.65
1,700	−43.434	−13.50	−29.94	47.79	17.85
1,800	−43.718	−13.97	−29.75	45.13	15.38
1,900	−43.988	−14.40	−29.59	42.76	13.17
2,000	−44.242	−14.82	−29.42	40.62	11.20
2,500	−45.360	−16.61	−28.75	32.50	3.75
3,000	−46.290	−18.06	−28.23	27.08	−1.15

Solid→Gas (Cu)

$C_p(g) = 4.97,$
$C_p(s) = 5.44 + 1.462 \times 10^{-3} T,$
$\Delta C_p = -0.47 - 1.462 \times 10^{-3} T,$
$\Delta H = 81{,}730 - 0.47\ T - 0.731 \times 10^{-3} T^2,$
$\Delta F^\circ = 81{,}730 + 1.08\ T \log T + 0.731 \times 10^{-3} T^2 - 35.41\ T,$
$\Delta H_{298.1} = 81{,}525;\ \Delta F^\circ_{298.1} = 72{,}036,$
$\Delta S_{298.1} = 31.83;\ S^\circ_{298.1}(g) = 39.75.$

Liquid→Gas (Cu)

$C_p(g) = 4.97,$
$C_p(l) = 7.50,$
$\Delta C_p = -2.53,$
$\Delta H = 80{,}070 - 2.53\ T,$
$\Delta F^\circ = 80{,}070 + 5.83\ T \log T - 48.08\ T,$
B. P. = 2,868°; $\Delta H_{2868} = 72{,}814;\ \Delta S_{2868} = 25.4,$
$\Delta H_{298.1} = 79{,}316;\ \Delta F^\circ_{298.1} = 70{,}037.$

Oxide.—Mack, Osterhof, and Kraner (*230*) (873–1,223°) have made vapor-pressure measurements reputed to be of cupric oxide, CuO. These data are for pressures below 0.001 mm and are consequently erratic, so that reliable free-energy calculations cannot be made. Moreover, due to the dissociation of cupric oxide, the significance of these measurements is at least questionable.

Bromide.—Liquid cuprous bromide, Cu_2Br_2, was studied by Jellinek and Rudat (*184*) (1,173–1,373°) and Von Wartenberg and Bosse (*431*) (1,270–1,624°). The data are in fair agreement, those of Von Wartenberg and Bosse appearing the better. $\Delta C_p = -14$ has been assumed in obtaining the following results.

Liquid→Gas (Cu_2Br_2)
$\Delta C_p = -14,$
$\Delta H = 39{,}100 - 14\ T,$
$\Delta F^\circ = 39{,}100 + 32.2\ T \log T - 127.43\ T,$
B. P. $= 1{,}628^\circ$; $\Delta H_{1628} = 16{,}308$; $\Delta S_{1628} = 10.0,$
$\Delta H_{298.1} = 34{,}927$; $\Delta F^\circ_{298.1} = 24{,}864.$

The entropy of vaporization is abnormally low, and the explanation is by no means apparent. The other cuprous halides will be seen to give even lower values. Assumption of dissociation of the vapor into CuBr molecules does not improve the situation much, since $\Delta S = 11.2$ if $\Delta C_p = -7$ and $\Delta S = 12.1$ if $\Delta C_p = 0$. Whatever the cause of this difficulty may be, the vapor-pressure relationship corresponding to the above free-energy equation represents the data obtained from two independent investigations. The author believes, however, that the equations for heat and free energy themselves have no significance.

Chloride.—Maier (*232*) (1,228–1,731°) and Von Wartenberg and Bosse (*431*) (1,151–1,642°) have measured the vapor pressure of liquid cuprous chloride, Cu_2Cl_2. In both investigations duplicate sets of determinations were made, Von Wartenberg and Bosse using both quartz and platinum containers. Maier found it necessary to have metallic copper present during the preparation of the sample and during the vapor-pressure measurements, since preliminary studies showed that chlorine was evolved in the vapor-pressure apparatus when cuprous chloride was heated alone. Up to about 1,400° the data from the two investigations are in agreement, but above this temperature Von Wartenberg and Bosse's results have a greater temperature coefficient than in the lower temperature range. It will be seen that the entropy of vaporization is abnormally low in this case. The comments made in discussing cuprous bromide apply here also.

Liquid→Gas (Cu_2Cl_2)
$\Delta C_p = -14,$
$\Delta H = 36{,}600 - 14\ T,$
$\Delta F^\circ = 36{,}600 + 32.2\ T \log T - 129.25\ T,$
B. P. $= 1{,}763^\circ$; $\Delta H_{1763} = 11{,}918$; $\Delta S_{1763} = 6.8,$
$\Delta H_{298.1} = 32{,}427$; $\Delta F^\circ_{298.1} = 21{,}822.$

Iodide.—Greiner and Jellinek (*134*) (1,073°), Jellinek and Rudat (*184*) (1,183–1,373°), and Von Wartenberg and Bosse (*431*) (1,264–1,427°) have measured the vapor pressure of liquid cuprous iodide. Greiner and Jellinek and Jellinek and Rudat claim the molecular species in the gas is CuI, and Von Wartenberg and Bosse state that the substance is strongly dissociated, $Cu_2I_2 = 2CuI$. For the present calculations the gas is assumed to be entirely CuI, and ΔC_p is taken as -7.

Liquid→Gas (CuI)
$\Delta C_p = -7,$
$\Delta H = 27{,}200 - 7\ T,$
$\Delta F^\circ = 27{,}200 + 16.1\ T \log T - 68.53\ T,$
B. P. $= 1{,}609^\circ$; $\Delta H_{1609} = 15{,}937$; $\Delta S_{1609} = 9.9,$
$\Delta H_{298.1} = 25{,}113$; $\Delta F^\circ_{298.1} = 18{,}647.$

Here again an abnormally low entropy of vaporization figure results, and the reader is referred to the remarks made in discussing cuprous bromide and chloride, especially with reference to the significance of these equations.

FLUORINE

Element.—The vapor pressure of liquid fluorine was measured by Cady and Hildebrand (*58*) (72–86°). In the absence of information concerning the specific heats ΔC_p is taken as zero. The extreme variation in I is 0.06 unit.

Liquid→Gas (F_2)

$\Delta H = 1{,}640,$

$\Delta F^\circ = 1{,}640 - 19.31\ T,$

B. P. = 84.9°; $\Delta S_{84.9} = 19.3.$

Monoxide.—Ruff and Menzel (*330, 331*) (80–128°) have measured the vapor pressure of liquid fluorine monoxide, F_2O. They report 49.3° for the melting point. If the preliminary measurements in their first paper are discarded, the remainder show an extreme deviation in I of 0.19 unit when ΔC_p is neglected in calculating Σ-function values.

Liquid→Gas (F_2O)

$\Delta H = 2{,}650,$

$\Delta F^\circ = 2{,}650 - 20.66\ T,$

B. P. = 128.3°; $\Delta S_{128.3} = 20.7.$

GALLIUM

Element.—Harteck (*144*) (1,198–1,391°) has measured the vapor pressure of liquid gallium. His results are quite scattered and depend upon the assumption of the molecular species present in the gas. (Harteck assumed the gas to be monatomic.) A log P equation only is justified in this case.

Liquid→Gas (Ga)

$$\log P\ (\text{at.}) = -\frac{16{,}280}{T} - 1.27 \log T + 11.242,$$

B. P. = 2,344°.

GERMANIUM

Monogermane.—The hydride of germanium, GeH_4, was studied by Corey, Laubengayer, and Dennis (*67*) (128–190°). Paneth and Rabinowitsch (*274*) (126–186°), and Schenck and Imker (*349*) (118–183°). This substance melts at 108°. The three sets of data do not agree, and those of Paneth and Rabinowitsch were adopted for the present purpose, since they are very consistent and about the mean of the other two sets. Taking ΔC_p as zero, the variation in the I values from Paneth and Rabinowitsch's data is 0.08 unit if one determination is omitted.

Liquid→Gas (GeH_4)

$\Delta H = 3{,}580,$

$\Delta F^\circ = 3{,}580 - 19.46\ T,$

B. P. = 184.0°; $\Delta S_{184.0} = 19.5.$

Bromide.—Vapor-pressure measurements on solid and liquid germanium bromide, $GeBr_4$, were made by Brewer and Dennis (*41*) (277–460°). Their results for the liquid above about 355° are consistent, but below this temperature they do not show a proper temperature coefficient. Also the heat of vaporization computed from their data for the solid is lower than that obtained for the liquid which, of course, is impossible. Consequently, equations for the liquid range only are given. These are based on the data above 355° and the assumption that $\Delta C_p = -18$. The melting point is 299.2°.

Liquid→Gas ($GeBr_4$)

$\Delta C_p = -18,$
$\Delta H = 16{,}880 - 18\,T,$
$\Delta F^\circ = 16{,}880 + 41.4\,T \log T - 146.87\,T,$
B. P. = 462°; $\Delta H_{462} = 8{,}564$; $\Delta S_{462} = 18.5,$
$\Delta H_{298.1} = 11{,}514$; $\Delta F^\circ_{298.1} = 3{,}635.$

Chloride.—Laubengayer and Tabern (*222*) (233–358°) and Nilson and Pettersson (*261*) (283–550°) have measured the vapor pressure of liquid germanium chloride, $GeCl_4$. The melting point is 223.6°. The two sets of data are in good agreement, the I values from the individual sets differing by only 0.06 unit. Nilson and Pettersson have taken their measurements up to 38 atmospheres. No attempt has been made to represent these high-pressure data, although it happens that the equations given do fit up to 7 atmospheres. ΔC_p has been assumed to be −18.

Liquid→Gas ($GeCl_4$)

$\Delta C_p = -18,$
$\Delta H = 13{,}460 - 18\,T,$
$\Delta F^\circ = 13{,}460 + 41.5\,T \log T - 143.63\,T,$
B. P. = 357°; $\Delta H_{357} = 7{,}034$; $\Delta S_{357} = 19.7,$
$\Delta H_{298.1} = 8{,}094$; $\Delta F^\circ_{298.1} = 1{,}255.$

Trichlormonogermane.—This substance, $GeHCl_3$, was studied by Dennis, Orndorff, and Tabern (*81*) (248–352°). This compound melts at about 202° and undergoes noticeable decomposition at 313° or above. These investigators showed the vapor to be monomolecular. Assuming $\Delta C_p = -18$ the following equations result.

Liquid→Gas ($GeHCl_3$)

$\Delta C_p = -18,$
$\Delta H = 14{,}250 - 18\,T,$
$\Delta F^\circ = 14{,}250 + 41.4\,T \log T - 146.17\,T,$
$\Delta H_{298.1} = 8{,}884$; $\Delta F^\circ_{298.1} = 1{,}214.$

The free energy becomes zero at 348°, which is a hypothetical boiling point assuming no dissociation.

Tetramethyl.—Germanium tetramethyl, $Ge(CH_3)_4$, in the liquid state was studied by Dennis and Hance (*79*) (184–320°). The melting point is about 185°. A Σ-function plot assuming $\Delta C_p = -10$ gives a straight line with an extreme deviation in I of 0.37 unit if two determinations are omitted.

Liquid→Gas ($Ge(CH_3)_4$)

$\Delta C_p = -10,$
$\Delta H = 9{,}625 - 10\,T,$
$\Delta F^\circ = 9{,}625 + 23.0\,T \log T - 87.90\,T,$
B. P. = 317°; $\Delta H_{317} = 6{,}455$; $\Delta S_{317} = 20.4,$
$\Delta H_{298.1} = 6{,}644$; $\Delta F^\circ_{298.1} = 387.$

Digermane.—Dennis, Corey, and Moore (*80*) (175–273°) have measured the vapor pressure of liquid digermane, Ge_2H_6, which melts at about 164°. In this case ΔC_p has been taken as −4, and the equations obtained are satisfactory above 217°. Below this temperature the calculated and observed vapor pressures deviate somewhat.

Liquid→Gas (Ge_2H_6)

$\Delta C_p = -4,$
$\Delta H = 7{,}120 - 4\ T,$
$\Delta F^\circ = 7{,}120 + 9.2\ T \log T - 46.23\ T,$
B. P. $= 304.5°$; $\Delta H_{304.5} = 5{,}902$; $\Delta S_{304.5} = 19.4,$
$\Delta H_{298.1} = 5{,}928$; $\Delta F^\circ_{298.1} = 125.$

Trigermane.—Dennis, Corey, and Moore (*80*) (275–385°) also studied trigermane, Ge_3H_8. The melting point given for this substance is 167.5°. Σ-function values calculated on the assumption that $\Delta C_p = -6$ give a straight line when plotted against $\frac{1}{T}$, with an extreme variation in I of 0.14 if two erratic points are omitted.

Liquid→Gas (Ge_3H_8)

$\Delta C_p = -6,$
$\Delta H = 9{,}850 - 6\ T,$
$\Delta F^\circ = 9{,}850 + 13.8\ T \log T - 61.33\ T,$
B. P. $= 383.7°$; $\Delta H_{383.7} = 7{,}548$; $\Delta S_{383.7} = 19.7,$
$\Delta H_{298.1} = 8{,}061$; $\Delta F^\circ_{298.1} = 1{,}747.$

GOLD

Element.—Vapor-pressure measurements of gold were made by Harteck (*144*) (1,436–1,463°), Ruff and Bergdahl (*316*) (2,588–2,883°), Ruff and Konschak (*327*) (2,258–2,783°), and Von Wartenberg (*425*) (B. P.>2,200°). Overstreet (*273*) has computed free-energy values for the gas from spectroscopic data at various temperatures between 298 and 3,000°. Harteck's determinations are used in conjunction with Overstreet's figures to obtain the free energy of vaporization values given in table 13. ΔE° was found from a smoothed value from Harteck's data, $\frac{\Delta F_0^\circ}{T} = -R \ln P = 30.06$, at 1,500°. The corresponding ΔE_0° value is 90,450.

TABLE 13.—*Free energy of vaporization data for gold*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_s - E^\circ_{s,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−38.160	−6.56	−31.60	303.42	271.82
400	−39.620	−8.04	−31.58	226.12	194.54
500	−40.729	−9.21	−31.52	180.90	149.38
600	−41.634	−10.20	−31.43	150.75	119.32
700	−42.400	−11.07	−31.33	129.21	97.88
800	−43.063	−11.84	−31.22	113.06	81.84
900	−43.648	−12.54	−31.11	100.50	69.39
1,000	−44.172	−13.16	−31.01	90.45	59.44
1,100	−44.645	−13.73	−30.91	82.23	51.32
1,200	−45.077	−14.28	−30.80	75.38	44.58
1,300	−45.476	−14.78	−30.70	69.58	38.88
1,400	−45.844	−15.36	−30.48	64.61	34.13
1,500	−46.187	−15.95	−30.24	60.30	30.06
1,600	−46.508	−16.49	−30.02	56.53	26.51
1,700	−46.811	−16.99	−29.82	53.21	23.39
1,800	−47.095	−17.47	−29.63	50.25	20.62
2,000	−47.624	−18.32	−29.30	45.22	15.92
2,500	−48.754	−20.09	−28.66	36.18	7.52
3,000	−49.703	−21.52	−28.18	30.15	1.97

In deriving equations from these free-energy results the value of I for the solid was computed from entropy figures at 298.1° and high-temperature thermal data, and ΔH_0 was obtained in the usual manner from the Σ-function values. The individual values of ΔH_0 varied over a range of 32 calories giving a mean of 90,740. The ΔH_0 value for the liquid, obtained from that of the solid, the heat of fusion, and the high-temperature specific heats, is 88,280. This latter figure when combined with Σ-function results for the liquid gives individual values of *I* having an extreme variation of 0.06 unit.

Solid→Gas (Au)

$C_p(g) = 5.00,$
$C_p(s) = 5.61 + 1.44\times10^{-3}T,$
$\Delta C_p = -0.61 - 1.44\times10^{-3}T,$
$\Delta H = 90{,}740 - 0.61\ T - 0.72\times10^{-3}T^2,$
$\Delta F^\circ = 90{,}740 + 1.40\ T\log T + 0.72\times10^{-3}T^2 - 36.23\ T,$
$\Delta H_{298.1} = 90{,}494;\ \Delta F^\circ_{298.1} = 81{,}037;\ S^\circ_{298.1}(g) = 43.13.$

Liquid→Gas. (Au)

$C_p(g) = 5.00,$
$C_p(l) = 7.00,$
$\Delta C_p = -2.00,$
$\Delta H = 88{,}280 - 2.00\ T,$
$\Delta F^\circ = 88{,}280 + 4.61\ T\log T - 43.44\ T,$
B. P. = 3,239°; $\Delta H_{3239} = 81{,}802;\ \Delta S_{3239} = 25.26,$
$\Delta H_{298.1} = 87{,}684;\ \Delta F^\circ_{298.1} = 78{,}731.$

Chloride.—Several investigators have attempted to obtain the partial pressures of the chloride, Au_2Cl_6, in the gaseous phase in equilibrium with the solid of the same composition—Biltz, Fischer, and Juza (*27*) (513°), Fischer and Biltz (*108*) (473–518°), Petit (*284*) (454–600°), and Rose (*314*) (343–551°). This substance decomposes readily, and at temperatures even as low as 343° the partial pressure of Au_2Cl_6 is only a small fraction of the total pressure. Consequently, the partial-pressure results obtained are very discordant, making it advisable to omit equations for this substance.

HELIUM

Element.—Vapor-pressure measurements of liquid helium were made by Keesom, Weber, and Norgaard (*197*) (1.72–4.22°), Keesom, Weber, and Schmidt (*198*) (0.843–4.90°), and Onnes and Weber (*270*) (1.47–5.16°). The liquid exists in two forms, the transition between which takes place over a range of temperature centered around 2.19°. The following vapor-pressure equations are those of Keesom and his coworkers, altered only by the change from millimeters to atmospheres.

Liquid→Gas (He)

$$\log P\,(at.) = -\frac{3.859}{T} + 0.922\log T + 0.154;\ (T < 2.19^\circ),$$

$$\log P\,(at.) = -\frac{3.024}{T} + 2.208\log T - 0.664;\ (T > 2.19^\circ),$$

B. P. = 4.22°.

HYDROGEN

Element.—Vapor pressures of hydrogen were measured by Bonhoeffer and Harteck (*35*) (13.8–20.4°, both normal and para), Bulle (*58*) (20–32°), Cath and Onnes (*62*) (24–33°), Henning (*153*) (14–21°), Keesom, Bijl, and Van der Horst (*195*) (15–20°), Onnes, Crommelin, and Cath (*271*) (32–33°), and Travers and Jaquerod (*417, 418*) (14–21°). It would be very difficult to derive entirely satisfactory heat and free energy of vaporization equations for this substance because of the very low temperatures involved and the difficulty in taking account of gas imperfection. Furthermore, liquid hydrogen has some unusual properties. For example, the heat of vaporization rises as the temperature is decreased below the boiling point, reaches a maximum at about 16°, and then decreases. Consequently, no free-energy relationships are given, but vapor-pressure equations are included for ordinary hydrogen and for the paraform.

Liquid→Gas (H_2)

Ordinary hydrogen

$$\log P\ (at.) = -\frac{51.15}{T} + 2.505,$$

B. P. = 20.42°.

Para hydrogen

$$\log P\ (at.) = -\frac{50.54}{T} + 2.496,$$

B. P. = 20.25°.

Simon (*361*) has derived a vapor-pressure equation for solid hydrogen from a consideration of the heat of vaporization of the solid and the specific heats of solid and gas. This equation, after changing from centimeters to atmospheres, follows.

Solid→Gas (H_2)

Ordinary hydrogen

$$\log P\ (at.) = -\frac{40.123}{T} + 2.5 \log T - \frac{1}{4.571}\int_0^T \frac{E(91)}{T^2}\,dT + 5.30\times10^{-10}T^6 + 3.67\times10^{-11}T^7 - 1.1108.$$

The symbol $E(91)$ refers to the energy corresponding to the Debye function of $\frac{h\nu}{k} = 91$. Table 14 gives vapor-pressure results computed from this relationship.

TABLE 14.—*Vapor pressures of solid hydrogen*

T	P(at.)	T	P(at.)
7.0	1.84×10^{-5}	11.0	6.79×10^{-3}
7.5	5.28×10^{-5}	11.5	1.09×10^{-2}
8.0	1.34×10^{-4}	12.0	1.69×10^{-2}
8.5	3.07×10^{-4}	12.5	2.54×10^{-2}
9.0	6.45×10^{-4}	13.0	3.70×10^{-2}
9.5	1.26×10^{-3}	13.5	5.28×10^{-2}
10.0	2.33×10^{-3}	13.94	7.08×10^{-2}
10.5	4.07×10^{-3}		

Water.—Many investigators have studied the vapor pressure of water—Crafts (*69*) (408–502°), Derby, Daniels, and Gutsche (*82*) (298°), Drücker, Jiméno, and Kangro (*91*) (139–156°), Fenby (*105*) (278–298°), Holborn and Baumann (*168*) (473–643°), Holborn and Henning (*169*) (273–473°), Jolly and Briscoe (*190*) (297–325°), Kahlbaum (*193*) (283–315°), Keyes and Smith (*202*) (373–583°), Osborne, Stimson, Fiock, and Ginnings (*272*) (383–647°), Scheel and Heuse (*344*, *345*) (213–323°), Smith and Menzies (*367*) (322–369°), Washburn (*433*) (183–273°), Wertheimer (*438*) (273–647°), and many others. With a few minor exceptions the data below 1 atmosphere are in very good agreement. The higher-pressure figures were not utilized for the present purpose. To avoid the effects due to associated molecules and other gas imperfections the equations have been based largely on the lower-pressure data, particularly on the figures for ice. It is to be noticed that the free-energy equation for the vaporization of the liquid gives $\Delta F^\circ = 0$ at 373.4°, which is 0.3° above the normal boiling point. According to this equation the fugacity of the monomolecular species is unity at this temperature. However, because of certain minor corrections which have not been made, this statement probably has but little significance.

Solid→Gas (H_2O)
$C_p(g) = 8.22 + 0.15 \times 10^{-3}T + 1.34 \times 10^{-6}T^2,$
$C_p(s) = 0.56 + 31.3 \times 10^{-3}T,$
$\Delta C_p = 7.66 - 31.2 \times 10^{-3}T + 1.34 \times 10^{-6}T^2,$
$\Delta H = 11{,}260 + 7.66\,T - 15.6 \times 10^{-3}T^2 + 0.446 \times 10^{-6}T^3,$
$\Delta F^\circ = 11{,}260 - 17.64\,T \log T + 15.6 \times 10^{-3}T^2 - 0.223 \times 10^{-6}T^3 + 7.656\,T,$
$\Delta H_{298.1} = 12{,}169;\ \Delta F^\circ_{298.1} = 1{,}910.$

Liquid→Gas (H_2O)
$C_p(g) = 8.22 + 0.15 \times 10^{-3}T + 1.34 \times 10^{-6}T^2,$
$C_p(l) = 18.03,$
$\Delta C_p = -9.81 + 0.15 \times 10^{-3}T + 1.34 \times 10^{-6}T^2,$
$\Delta H = 13{,}425 - 9.81\,T + 0.075 \times 10^{-3}T^2 + 0.446 \times 10^{-6}T^3,$
$\Delta F^\circ = 13{,}425 + 22.59\,T \log T - 0.075 \times 10^{-3}T^2 - 0.223 \times 10^{-6}T^3 - 94.00\,T,$
$\Delta H_{298.1} = 10{,}520;\ \Delta F^\circ_{298.1} = 2{,}054.$

It is to be noted that the value $\Delta F^\circ_{298.1} = 2{,}054$ for the free-energy difference between gas and liquid is virtually identical with the figure 2,053 given by Lewis and Randall (*226*).

An approximate equation also is included for the vapor pressure of water composed of the heavy isotope (atomic weight 2) of hydrogen. Lewis and Macdonald (*225*) compared the vapor pressure of a sample of this water of over 99 percent purity with that of ordinary water in a differential tensimeter. Their pressure differences have been subtracted from the results of Holborn and Henning for ordinary water at the corresponding temperatures.

Liquid→Gas (H^2H^2O)
$\log P\ (at.) = -\frac{2{,}286}{T} + 6.105,$
B. P. = 374.5°.

Water composed of the heavy isotope of hydrogen has a heat of vaporization greater than that of ordinary water by about 260 calories per mole. This corresponds to about 0.6 unit in the entropy of vaporization at the boiling point.

Peroxide.—The vapor pressure of liquid hydrogen peroxide, H_2O_2, was measured by Maass and Hiebert (*228*) (296–349°). Some decomposition of their sample occurred during the course of the measurements. Σ-function values, computed on the assumption that $\Delta C_p = -14$, when plotted against $\frac{1}{T}$ may be fitted by a straight line with an extreme variation in I of 0.34 unit if one obviously erratic point is omitted.

Liquid→Gas (H_2O_2)
$\Delta C_p = -14,$
$\Delta H = 16{,}300 - 14\,T,$
$\Delta F^\circ = 16{,}300 + 32.2\,T \log T - 122.67\,T,$
B. P. = 431°; $\Delta H_{431} = 10{,}266;\ \Delta S_{431} = 23.8,$
$\Delta H_{298.1} = 12{,}127;\ \Delta F^\circ_{298.1} = 3{,}483.$

Sulphide.—Blue (*30*) (164–214°), Klemenc (*204*) (153–207°), Klemenc and Bankowski (*205*) (153–213°), Regnault (*300*) (247–341°), Steele and Bagster (*377*) (198–214°), and Steele and McIntosh (*378*) (185–213°) have measured the vapor pressure of hydrogen sulphide. The solid exists in three different polymorphic forms, and Blue has measured the temperatures and heats of transition as well as the heat and temperature of fusion, boiling point, and heat of vaporization. The free-energy and heat of vaporization equations are obtained from his thermal data. Correction to the ideal state was made for the heat of vaporization. The specific heat of the liquid may be taken as constant at 16.25, and that of the solid state stable between 126.2° and the melting point, 187.6°, is approximated by $C_p(S_I)=9.83+0.024\ T$. For the specific heat of the gas the value $7.95=4\ R$ is used.

Liquid→Gas (H_2S)
$C_p(g)=7.95,$
$C_p(l)=16.25,$
$\Delta C_p=-8.30,$
$\Delta H=6{,}254-8.30\ T,$
$\Delta F^\circ=6{,}254+19.11\ T\log T-73.83\ T.$
Solid (S_I)→Gas (H_2S)
$C_p(g)=7.95,$
$C_p(S_I)=9.83+0.024\ T,$
$\Delta C_p=-1.88-0.024\ T,$
$\Delta H=6{,}040-1.88\ T-0.012\ T^2,$
$\Delta F^\circ=6{,}040+4.33\ T\log T+0.012\ T^2-41.34\ T.$

No equations are given for the other solid forms, since the transition between S_I and S_{II} is not sharp but is of the ammonium chloride type. The vapor pressure of the liquid is represented by the following equation, which agrees with Blue's data and is also a fair representation of the mean of the others:

Liquid→Gas (H_2S)
$$\log P\ (at.)=-\frac{1{,}377.0}{T}-4.177\log T+16.195,$$
B. P.=212.8°.

Disulphide.—Liquid hydrogen disulphide, H_2S_2, was studied by Butler and Maass (*57*) (273–318°). Their data are quite erratic, and therefore a log *P* equation only is included. They give 183.5° as the melting point.

Liquid→Gas (H_2S_2)
$$\log P\ (at.)=-\frac{2{,}077}{T}+6.160,$$
B. P.=337°.

Bromide.—Vapor-pressure measurements of hydrogen bromide were made by Drozdowski and Pietrzak (*90*) (83–360°), Henglein (*149*) (177–209°), Steele and Bagster (*377*) (197–207°), and Steele and McIntosh (*378*) (168–208°). Heat and free energy of vaporization equations are obtained from low-temperature thermal data, correction being made for gas imperfection. This substance undergoes three transformations in the solid state between 15° and the melting point, 186.2°. Only the liquid and highest-temperature solid form are considered. The specific heat of the former is nearly constant, 14.26, and that of the latter may be represented down to 120° by the average value, 11.40.

Liquid→Gas (HBr)

$C_p(g)=6.95,$
$C_p(l)=14.26,$
$\Delta C_p=-7.31,$
$\Delta H=5{,}752-7.31\ T,$
$\Delta F^\circ=5{,}752+16.83\ T\log T-66.77\ T.$

Solid (S_I)→**Gas (HBr)**

$C_p(g)=6.95,$
$C_p(S_I)=11.40,$
$\Delta C_p=-4.45,$
$\Delta H=5{,}795-4.45\ T,$
$\Delta F^\circ=5{,}795+10.25\ T\log T-52.06\ T.$

The equation for vapor pressure of the liquid derivable from the above free-energy relationship, on the assumption $\Delta F^\circ=-RT\ ln\ P$, does not fit the experimental data. However, that for the solid similarly derived is satisfactory, since under the low pressures involved fugacity and pressure are virtually equal. The following equation is a good representation of the experimentally determined vapor pressures for the liquid range.

Liquid→Gas (HBr)

$$\log P\ (at.)=-\frac{1{,}290}{T}-3.679\log T+14.772.$$

Chloride.—Vapor pressures of hydrogen chloride were measured by Briner (*45*) (298–324°), Cardoso and Germann (*60*) (248–324°), Drozdowski and Pietrzak (*90*) (83–299°), Giauque and Wiebe (*122*) (132–196°), Henglein (*149*) (115–161°), Henning and Stock (*155*) (155–186°), Karwat (*194*) (122–160°), Steele and McIntosh (*378*) (163–193°), and Stock, Henning, and Kusz (*400*) (162–188°). This substance exhibits two solid modifications with the transition point at 98.4°. The melting point is 158.9°. These values and the corresponding latent-heat results and the heat of vaporization obtained by Giauque and Wiebe are used to derive heat and free energy of vaporization equations. Correction has been made for gas imperfection. The following specific-heat equations are employed—$C_p(g)=6.95$, $C_p(l)=13.97$, $C_p(S_I)=5.70+0.038T$, and $C_p(S_{II})=0.86+0.0074\ T$. Those for the solid and liquid forms are in agreement with the measurements of Giauque and Wiebe, that for S_{II} being good only down to 40°, however. The equation for the gas is the classical $C_p=\frac{7}{2}R$.

Liquid→Gas (HCl)

$C_p(g)=6.95,$
$C_p(l)=13.97,$
$\Delta C_p=-7.02,$
$\Delta H=5{,}209-7.02\ T,$
$\Delta F^\circ=5{,}209+16.17\ T\log T-64.42\ T.$

Solid (S_I)→**Gas (HCl)**

$C_p(g)=6.95,$
$C_p(S_I)=5.70+0.038\ T,$
$\Delta C_p=1.25-0.038\ T,$
$\Delta H=4{,}851+1.25\ T-0.019\ T^2,$
$\Delta F^\circ=4{,}851-2.88\ T\log T+0.019\ T^2-23.25\ T.$

Solid (S_{II})→**Gas (HCl)**

$C_p(g)=6.95,$
$C_p(S_{II})=0.86+0.074\ T,$
$\Delta C_p=6.09-0.074\ T,$
$\Delta H=4{,}833+6.09\ T-0.037\ T^2,$
$\Delta F^\circ=4{,}833-14.03\ T\log T+0.037\ T^2-2.622\ T.$

The corresponding vapor-pressure equations are satisfactory for the two solid forms where the vapor pressures are low, but in the case of the liquid the correction for gas imperfection is important. For the latter the following equation is suggested:

Liquid→Gas (HCl)

$$\log P\ (\text{at.}) = -\frac{1158.5}{T} - 3.534 \log T + 14.199,$$

B. P. = 188.1°.

Fluoride.—The vapor pressure of liquid hydrogen fluoride was measured by Simons (*362*) (192–320°), and Simons and Hildebrand (*363*) have studied the density and complexity of the gas. They find that the properties are explainable on the assumption of the presence of the two molecular species, HF and $(HF)_6$, and have given information sufficient for obtaining the partial pressures of these two species in equilibrium with the liquid at various temperatures. Ignoring ΔC_p, the following results are obtained.

Liquid→Gas (HF)

$\Delta H = 7{,}460,$
$\Delta F^\circ = 7{,}460 - 24.35\,T,$
$P\ (\text{HF}) = 1$ at. at 306.4°.
$\Delta F^\circ_{298.1} = 201.$

Liquid→Gas $[(HF)_6]$

$\Delta H = 5{,}020,$
$\Delta F^\circ = 5{,}020 - 15.48\,T,$
$P\ (\text{HF})_6 = 1$ at. at 324.3°,
$\Delta F^\circ_{298.1} = 405.$

The total vapor pressure is adequately represented by the following equation:

Liquid→Gas $[HF + (HF)_6]$

$$\log P\ (\text{at.}) = -\frac{1{,}331}{T} + 4.549,$$

B. P. = 293°.

Iodide.—The vapor pressure of hydrogen iodide was measured by Drozdowski and Pietrzak (*90*) (83–420°), Henglein (*149*) (177–209°), Steele and Bagster (*377*) (220–234°), and Steele and McIntosh (*378*) (195–238°). The heat and free energy of vaporization equations are based on low-temperature thermal data, as was done with HCl and HBr. The data used for this purpose are those of Giauque and Wiebe (*123*). The heat and free energy necessary to convert the actual gas into the hypothetical ideal gas at the boiling point were computed, as usual, on the assumption of Berthelot's equation of state.

The specific heat of the liquid is nearly constant, 14.25, while for the solid form stable below the melting point the average value for the temperature range 125 to 222.3° (melting point) is 11.15. (This substance shows two transitions between 15 and 222.3°, the character of which precludes the utilization of simple specific-heat equations for the lowest and intermediate temperature solid forms. The highest temperature solid form above 125° gives a specific-heat curve having a relatively small temperature coefficient and this form only is considered with the understanding that the equations are not valid below 125°.)

Liquid→Gas (HI)

$C_p(g)=6.95,$
$C_p(l)=14.25,$
$\Delta C_p=-7.30,$
$\Delta H=6{,}502-7.30\ T,$
$\Delta F^\circ=6{,}502+16.81\ T\log T-67.23\ T.$

Solid (S_I)→Gas (HI)

$C_p(g)=6.95,$
$C_p(S_I)=11.15,$
$\Delta C=-4.20,$
$\Delta H=6{,}499-4.20\ T,$
$\Delta F^\circ=6{,}499+9.67\ T\log T-50.46\ T.$

The following equations represent the experimental vapor-pressure measurements with the exception of those of Steele and Bagster, which appear to be in considerable error.

Liquid→Gas (HI)

$$\log P\ (at.)=-\frac{1{,}456}{T}-3.764\log T+14.859.$$

Solid (S_I)→Gas (HI)

$$\log P\ (at.)=-\frac{1{,}309}{T}-2.114\log T+10.516.$$

Cyanide.—Bredig and Teichmann (*40*) (258–453°), Hara and Sinozaki (*143*) (273–320°), Perry and Porter (*282*) (243–301°), Shirado (*359*) (291°), and Sinozaki, Hara, and Mitsukuri (*365*) (187–320°) have studied the vapor pressure of hydrogen cyanide, HCN. All the results are in good agreement. Taking ΔC_p as zero, it was found that for the liquid the Σ-function values plotted against $\frac{1}{T}$ give a straight line, and the I values from the data of the individual investigations lie in a range of 0.01 unit, while for the solid similar calculations give 0.13 unit.

Liquid→Gas (HCN)

$\Delta H=6{,}660,$
$\Delta F^\circ=6{,}660-22.29\ T,$
B. P.$=298.8^\circ$; $\Delta S_{298.1}=22.3,$
$\Delta F^\circ_{298.1}=15.$

Solid→Gas (HCN)

$\Delta H=8{,}940,$
$\Delta F^\circ=8{,}940-31.06\ T,$
$\Delta F^\circ_{298.1}=-319.$

The melting point and heat of fusion corresponding to these equations are, respectively, 260.0° and 2,280 calories per gram formula weight.

Selenide.—The vapor pressure of hydrogen selenide was measured by Bruylants and Dondeyne (*51*) (194–253°), De Forcrand and Fonezes-Diacon (*111*) (231–304°), and Stein (*379*) (173–229°). This substance melts at 207°. For the liquid range the results of Bruylants and Dondeyne are the most consistent and not far different from the mean of the others. The experimental data for the solid are sketchy and show an abnormally high temperature coefficient. Consequently, equations for this form are omitted. Taking ΔC_p as zero, the individual I values obtained from Bruylants and Dondeyne's data vary over a range of only 0.05 unit.

Liquid→Gas (H_2Se)
$\Delta H = 4{,}880,$
$\Delta F^\circ = 4{,}880 - 21.05\ T,$
B. P. $= 231.8^\circ$; $\Delta S_{231.8} = 21.0.$

Telluride.—Bruylants (*50*) (213–273°) and Stein (*379*) (195–273°) have measured the vapor pressure of hydrogen telluride, H_2Te. The results of Bruylants are undoubtedly the better, and about half of Stein's data fall on Bruylants' curve. Again taking ΔC_p as zero, it is found that Bruylants' results give a variation in I of 0.09 unit for the liquid and 0.20 unit for the solid.

Liquid→Gas (H_2Te)
$\Delta H = 5{,}650,$
$\Delta F^\circ = 5{,}650 - 20.86\ T,$
B. P. $= 270.9^\circ$; $\Delta S_{270.9} = 20.9,$
$\Delta F^\circ_{298.1} = -568.$

Solid→Gas (H_2Te)
$\Delta H = 7{,}320,$
$\Delta F^\circ = 7{,}320 - 28.31\ T.$

From these equations the melting point is 224.2° and the heat of fusion 1,670 calories per gram formula weight. However, since there are only a few vapor-pressure results for the solid, this heat of fusion value may be quite seriously in error.

IODINE

Element.—Arctowski (*8*) (286–345°), Baxter and Grose (*18*) (273–368°), Baxter, Hickey, and Holmes (*20*) (273–328°), Dewar (*83*) (273–303°), Gerry and Gillespie (*117*) (305–358°), Haber and Kerschbaum (*138*) (225–264°), Naumann (*257*) (232–286°), Ramsay and Young (*298*) (331–459°), Richter (*302*) (358–386°), Strassmann (*403*) (305–358°), Wiedemann (*440*) (273–453°), and Wright (*442*) (352–373°) have given vapor-pressure data for iodine. For the solid, the results of Baxter and his coworkers and Ramsay and Young are in good agreement. The data of Haber and Kerschbaum also are consistent among themselves, but the pressure range studied is below 0.009 mm, and, because of increased experimental error at these low pressures, their results do not agree very well with the extrapolation of Baxter and his coworkers' data.

Giauque (*119*) has obtained a vapor-pressure equation for solid iodine based on gas-free energies calculated from spectroscopic data and the vapor-pressure data of Baxter and his coworkers. The heat and free-energy equations given here for the solid correspond to the vapor-pressure relationship of Giauque.

Solid→Gas (I_2)
$C_p(g) = 9.0,$
$C_p(s) = 13.0,$
$\Delta C_p = -4.0,$
$\Delta H = 16{,}069 - 4.0\ T,$
$\Delta F^\circ = 16{,}069 + 9.2\ T \log T - 61.186\ T,$
$\Delta H_{298.1} = 14{,}877$; $\Delta F^\circ_{298.1} = 4{,}615.$

For the vaporization of the liquid, the constant I was obtained from the free energy of vaporization at the melting point, 386.1°, and ΔH_0 was taken from the Σ-function plot of the data of Ramsay and Young and of Wiedemann, which are the only ones extending into the liquid range. The equations finally adopted agree with the measurements of Wiedemann, who found slightly higher pressures than did Ramsay and Young.

Liquid→Gas (I_2)

$C_p(g)=9.0,$
$C_p(l)=16.0,$
$\Delta C_p=-7.0,$
$\Delta H=13{,}580-7.0\,T,$
$\Delta F^\circ=13{,}580+16.1\,T\log T-72.59\,T,$
B. P.=456°; $\Delta H_{456}=10{,}388$; $\Delta S_{456}=22.8,$
$\Delta H_{298.1}=11{,}493$; $\Delta F^\circ_{298.1}=3{,}817.$

The heat of fusion is computed to be 3,650 calories per mole at the melting point, 386.1°. The entropy of fusion is 9.45 units.

Heptafluoride.—Solid iodine heptafluoride, IF_7, was studied by Ruff and Keim (*326*) (210–273°). They state that this substance has the theoretical molecular weight in the gaseous state corresponding to the formula IF_7. The melting point reported is 278–279°. ΔC_p has been neglected in this case.

Solid→Gas (IF_7)

$\Delta H=7{,}460,$
$\Delta F^\circ=7{,}460-26.92\,T,$
S. P.=277°; $\Delta S_{277}=26.9,$
$\Delta F^\circ_{298.1}=-565.$

IRON

Element.—Vapor-pressure measurements of iron were made by Greenwood (*131*) (2,723°), Jones, Langmuir, and Mackay (*191*) (1,270–1,580°), and Ruff and Bormann (*319*) (2,723°). Overstreet (*273*) has computed free-energy values for iron gas at various temperatures up to 3,000° from spectroscopic data. The vapor-pressure results of Jones, Langmuir, and Mackay, of γ-iron, are the most reliable experimental data. From their figures is selected the smoothed value—$R\ln P=\frac{\Delta F^\circ}{T}=33.85$ at 1,400°. From this value, Overstreet's results, and the $\frac{F^\circ_c-E^\circ_{c,0}}{T}$ data for γ-iron there is found $\Delta E^\circ_0=$ 96,030. The summary of the free energy of vaporization calculations is given in table 15.

TABLE 15.—*Free energy of vaporization data for iron*

T	$\frac{F^\circ-E^\circ_0}{T}$	$\frac{F^\circ_c-E^\circ_{c,0}}{T}$	$\frac{\Delta F^\circ-\Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−37.631	−2.88	−34.75	322.14	287.39
400	−39.272	−4.04	−35.23	240.08	204.85
600	−41.504	−5.89	−35.61	160.05	124.44
800	−43.250	−7.62	−35.63	120.04	84.41
1,000	−44.515	−9.07	−35.45	96.03	60.58
1,100	−45.054	−9.77	−35.28	87.30	52.02
1,200	−45.543	−10.44	−35.10	80.02	44.92
1,300	−45.993	−11.07	−34.92	73.87	38.95
1,400	−46.406	−11.67	−34.74	68.59	33.85
1,500	−46.788	−12.23	−34.56	64.02	29.46
1,600	−47.145	−12.75	−34.39	60.02	25.63
1,700	−47.481	−13.24	−34.24	56.49	22.25
1,800	−47.796	−13.72	−34.08	53.35	19.27
1,900	−48.095	−14.26	−33.84	50.54	16.70
2,000	−48.378	−14.78	−33.60	48.02	14.42
2,100	−48.647	−15.27	−33.38	45.73	12.35
2,200	−48.904	−15.74	−33.16	43.65	10.49
2,300	−49.150	−16.17	−32.98	41.75	8.77

Designating the solid forms of iron by α, β, γ, and δ, as is customary, the following results are obtained from the data in the last column of table 15. The figure 5.63 used for the specific heat of iron gas is an approximate, average value for the temperature range 298 to 3,000°. The increase over the classical value $\frac{3}{2}R=4.97$ is due to the energy absorbed in electronic degrees of freedom.

Solid (α)→Gas (Fe) (273–1,041°)
$C_p(g)=5.63,$
$C_p(\alpha)=4.13+6.38\times10^{-3}T,$
$\Delta C_p=1.50-6.38\times10^{-3}T,$
$\Delta H=96{,}520+1.50\ T-3.19\times10^{-3}T^2,$
$\Delta F^\circ=96{,}520-3.45\ T\log T+3.19\times10^{-3}T^2-28.77\ T,$
$\Delta H_{298.1}=96{,}684;\ \Delta F^\circ_{298.1}=85{,}682;\ S^\circ_{298.1}(g)=43.38.$
Solid (β)→Gas (Fe) (1,041–1,179°)
$C_p(g)=5.63,$
$C_p(\beta)=6.12+3.36\times10^{-3}T,$
$\Delta C_p=-0.49-3.36\times10^{-3}T,$
$\Delta H=96{,}620-0.49\ T-1.68\times10^{-3}T^2,$
$\Delta F^\circ=96{,}620+1.13\ T\log T+1.68\times10^{-3}T^2-41.10\ T,$
$\Delta H_{298.1}=96{,}325;\ \Delta F^\circ_{298.1}=85{,}351.$
Solid (γ)→Gas (Fe) (1,179–1,674°)
$C_p(g)=5.63,$
$C_p(\gamma)=8.40,$
$\Delta C_p=-2.77,$
$\Delta H=96{,}610-2.77\ T,$
$\Delta F^\circ=96{,}610+6.38\ T\log T-55.22\ T,$
$\Delta H_{298.1}=95{,}784;\ \Delta F^\circ_{298.1}=84{,}855.$
Solid (δ)→Gas (Fe) (1,674–1,803°)
$C_p(g)=5.63,$
$C_p(\delta)=10.00,$
$\Delta C_p=-4.37,$
$\Delta H=99{,}090-4.37\ T,$
$\Delta F^\circ=99{,}090+10.06\ T\log T-68.54\ T,$
$\Delta H_{298.1}=97{,}787;\ \Delta F^\circ_{298.1}=86{,}078.$
Liquid→Gas (Fe) (1,803°–)
$C_p(g)=5.63,$
$C_p(l)=8.15,$
$\Delta C_p=-2.52,$
$\Delta H=92{,}200-2.52\ T,$
$\Delta F^\circ=92{,}200+5.80\ T\log T-50.83\ T,$
B. P.$=3{,}008°$; $\Delta H_{3008}=84{,}620;\ \Delta S_{3008}=28.1,$
$\Delta H_{298.1}=91{,}449;\ \Delta F^\circ_{298.1}=81{,}126.$

Ferrous chloride.—The vapor pressure of ferrous chloride was measured by Maier (*232*) (972–1,268°). The data are quite concordant. If one point is omitted, the extreme variation in I is 0.43 unit when Σ-function values are computed on the assumption that $\Delta C_p=-10$.

Liquid→Gas ($FeCl_2$)
$\Delta C_p=-10,$
$\Delta H=43{,}200-10\ T,$
$\Delta F^\circ=43{,}200+23.0\ T\log T-104.87\ T,$
B. P.$=1{,}299°$; $\Delta H_{1299}=30{,}210;\ \Delta S_{1299}=23.3,$
$\Delta H_{298.1}=40{,}219;\ \Delta F^\circ_{298.1}=28{,}903.$

Ferric chloride.—Jellinek and Koop (*183*) (473–553°), Maier (*232*) (489–592°), and Stirnemann (*381*) (526–766°) have measured the vapor pressure of ferric chloride. Stirnemann has obtained the most extensive data, covering the temperature range of importance for the solid and extending well into the liquid range. His results, corrected for dissociation, for the solid fall between those of Jellinek and Koop and of Maier, while for the liquid he is in approximate agreement with Maier, who covered only a short temperature interval. The equations that follow are based on Stirnemann's work. The specific heat of the gas is taken as 34 calories per mole of Fe_2Cl_6. The variation in I for the solid is 0.16 unit and for the liquid 0.05 unit. The latter figure applies only to vapor pressures below 2 atmospheres. The data of Stirnemann go up to over 9 atmospheres, but the figures above 2 atmospheres have not been considered because of the effects of gas imperfection, which are readily apparent in the Σ-function plot.

Solid→Gas (Fe_2Cl_6)
$C_p(g)=34,$
$C_p(s)=40.8+26.4\times10^{-3}T,$
$\Delta C_p=-6.8-26.4\times10^{-3}T,$
$\Delta H=41{,}400-6.8\ T-13.2\times10^{-3}T^2,$
$\Delta F°=41{,}400+15.7\ T\log T+13.2\times10^{-3}T^2-122.17\ T,$
$\Delta H_{298.1}=38{,}200;\ \Delta F°_{298.1}=17{,}735.$

Liquid→Gas (Fe_2Cl_6)
$C_p(g)=34,$
$C_p(l)=64,$
$\Delta C_p=-30,$
$\Delta H=29{,}800-30\ T,$
$\Delta F°=29{,}800+69.1\ T\log T-241.90\ T,$
B. P. = 592°; $\Delta H_{592}=12{,}040;\ \Delta S_{592}=20.3,$
$\Delta H_{298.1}=20{,}860;\ \Delta F°_{298.1}=8{,}659.$

From these equations it follows that the heat of fusion at the melting point, 577°, is 20,590 calories per gram formula weight.

Carbonyl.—Iron pentacarbonyl, $Fe(CO)_5$, was studied in the liquid state by Trautz and Badstübner (*413*) (320–378°). If ΔC_p is neglected, their extensive set of data shows a variation in I of 0.12 unit, two determinations being discarded.

Liquid→Gas ($Fe(CO)_5$)
$\Delta H=9{,}000,$
$\Delta F°=9{,}000-23.83\ T,$
B. P. = 378°; $\Delta S_{378}=23.8$
$\Delta F°_{298.1}=1{,}896.$

KRYPTON

Element.—The vapor pressure of krypton was studied by Allen and Moore (*3*) (114–121°), Peters and Weil (*283*) (81–122°), and Ramsay and Travers (*296*) (84–291°). The most extensive data for the solid are those of Peters and Weil, with which the other results are in fair agreement. The liquid range is not considered here, since the results of Allen and Moore and of Peters and Weil cover only a short temperature interval and those of Ramsay and Travers are very erratic. The melting point is 116.5°, and the boiling point of the liquid is 120.2°, according to Allen and Moore.

Solid→Gas (Kr)
$\Delta H=2{,}540,$
$\Delta F°=2{,}540-21.03\ T.$

LEAD

Element.—Several investigators have studied the vapor pressure of liquid lead—Egerton (*90*) (600–1,200°), Greenwood (*131, 132, 133*) (1,593–2,373°), Harteck (*144*) (1,353–1,477°), Ingold (*175*) (1,195–1,611°), Leitgebel (*223*) (2,013°), Rodebush and Dixon (*309, 310*) (1,391–1,597°), Ruff and Bergdahl (*316*) (1,548–1,828°), and Von Wartenberg (*425, 427*) (1,081–1,903°). The results show considerable disagreement and on the Σ-function plot fall into three groups. The data of Egerton, Harteck, Leitgebel, and Rodebush and Dixon are in fair agreement, while those of Ingold and some of Von Wartenberg's results form a second distinct set. The third consists of the data of Greenwood and of Ruff and Bergdahl. The present author believes that the results of Egerton, Harteck, Leitgebel, and Rodebush and Dixon are the most reliable. Greenwood, and Ruff and Bergdahl generally find too high a pressure for the corresponding temperature reported, and Rodebush and Dixon have made it appear highly probable that Ingold's temperature measurements are in serious error. The value of I for the vaporization of the liquid was obtained from the entropy of the gas as given by the Sackur equation, $S^\circ_{298.1}=41.90$, the entropy of the solid at 298.1°, and the high-temperature thermal data. Application of this value of I to the Σ-function figures from the four investigations considered leads to four values for ΔH_0—46,360, 45,700, 45,660, and 45,890, respectively. A weighted mean, 45,750, has been adopted. Heat and free-energy equations for the vaporization of the solid were obtained from those for the liquid and the necessary thermal data.

Liquid→Gas (Pb)

$C_p(g)=4.97,$
$C_p(l)=6.80,$
$\Delta C_p=-1.83,$
$\Delta H=45{,}750-1.83\ T,$
$\Delta F^\circ=45{,}750+4.21\ T\log T-36.59\ T,$
B. P. = 2,017°; $\Delta H_{2017}=42{,}059$; $\Delta S_{2017}=20.85,$
$\Delta H_{298.1}=45{,}204$; $\Delta F^\circ_{298.1}=37{,}948.$

Solid→Gas (Pb)

$C_p(g)=4.97,$
$C_p(s)=5.77+2.02\times10^{-3}T,$
$\Delta C_p=-0.80-2.02\times10^{-3}T,$
$\Delta H=46{,}720-0.80\ T-1.01\times10^{-3}T^2,$
$\Delta F^\circ=46{,}720+1.84\ T\log T+1.01\times10^{-3}T^2-32.23\ T,$
$\Delta H_{298.1}=46{,}392$; $\Delta F^\circ_{298.1}=38{,}559$; $S^\circ_{298.1}(g)=41.90.$

Oxide.—Feiser (*103*) (1,023–1,745°) has given some indirectly determined vapor-pressure approximations for lead oxide, PbO, and a directly determined boiling point at 1 atmosphere pressure, 1,745°. Maier (*234*) has obtained the following heat and free energy of vaporization equations from Feiser's boiling-point temperature, a computed value for the entropy of vaporization of the solid, $\Delta S_{298.1}=39.3$, and a heat of fusion, 2,820 calories per gram formula weight, computed from melting-point data for the $PbO-Sb_4O_6$ and $PbO-PbF_2$ systems. The melting point is 1,163°.

Solid→Gas (PbO)

$C_p(g)=8.5,$
$C_p(s)=10.33+3.18\times10^{-3}T,$
$\Delta C_p=-1.83-3.18\times10^{-3}T,$
$\Delta H=61{,}610-1.83\ T-1.59\times10^{-3}T^2,$
$\Delta F^\circ=61{,}610+4.21\ T\log T+1.59\times10^{-3}T^2-52.51\ T,$
$\Delta H_{298.1}=60{,}923$; $\Delta F^\circ_{298.1}=49{,}203.$

Liquid→Gas (PbO)

$\Delta C_p=-5.5,$
$\Delta H=60{,}910-5.5\ T,$
$\Delta F^\circ=60{,}910+12.67\ T\log T-75.96\ T,$
B. P. = 1,745°; $\Delta H_{1745}=51{,}312$; $\Delta S_{1745}=29.4,$
$\Delta H_{298.1}=59{,}270$; $\Delta F^\circ_{298.1}=47{,}612.$

Sulphide.—Vapor-pressure measurements of solid lead sulphide, PbS, were made by Schenck and Albers (*348*) (1,123–1,205°). Taking the specific heat of the gas as 9 calories per mole of PbS in computing Σ-function values, it was found that the data could be represented with an extreme variation in *I* of 0.13 unit after two obviously erratic results are discarded. This substance melts at about 1,387°.

Solid→Gas (PbS)
$C_p(g)=9.0,$
$C_p(s)=10.63+4.01\times10^{-3}T,$
$\Delta C_p=-1.63-4.01\times10^{-3}T,$
$\Delta H=60{,}880-1.63\ T-2.00\times10^{-3}T^2,$
$\Delta F^\circ=60{,}880+3.75\ T\log T+2.00\times10^{-3}T^2-54.62\ T,$
$\Delta H_{298.1}=60{,}216;\ \Delta F^\circ_{298.1}=47{,}542.$

Bromide.—Greiner and Jellinek (*134*) (1,043°), Volmer (*424*) (683–843°), and Von Wartenberg and Bosse (*431*) (1,008–1,191°) have studied the vapor pressure of lead bromide. Since Von Wartenberg and Bosse report a slight dissociation near the boiling point, at first sight it would appear better to base the heat and free-energy equations on the data obtained by Volmer for the solid. However, Volmer's data for solid and liquid lead bromide cannot be reconciled with the directly measured heat of fusion, this also being true in the case of lead chloride. His results for the liquid range appear to be very reliable when compared with other investigators, but if his data for the solid also are adopted in the present instance an error in the heat of fusion of about 2,000 calories, or approximately 50 percent of the measured value, must be postulated. Consequently, the heat and free energy of vaporization equations below are based on the vapor-pressure data for the liquid and the directly measured thermal data. Σ-function values for the liquid show an extreme variation in *I* of 0.27 unit, all the available data being considered.

Liquid→Gas ($PbBr_2$)
$C_p(g)=14.0,$
$C_p(l)=27.4,$
$\Delta C_p=-13.4,$
$\Delta H=43{,}600-13.4\ T,$
$\Delta F^\circ=43{,}600+30.9\ T\log T-131.73\ T,$
B. P. = 1,187°; $\Delta H_{1187}27{,}694;\ \Delta S_{1187}=23.3,$
$\Delta H_{298.1}=39{,}605;\ \Delta F^\circ_{298.1}=27{,}123.$

Solid→Gas ($PbBr_2$)
$C_p(g)=14,$
$C_p(s)=18.13+3.10\times10^{-3}T,$
$\Delta C_p=-4.13-3.10\times10^{-3}T,$
$\Delta H=41{,}730-4.13\ T-1.55\times10^{-3}T^2,$
$\Delta F^\circ=41{,}730+9.51\ T\log T+1.55\times10^{-3}T^2-68.82\ T,$
$\Delta H_{298.1}=40{,}361;\ \Delta F^\circ_{298.1}=28{,}368.$

Chloride.—Eastman and Duschak (*92*) (775–1,218°), Greiner and Jellinek (*134*) (1,033–1,043°), Jellinek and Golubowski (*182*) (933–1,053°; extrapolation from a study of mixtures), Maier (*232*) (880–1,266°), Volmer (*424*) (713–873°), and Von Wartenberg and Bosse (*431*) (1,043–1,227°) have measured the vapor pressure of lead chloride. The results for the liquid range show disagreement, and the data of Greiner and Jellinek, Maier, and Volmer are adopted, since they give the more reasonable value for the entropy of vaporization. The same procedure was followed as in the case of the bromide, no weight being given to Volmer's results for the solid on account of the lack of agreement between his results and the directly measured heat of fusion.

Liquid→Gas ($PbCl_2$)

$C_p(g)=14.0,$
$C_p(l)=27.2,$
$\Delta C_p=-13.2,$
$\Delta H=45,800-13.2\ T,$
$\Delta F^{\circ}=45,800+30.4\ T\log T-131.22\ T,$
$\text{B. P.}=1,227^{\circ};\ \Delta H_{1227}=29,604;\ \Delta S_{1227}=24.1,$
$\Delta H_{298.1}=41,865;\ \Delta F^{\circ}_{298.1}=29,107.$

Solid→Gas ($PbCl_2$)

$C_p(g)=14.0,$
$C_p(s)=15.88+8.35\times10^{-3}T,$
$\Delta C_p=-1.88-8.35\times10^{-3}T,$
$\Delta H=45,210-1.88\ T-4.18\times10^{-3}T^2,$
$\Delta F^{\circ}=45,210+4.33\ T\log T+4.18\times10^{-3}T^2-58.41\ T,$
$\Delta H_{298.1}=44,279;\ \Delta F^{\circ}_{298.1}=31,363.$

Fluoride.—The only available vapor-pressure measurements of lead fluoride are those of Von Wartenberg and Bosse (*431*) (1,351–1,562°) for the liquid. These measurements are very concordant, the variation in I being only 0.1 unit if Σ-values are computed on the assumption that $\Delta C_p=-10$.

Liquid→Gas (PbF_2)

$\Delta C_p=-10,$
$\Delta H=54,000-10\ T,$
$\Delta F^{\circ}=54,000+23.0\ T\log T-107.96\ T,$
$\text{B. P.}=1,566^{\circ};\ \Delta H_{1566}=38,340;\ \Delta S_{1566}=24.5,$
$\Delta H_{298.1}=51,019;\ {}^{\circ}F_{298.1}=38,782.$

Thermal data for obtaining equations for the solid are not available.

Iodide.—Liquid lead iodide was studied by Greiner and Jellinek (*134*) (1,033–1,073°) and Jellinek and Rudat (*184*) (923–1,073°). Their results are in good agreement, the variation in I being 0.13 unit. The equations for the solid are obtained from those for the liquid and high-temperature thermal data.

Liquid→Gas (PbI_2)

$C_p(g)=14.0,$
$C_p(l)=32.3,$
$\Delta C_p=-18.3,$
$\Delta H=45,800-18.3\ T,$
$\Delta F^{\circ}=45,800+42.1\ T\log T-168.78\ T,$
$\text{B. P.}=1,145^{\circ};\ \Delta H_{1145}=24,846;\ \Delta S_{1145}=21.7,$
$\Delta H_{298.1}=40,345;\ \Delta F^{\circ}_{298.1}=26,541.$

Solid→Gas (PbI_2)

$C_p(g)=14.0,$
$C_p(s)=18.66+2.93\times10^{-3}T,$
$\Delta C_p=-4.66-2.93\times10^{-3}T,$
$\Delta H=42,760-4.66\ T-1.46\times10^{-3}T^2,$
$\Delta F^{\circ}=42,760+10.73\ T\log T+1.46\times10^{-3}T^2-76.83\ T,$
$\Delta H_{298.1}=41,241;\ \Delta F^{\circ}_{298.1}=27,902.$

Tetramethyl-lead.—Tanaka and Nagai (*404*) (298–308°) have given two vapor-pressure results for tetramethyl-lead, $Pb(CH_3)_4$. These results indicate a heat of vaporization of about 9,100 calories per gram formula weight and a boiling point of 376.5°. However, two determinations which are separated by only 10° in temperature and 10 mm in pressure do not really warrant such calculations, and consequently these results are not considered significant.

LITHIUM

Element.—Bogros (*33*, *34*) (723–845°), Hartmann and Schneider (*146*) (1,204–1,353°), and Lewis (*227*) (852–926°) have measured the vapor pressure of lithium in the liquid state, and Ruff and Johannsen (*324*) have stated that the boiling point is above 1,673°. Calculations from spectroscopic data of the free energy of the gas at various temperatures up to 3,000° were made by Overstreet (*273*). Since the results of the three investigations on liquid lithium do not agree, some arbitrary choice must be made. In this case, the data of Hartmann and Schneider are selected, since they have studied several of the metals and it is possible to obtain information concerning the accuracy of their work by comparison with the results of other investigators. At 1,250° a smoothed value, $\frac{\Delta F^{\circ}}{T} = -R \ ln \ P = 6.32$, is obtained from their results. This leads to the figure, 36,100 calories, for ΔE°_0. Table 16 summarizes the free energy of vaporization calculations.

TABLE 16.—*Free energy of vaporization data for lithium*

T	$\frac{F^{\circ}-E^{\circ}_0}{T}$	$\frac{F^{\circ}_s-E^{\circ}_{s,0}}{T}$	$\frac{\Delta F^{\circ}-\Delta E^{\circ}_0}{T}$	$\frac{\Delta E^{\circ}_0}{T}$	$\frac{\Delta F^{\circ}}{T}$
298.1	−28.184	−3.68	−24.50	121.10	96.60
400	−29.644	−4.93	−24.71	90.25	65.54
500	−30.753	−6.20	−24.55	72.20	47.65
600	−31.658	−7.48	−24.18	60.17	35.99
700	−32.424	−8.56	−23.86	51.57	27.71
800	−33.087	−9.52	−23.57	45.12	21.55
900	−33.672	−10.36	−23.31	40.11	16.80
1,000	−34.196	−11.12	−23.08	36.10	13.02
1,100	−34.669	−11.80	−22.87	32.82	9.95
1,200	−35.101	−12.44	−22.66	30.08	7.42
1,300	−35.499	−13.02	−22.48	27.77	5.29

A Σ-function plot for the values in the last column of table 16 for the liquid state gives $\Delta H_0 = 36{,}410$ with an extreme deviation in I of 0.04 unit, while for the solid $\Delta H_0 = 35{,}960$, with a deviation in I of 0.05 unit.

Solid→Gas (Li)

$C_p(g) = 4.97,$
$C_p(s) = 0.68 + 18.0 \times 10^{-3} T,$
$\Delta C_p = 4.29 - 18.0 \times 10^{-3} T,$
$\Delta H = 35{,}960 + 4.29 \ T - 9.0 \times 10^{-3} T^2,$
$\Delta F^{\circ} = 35{,}960 - 9.88 \ T \log T + 9.0 \times 10^{-3} T^2 - 2.23 \ T,$
$\Delta H_{298.1} = 36{,}439; \ \Delta F^{\circ}_{298.1} = 28{,}807; \ S^{\circ}_{298.1}(g) = 33.15.$

Liquid→Gas (Li)

$C_p(g) = 4.97,$
$C_p(l) = 7.50,$
$\Delta C_p = -2.53,$
$\Delta H = 36{,}410 - 2.53 \ T,$
$\Delta F^{\circ} = 36{,}410 + 5.83 \ T \log T - 40.88 \ T,$
$\text{B. P.} = 1{,}645^{\circ}; \ \Delta H_{1645} = 32{,}248; \ \Delta S_{1645} = 19.6,$
$\Delta H_{298.1} = 35{,}656; \ \Delta F^{\circ}_{298.1} = 28{,}524.$

Bromide.—Ruff and Mugdan (*333*) (1,283–1,538°) and Von Wartenberg and Schulz (*432*) (1,387–1,590°) have measured the vapor pressure of liquid lithium bromide. The results of the former authors are very erratic and are given no weight. Taking $\Delta C_p = -7$, the Σ-function values from Von Wartenberg and Schulz's data, when plotted against $\frac{1}{T}$, fall on a straight line with an extreme variation in I of 0.14 unit.

Liquid→Gas (LiBr)
$\Delta C_p = -7,$
$\Delta H = 46{,}500 - 7\ T,$
$\Delta F° = 46{,}500 + 16.1\ T \log T - 80.88\ T,$
B. P. = 1,583°; $\Delta H_{1583} = 35{,}420$; $\Delta S_{1583} = 22.4,$
$\Delta H_{298.1} = 44{,}413$; $\Delta F°_{298.1} = 34{,}266.$

Chloride.—Maier (*232*) (1,154–1,525°), Ruff and Mugdan (*333*) (1,318–1,598°), and Von Wartenberg and Schulz (*432*) (1,442–1,657°) have measured the vapor pressure of liquid lithium chloride. The results of Von Wartenberg and Schulz are the most consistent. Maier agrees with them, except for his two highest and one intermediate temperature determinations, while the vapor pressures given by Ruff and Mugdan appear to be considerably too high. The extreme variation in I for Von Wartenberg and Schulz's data is 0.25 unit when Σ-function values are calculated with $\Delta C_p = -8$.

Liquid→Gas (LiCl)
$\Delta C_p = -8,$
$\Delta H = 49{,}200 - 8\ T,$
$\Delta F° = 49{,}200 + 18.4\ T \log T - 88.95\ T,$
B. P. = 1,655°; $\Delta H_{1655} = 35{,}960$; $\Delta S_{1655} = 21.7,$
$\Delta H_{298.1} = 46{,}815$; $\Delta F°_{298.1} = 36{,}256.$

Fluoride.—The vapor pressure of liquid lithium fluoride was measured by Ruff, Schmidt, and Mugdan (*339*) (1,671–1,939°) and Von Wartenberg and Schulz (*432*) (1,626–1,820°). The two sets of data are in fair agreement but permit considerable latitude in the drawing of the straight line in the Σ v. $\frac{1}{T}$ plot.

Liquid→Gas (LiF)
$\Delta C_p = -8,$
$\Delta H = 66{,}600 - 8\ T,$
$\Delta F° = 66{,}600 + 18.4\ T \log T - 94.64\ T,$
B. P. = 1,954°; $\Delta H_{1954} = 50{,}968$; $\Delta S_{1954} = 26.1,$
$\Delta H_{298.1} = 64{,}215$; $\Delta F°_{298.1} = 51{,}960.$

The entropy of vaporization value seems high, but the experimental data themselves do not permit a lower value. However, the equations for this substance are certainly less accurate than those for the chloride and bromide.

Iodide.—Ruff and Mugdan (*333*) (1,223–1,273°) and Von Wartenberg and Schulz (*432*) (1,223–1,273°) have reported the same set of measurements for lithium iodide. The results, extending over the short temperature range of 50°, allow considerable choice in the slope of the Σ v. $\frac{1}{T}$ line and probably do not warrant free-energy calculations. The magnitude of the entropy of vaporization at least indicates that such calculations are uncertain. However, the following equations are given as approximations and, with the exception of the lowest temperature determination, the corresponding vapor-pressure relationship fits the experimental results.

Liquid→Gas (LiI)

$\Delta C_p = -7,$
$\Delta H = 50{,}880 - 7T,$
$\Delta F^\circ = 50{,}880 + 16.1T \log T - 86.11T,$
$\text{B. P.} = 1{,}444^\circ;\ \Delta H_{1444} = 40{,}772;\ \Delta S_{1444} = 28.2,$
$\Delta H_{298.1} = 48{,}793;\ \Delta F^\circ_{298.1} = 37{,}087.$

MAGNESIUM

Element.—Vapor-pressure measurements of magnesium were made by Greenwood (*131*) (1,393°), Hartmann and Schneider (*146*) (1,009–1,293°), and Ruff and Hartmann (*322*) (911–1,344°). Von Wartenberg (*425*) has stated that the normal boiling point is at a temperature above 2,573°. The data of Hartmann and Schneider are undoubtedly the best and will be used in conjunction with Overstreet's (*273*) free-energy calculations for the gas to obtain the heat and free energy of vaporization equations for the solid and liquid. At 1,200° a smoothed curve through the results of Hartmann and Schneider gives $\frac{\Delta F^\circ}{T} = -R \ln P = 3.55$. From this figure and the gas- and liquid-free energies, $\Delta E^\circ_0 = 35{,}560$ is computed. Table 17 gives the resulting free energy of vaporization calculations.

TABLE 17.—*Free energy of vaporization data for magnesium*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_s - E^\circ_{s,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−30.545	−3.80	−26.74	119.29	92.55
400	−32.005	−5.15	−26.85	88.90	62.05
500	−33.114	−6.20	−26.91	71.12	44.21
600	−34.019	−7.12	−26.90	59.27	32.37
700	−34.785	−7.95	−26.83	50.80	23.97
800	−35.448	−8.68	−26.77	44.45	17.68
900	−36.033	−9.37	−26.66	39.51	12.85
1,000	−36.557	−10.08	−26.48	35.56	9.08
1,100	−37.030	−10.77	−26.26	32.33	6.07
1,200	−37.462	−11.38	−26.08	29.63	3.55
1,300	−37.860	−11.96	−25.90	27.35	1.45
1,400	−38.228	−12.49	−25.74	25.40	−.34
1,500	−38.571	−12.99	−25.58	23.71	−1.87

The value of I in the free-energy equation for the solid was obtained from the entropy of vaporization at 298.1°, which is the difference between the entropy of the gas as given by the Sackur equation, 35.51, and the entropy of the solid. The I value when subtracted from Σ gives $\frac{\Delta H_0}{T}$. ΔH_0 for the liquid may be obtained from the ΔH_0 value for the solid and the high-temperature thermal data. This in turn when applied to the Σ- values makes possible the calculation of I for the liquid.

Solid→Gas (Mg)

$C_p(g) = 4.97,$
$C_p(s) = 6.20 + 1.33 \times 10^{-3}\ T - 0.678 \times 10^{5} T^{-2},$
$\Delta C_p = -1.23 - 1.33 \times 10^{-3} T + 0.678 \times 10^{5} T^{-2},$
$\Delta H = 36{,}560 - 1.23\ T - 0.665 \times 10^{-3} T^2 - 0.678 \times 10^{5} T^{-1},$
$\Delta F^\circ = 36{,}560 + 2.83\ T \log T + 0.665 \times 10^{-3} T^2 - 0.339 \times 10^{5} T^{-1} - 36.74\ T,$
$\Delta H_{298.1} = 35{,}907;\ \Delta F^\circ_{298.1} = 27{,}640;\ S^\circ_{298.1}(g) = 35.51.$

Liquid→Gas (Mg)

$C_p(g)=4.97,$
$C_p(l)=7.40,$
$\Delta C_p=-2.43,$
$\Delta H=35{,}870-2.43\ T,$
$\Delta F°=35{,}870+5.60\ T\log T-43.58\ T,$
B. P. $=1{,}380°$; $\Delta H_{1380}=32{,}517$; $\Delta S_{1380}=23.6,$
$\Delta H_{298.1}=35{,}146$; $\Delta F°_{298.1}=27{,}010.$

Oxide.—Ruff and Schmidt (*335*) (2,223–3,033°) report some vapor-pressure studies of magnesium oxide. The results are very uncertain, the same pressure being recorded at temperatures differing by as much as 600°, consequently equations for the substance are omitted.

Chloride.—Maier (*232*) (1,056–1,401°) has measured the vapor pressure of liquid magnesium chloride. Except for his three lowest temperature points the data are very consistent, showing an extreme variation in I of only 0.09 unit when Σ- values are computed on the assumption that $\Delta C_p=-10.$

Liquid→Gas ($MgCl_2$)

$\Delta C_p=-10,$
$\Delta H=49{,}600-10\ T,$
$\Delta F°=49{,}600+23.0\ T\log T-103.58\ T,$
B. P. $=1{,}691°$; $\Delta H_{1691}=32{,}690$; $\Delta S_{1691}=19.3,$
$\Delta H_{298.1}=46{,}619$; $\Delta F_{298.1}=35{,}688.$

The entropy of vaporization figure may be a little low and considerable extrapolation is involved in its calculation since Maier's determinations are all below 10 cm.

MANGANESE

Element.—Only two vapor-pressure determinations are available for manganese, those of Greenwood (*131*) (2,173°) and Ruff and Bormann (*317*) (1,783°). Gayler (*114*) has stated that just above the melting point manganese vaporizes under a pressure of 1 to 2 mm. A comparison of Greenwood's boiling-point determinations of the metals with those of other investigators leads to an adjusted boiling-point temperature, 2,425°, which is used in conjunction with Overstreet's (*273*) free-energy calculations for manganese gas and high-temperature thermal data to obtain the heat and free energy of vaporization equations for the various forms of manganese. Taking $\frac{\Delta F°}{T}=0$ at 2,425°, there is obtained $\Delta E_0°=69{,}400$ calories. Table 18 gives the calculated $\frac{\Delta F°}{T}$ values for the vaporization of manganese. These values differ somewhat from the figures found previously by Maier (*233*), because different data were taken to obtain $\Delta E_0°$. However, Maier's calculations do not lead to the correct entropy of manganese gas at 298.1°, while the present results are in accordance with the spectroscopic calculation of this quantity.

TABLE 18.—*Free energy of vaporization data for manganese*

T	$\frac{F^\circ-E^\circ_0}{T}$	$\frac{F^\circ_s-E^\circ_{s,0}}{T}$	$\frac{\Delta F^\circ-\Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−36.534	−3.44	−33.09	232.81	199.72
400	−37.994	−4.66	−33.33	173.50	140.17
600	−40.008	−6.68	−33.33	115.67	82.34
800	−41.437	−8.39	−33.05	86.75	53.70
1,000	−42.546	−9.90	−32.65	69.40	36.75
1,110	−43.019	−10.61	−32.41	63.09	30.68
1,200	−43.451	−11.28	−32.17	57.83	25.66
1,300	−43.849	−11.92	−31.93	53.38	21.45
1,400	−44.217	−12.51	−31.71	49.57	17.86
1,500	−44.560	−13.09	−31.47	46.27	14.80
1,600	−44.880	−13.84	−31.04	43.38	12.34
1,700	−45.182	−14.49	−30.69	40.82	10.13
1,800	−45.465	−15.11	−30.35	38.56	8.21
1,900	−45.734	−15.69	−30.04	36.53	6.49
2,000	−45.989	−16.19	−29.80	34.70	4.90
2,100	−46.231	−16.77	−29.46	33.05	3.59
2,200	−46.462	−17.27	−29.19	31.55	2.36
2,300	−46.683	−17.75	−28.93	30.17	1.24
2,400	−46.894	−18.21	−28.68	28.92	.24
2,500	−47.098	−18.66	−28.44	27.76	−.68

The following extreme variations in I for the different forms of manganese indicate the accuracy with which the free-energy values of table 18 are fitted by the equations presented below—0.02 unit for α, 0.03 for β, 0.02 for γ, and 0.07 for liquid.

Solid (α)→Gas (Mn) (273–1,108°)
$C_p(g)=4.97$,
$C_p(\alpha)=3.76+7.47\times10^{-3}T$,
$\Delta C_p=1.21-7.47\times10^{-3}T$,
$\Delta H=69{,}700+1.21\ T-3.74\times10^{-3}T^2$,
$\Delta F^\circ=69{,}700-2.79\ T\log T+3.74\times10^{-3}T^2-28.31\ T$,
$\Delta H_{298.1}=69{,}729$; $\Delta F^\circ_{298.1}=59{,}535$; $S^\circ_{298.1}(g)=41.5$.

Solid (β)→Gas (Mn) (1,108–1,317°)
$C_p(g)=4.97$,
$C_p(\beta)=5.06+3.95\times10^{-3}T$,
$\Delta C_p=0.09-3.95\times10^{-3}T$,
$\Delta H=68{,}910-0.09\ T-1.98\times10^{-3}T^2$,
$\Delta F^\circ=68{,}910+0.21\ T\log T+1.98\times10^{-3}T^2-34.78\ T$,
$\Delta H_{298.1}=68{,}707$; $\Delta F^\circ_{298.1}=58{,}873$.

Solid (γ)→Gas (Mn) (1,317–1,493°)
$C_p(g)=4.97$,
$C_p(\gamma)=4.80+4.22\times10^{-3}T$,
$\Delta C_p=0.17-4.22\times10^{-3}T$,
$\Delta H=68{,}670+0.17\ T-2.11\times10^{-3}T^2$,
$\Delta F^\circ=68{,}670-0.39\ T\log T+2.11\times10^{-3}T^2-32.91\ T$,
$\Delta H_{298.1}=68{,}533$; $\Delta F^\circ_{298.1}=58{,}760$.

Liquid→Gas (Mn) (1,493°–)
$C_p(g)=4.97$,
$C_p(l)=11.0$,
$\Delta C_p=-6.03$,
$\Delta H=69{,}770-6.03\ T$,
$\Delta F^\circ=69{,}770+13.89\ T\log T-75.79\ T$,
B. P. $=2{,}425°$; $\Delta H_{2425}=55{,}147$; $\Delta S_{2425}=22.75$,
$\Delta H_{298.1}=67{,}972$; $\Delta F^\circ_{298.1}=57{,}423$.

Chloride.—Maier (*232*) (1,071–1,424°) has measured the vapor pressure of manganous chloride, $MnCl_2$. Σ-function values were computed on the assumption that $\Delta C_p=-10$. The data permit but little choice in the manner of drawing the straight line in the Σ-function plot, although they are somewhat erratic near the ends of the temperature range covered, the extreme variation in I being 0.97 unit if the lowest temperature point is omitted.

Liquid→Gas ($MnCl_2$)

$\Delta C_p = -10,$

$\Delta H = 44{,}260 - 10\ T,$

$\Delta F^\circ = 44{,}260 + 23.0\ T \log T - 103.05\ T,$

B. P. = 1,463°; $\Delta H_{1463} = 29{,}630$; $\Delta S_{1463} = 20.3,$

$\Delta H_{298.1} = 41{,}279$; $\Delta F^\circ_{298.1} = 30{,}506.$

MERCURY

Element.—Many investigators have studied the vapor pressure of mercury. Among them are Bernhardt (*24*) (673–1,708°), Bodenstein (*32*) (356°), Egerton (*95*) (273–309°), Gebhardt (*115*) (403–583°), Haber and Kerschbaum (*138*) (293°), Hertz (*158*) (273–493°), Heycock and Lamplough (*161*) (630°), Hill (*162*) (272–308°), Hirst and Olson (*165*) (299°), Jenkins (*186*) (479–671°), Kahlbaum (*193*) (393–493°), Knudsen (*208, 209*) (263–428°), Kordez and Raaz (*212*) (631°), Menzies (*245*) (394–708°), Millar (*248*) (468–614°), Morley (*253, 254*) (273–343°), Neumann and Völker (*258*) (289–344°), Pfaundler (*285*) (288–372°), Van der Platts (*287*) (273–358°), Poindexter (*289*) (194–293°), Ramsay and Young (*297*) (495–721°), Regnault (*300*) (273–785°), Rodebush and Dixon (*309*) (443–476°), Ruff and Bergdahl (*316*) (478–630°), Stock and Zimmermann (*397, 398*) (213–283°), and Young (*449, 451*) (323–633°).

Most of the measurements for the liquid are in good agreement, and the data of the following, more recent investigators may be mentioned as being most concordant—Menzies, Rodebush and Dixon, Neumann and Völker, and Stock and Zimmermann. The results on the solid are quite scattered, however.

Free-energy calculations from spectroscopic data for mercury gas were made by Overstreet (*273*). Mercury vapor contains a small proportion of diatomic molecules. To avoid error from this cause, ΔE_0° is computed from the smoothed value $-R \ln P = 13.11$ at 400°. The pressure is low enough at this temperature to warrant the assumption of a virtually negligible proportion of diatomic molecules. From this value of $-R \ln P$, Overstreet's results, and thermal data $\Delta E_0^\circ = 15{,}320$ is computed. The resulting free energy of vaporization calculations are given in table 19.

TABLE 19.—*Free energy of vaporization data for mercury*

T	$\frac{F^\circ - E^\circ_0}{T}$[1]	$\frac{F^\circ_l - E^\circ_{l,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−36.834	−10.91	−25.92	51.39	25.47
300	−36.865	−10.95	−25.91	51.07	25.16
350	(−37.60)	−12.11	−25.49	43.77	18.28
400	−38.294	−13.10	−25.19	38.30	13.11
450	(−38.88)	−13.96	−24.92	34.04	9.12
500	−39.403	−14.72	−24.68	30.64	5.96
550	(−39.89)	−15.41	−24.48	27.85	3.37
600	−40.308	−16.02	−24.29	25.53	1.24
630	(−40.55)	−16.38	−24.17	24.32	.15
700	−41.074	−17.11	−23.96	21.89	−2.07

[1] The figures in parentheses are interpolated from a smoothed curve.

The value of I was obtained from the entropies at 298.1° and the specific heats of gas and liquid. The extreme variation in ΔH_0 for the data in table 19 is 10 calories. The equations for the solid were obtained from those for the liquid and thermal data. Down to 100° the specific heat of the solid is represented by $C_p(s)=5.37+0.006\ T$.

Liquid→Gas (Hg)

$$\begin{aligned}
&C_p(g)=4.97,\\
&C_p(l)=6.61,\\
&\Delta C_p=-1.64,\\
&\Delta H=15{,}024-1.64\ T,\\
&\Delta F^\circ=15{,}024+3.78\ T\log T-34.29\ T,\\
&P(\mathrm{Hg})=1\text{ at. at }634^\circ;\ \Delta H_{634}=13{,}984;\ \Delta S_{634}=22.06,\\
&\Delta H_{298.1}=14{,}535;\ \Delta F^\circ_{298.1}=7{,}590;\ S^\circ_{298.1}(g)=41.80.
\end{aligned}$$

Solid→Gas (Hg)

$$\begin{aligned}
&C_p(g)=4.97,\\
&C_p(s)=5.37+0.006\ T,\\
&\Delta C_p=-0.40-0.006\ T,\\
&\Delta H=15{,}455-0.40\ T-0.003\ T^2,\\
&\Delta F^\circ=15{,}455+0.92\ T\log T+0.003\ T^2-30.06\ T.
\end{aligned}$$

The free-energy equation for the vaporization of the liquid indicates about 7 percent Hg_2 molecules at the normal boiling point, 630°. An expression for the total vapor pressure of the liquid follows.

Liquid→Gas (Hg+Hg$_2$)

$$\log P\ (at.)=-\frac{3{,}327}{T}-0.826\log T+7.593,$$

B. P.=630°.

For the solid the vapor pressures derived from the free energy of vaporization equation and $\Delta F^\circ=-R\ T\ ln\ P$ are satisfactory.

Oxide.—Stock and Zimmermann (*397*) (273.1°) have determined the vapor pressure of mercuric oxide, HgO, at a single temperature.

Bromide.—The vapor pressure of mercuric bromide was studied by Johnson (*187*) (435–592°), Prideaux (*293*) (539–604°), Völmer (*424*) (363–463°), and Wiedemann (*440*) (363–593°). These data agree exceptionally well. Σ-function values were calculated on the assumption that $C_p(g)=14$ for the gas. The average I values from the individual sets of data fall in a range of 0.24 unit for the solid and 0.06 unit for the liquid.

Solid→Gas (HgBr$_2$)

$$\begin{aligned}
&C_p(g)=14,\\
&C_p(s)=13.9+13.8\times10^{-3}T,\\
&\Delta C_p=0.1-13.8\times10^{-3}T,\\
&\Delta H=20{,}590+0.1\ T-6.9\times10^{-3}\ T^2,\\
&\Delta F^\circ=20{,}590-0.23\ T\log T+6.9\times10^{-3}T^2-39.26\ T,\\
&\Delta H_{298.1}=20{,}007;\ \Delta F^\circ_{298.1}=9{,}330
\end{aligned}$$

Liquid→Gas (HgBr$_2$)

$$\begin{aligned}
&C_p(g)=14,\\
&C_p(l)=24,\\
&\Delta C_p=-10,\\
&\Delta H=20{,}000-10\ T,\\
&\Delta F^\circ=20{,}000+23.0\ T\log T-97.54\ T,\\
&\text{B. P.}=592^\circ;\ \Delta H_{865}=14{,}080;\ \Delta S_{865}=23.8,\\
&\Delta H_{298.1}=17{,}019;\ \Delta F^\circ_{298.1}=7{,}888.
\end{aligned}$$

These equations give for the melting point, heat of fusion, and entropy of fusion, respectively, 514°, 3,960 calories per gram formula weight and 7.70 calories per degree per gram formula weight.

Chloride.—Fischer and Biltz (*108*) (439–489°), Johnson (*187*) (423–575°), Prideaux (*293*) (559–582°), Richter (*302*) (473–550°), Schmidt and Walter (*352*) (373–453°), Stock and Zimmermann (*397*) (273.1°), and Wiedemann (*440*) (333–573°) have measured the vapor pressure of mercuric chloride. Their results are in good agreement, although those of Johnson and of Wiedemann appear somewhat the best for the solid, while Prideaux's results for the liquid are the best. However, the variation in the individual average *I* values is only 0.08 unit for the liquid and 0.47 unit for the solid.

Solid→Gas ($HgCl_2$)

$C_p(g)=14,$
$C_p(s)=15.3+10.3\times10^{-3}T,$
$\Delta C_p=-1.3-10.3\times10^{-3}T,$
$\Delta H=20{,}770-1.3\ T-5.15\times10^{-3}T^2,$
$\Delta F^\circ=20{,}770+2.99\ T\log T+5.15\times10^{-3}T^2-47.57\ T,$
$\Delta H_{298.1}=19{,}924;\ \Delta F^\circ_{298.1}=9{,}252.$

Liquid→Gas ($HgCl_2$)

$C_p(g)=14,$
$C_p(l)=24,$
$\Delta C_p=-10,$
$\Delta H=19{,}850-10\ T,$
$\Delta F^\circ=19{,}850+23.0\ T\log T-97.90\ T,$
B. P. = 577°; $\Delta H_{577}=14{,}080;\ \Delta S_{577}=24.4,$
$\Delta H_{298.1}=16{,}869;\ \Delta F^\circ_{298.1}=7{,}631.$

The melting point is 550°, and the heat and entropy of fusion per gram formula weight are computed to be 4,150 calories and 7.54 calories per degree, respectively.

Iodide.—The vapor pressure of mercuric iodide was investigated by Ditte (*85*) (468–581°), Rinse (*306*) (403–621°), Johnson (*187*) (450–614°), Prideaux (*293*) (570–634°), Stock and Zimmermann (*397*) (273.1°), and Wiedemann (*440*) (373–603°). Rinse detected no dissociation below 723° but estimates about 5 percent at 873°. In the liquid range there are five sets of determinations, and the agreement is good except for the data of Ditte. The other four sets show a variation in average *I* values of only 0.03. For the high-temperature or β-crystalline form there are four sets of determinations, and again Ditte is in disagreement. The average *I* values of the others have a spread of 0.22 unit. In the temperature range where the low-temperature or α-crystalline form is stable, there are four measurements of Wiedemann and the one of Stock and Zimmermann. These results are scattered, but fortunately thermal data are available for obtaining results for this form from those for the β modification.

Solid (α)→Gas (HgI_2) (273–403°)

$C_p(g)=14,$
$C_p(\alpha)=17.41+4.00\times10^{-3}T,$
$\Delta C_p=-3.41-4.00\times10^{-3}T,$
$\Delta H=22{,}960-3.41\ T-2.00\times10^{-3}T^2,$
$\Delta F^\circ=22{,}960+7.85\ T\log T+2.00\times10^{-3}T^2-61.93\ T,$
$\Delta H_{298.1}=21{,}765;\ \Delta F^\circ_{298.1}=10{,}467.$

Solid (β)→Gas (HgI_2) (403–524°)

$C_p(g)=14,$
$C_p(\beta)=20.2,$
$\Delta C_p=-6.2,$
$\Delta H=23{,}150-6.2\ T,$
$\Delta F^\circ=23{,}150+14.3\ T\log T-78.40\ T,$
$\Delta H_{298.1}=21{,}302;\ \Delta F^\circ_{298.1}=10{,}327.$

Liquid→Gas (HgI_2) (524°-)

$C_p(g) = 14,$
$C_p(l) = 25,$
$\Delta C_p = -11,$
$\Delta H = 21{,}160 - 11\ T,$
$\Delta F^\circ = 21{,}160 + 25.3\ T \log T - 104.51\ T,$
B. P. = 627°; $\Delta H_{627} = 14{,}263$; $\Delta S_{627} = 22.7,$
$\Delta H_{298.1} = 17{,}881$; $\Delta F^\circ_{298.1} = 8{,}668.$

MOLYBDENUM

Element.—Langmuir and Mackay (*221*) (1,800–3,890°) and Jones, Langmuir, and Mackay (*191*) (1,000–5,960°) have given vapor-pressure data and calculations for molybdenum. The actual measurements of the latter authors are rates of evaporation of molybdenum filaments in the temperature range 2,070 to 2,504°. The experimental results and not the calculated values have been used here. These results are excellent for the high temperatures involved but nevertheless permit considerable choice in the manner of drawing the straight line in the Σ-function plot. This may be shown by applying the I value given below to the individual Σ-function values to obtain ΔH_0 results. These values have a spread of 3,600 calories. Attention also is called to the facts that at the high temperatures involved the specific heat of molybdenum gas probably is higher than the classical value, 4.97, and the specific heat of the solid is an extrapolation from experimental results which only extend up to 1,773°.

Solid→Gas (Mo)

$C_p(g) = 4.97,$
$C_p(s) = 5.69 + 1.88\times10^{-3}T - 0.503\times10^{5}T^{-2},$
$\Delta C_p = -0.72 - 1.88\times10^{-3}T + 0.503\times10^{5}T^{-2},$
$\Delta H = 155{,}960 - 0.72\ T - 0.94\times10^{-3}T^{2} - 0.503\times10^{5}T^{-1},$
$\Delta F^\circ = 155{,}960 + 1.66\ T \log T + 0.94\times10^{-3}T^{2} - 0.2515\times10^{5}T^{-1} - 42.31\ T,$
$\Delta H_{298.1} = 155{,}493$; $\Delta F^\circ_{298.1} = 144{,}571$; $S^\circ_{298.1}(g) = 43.5.$

Approximate equations may be obtained for the liquid from those for the solid, provided one is willing to make sufficient assumptions. The melting point of molybdenum is 2,895° (*218*), and if the assumption is made that molybdenum has an entropy of fusion which is the average value given by all the metals whose heats of fusion have been measured, 2.3 units, then a heat of fusion of 2.3×2,895=6,660 calories may be obtained. The heat and free energy of vaporization of the liquid at the melting point may now be found. These results and the assumption that $\Delta C_p = -5$ make possible the deriving of the following results:

Liquid→Gas (Mo)

$\Delta C_p = -5,$
$\Delta H = 153{,}800 - 5\ T,$
$\Delta F^\circ = 153{,}800 + 11.5\ T \log T - 72.91\ T,$
B. P. = 5,077°; $\Delta H_{5077} = 128{,}415$; $\Delta S_{5077} = 25.3,$
$\Delta H_{298.1} = 152{,}310$; $\Delta F^\circ_{298.1} = 140{,}549.$

Oxide.—Feiser (*104*) (873–1,428°) has made some indirect vapor-pressure determinations of molybdenum oxide, MoO_3. He has calculated his results, which are based on measured evaporation rates, according to three assumptions and reports three different sets of figures which are not in agreement. Furthermore, it is difficult to reconcile these results with the melting-point determination of Jaeger and Germs (*180*), 1,068°. Consequently, only vapor-pressure equations will be included. These reproduce well Feiser's set of figures based on the assumption that the vapor pressure is proportional to the mass of material vaporized in a definite time interval from a surface of definite area.

Liquid→Gas (MoO_3)

$$\log P\ (at.) = -\frac{11{,}820}{T} - 7.04 \log T + 30.494,$$

B. P. = 1,424°.

Solid→Gas (MoO_3)

$$\log P\ (at.) = -\frac{15{,}110}{T} + 1.46 \log T - 1.32\times10^{-3}T + 9.071.$$

Hexafluoride.—The vapor pressure of molybdenum hexafluoride, MoF_6, was measured by Ruff and Ascher (*315*) (225–295°). Their results extend into both the solid and liquid ranges, those for the liquid being much more consistent than those for the solid but covering a narrower temperature range. ΔC_p has been neglected.

Solid→Gas (MoF_6)

$\Delta H = 8{,}500,$
$\Delta F^\circ = 8{,}500 - 28.03\ T,$
$\Delta F^\circ_{298.1} = 144.$

Liquid→Gas (MoF_6)

$\Delta H = 6{,}000,$
$\Delta F^\circ = 6{,}000 - 19.4\ T,$
B. P. = 309°; $\Delta S_{309} = 19.4,$
$\Delta F^\circ_{298.1} = 214.$

The melting point is 290°, and the heat of fusion is 2,500 calories per gram formula weight. The corresponding entropy of fusion is 8.6 units.

NEON

Element.—Cath and Onnes (*62*) (24–44.4°), Crommelin and Gibson (*75, 76*) (15–44.4°), and Travers and Jacquerod (*417*) (15–21°) have measured the vapor pressure of neon. The results of Cath and Onnes and Crommelin and Gibson are in good agreement. The melting point is 24.59°. The following simple vapor-pressure equations represent the data below 4 atmospheres.

Solid→Gas (Ne)

$$\log P\ (at.) = -\frac{113.66}{T} + 4.251.$$

Liquid→Gas (Ne)

$$\log P\ (at.) = -\frac{96.74}{T} + 3.563,$$

B. P. = 27.15°.

NICKEL

Element.—The vapor pressure of nickel was measured by Ruff and Bormann (*318*) (2,614°) and Jones, Langmuir, and Mackay (*191*) (1,318–1,602°). The latter results are the more reliable and were used with Overstreet's (*273*) free-energy values for nickel gas to obtain the free energy of vaporization. A smoothed curve through the data of Jones, Langmuir, and Mackay gives $\frac{\Delta F^\circ}{T} = -R \ln P = 30.43$ at 1,500°. This makes possible the calculation of $\Delta E^\circ_0 = 97{,}800$ calories. Free energy of vaporization calculations are shown in table 20.

TABLE 20.—*Free energy of vaporization data for nickel*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_s - E^\circ_{s,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−38.058	−3.28	−34.78	328.08	293.30
400	−39.672	−4.52	−35.15	244.50	209.35
500	−40.908	−5.58	−35.33	195.60	160.27
600	−41.929	−6.53	−35.40	163.00	127.60
700	−42.796	−7.42	−35.38	139.71	104.33
800	−43.557	−8.23	−35.33	122.25	86.92
900	−44.231	−8.96	−35.27	108.67	73.40
1,000	−44.833	−9.64	−35.19	97.80	62.61
1,100	−45.382	−10.28	−35.10	88.91	53.81
1,200	−45.885	−10.86	−35.02	81.50	46.48
1,300	−46.348	−11.39	−34.96	75.23	40.27
1,400	−46.777	−11.91	−34.87	69.86	34.99
1,500	−47.174	−12.40	−34.77	65.20	30.43
1,600	−47.548	−12.85	−34.70	61.12	26.42
1,700	−47.901	−13.28	−34.62	57.53	22.91
1,800	−48.230	−13.79	−34.44	54.33	19.89
1,900	−48.540	−14.31	−34.23	51.47	17.24
2,000	−48.833	−14.80	−34.03	48.90	14.87
2,500	−50.110	−16.89	−33.22	39.12	5.90

Equations were derived in the usual manner from the figures in table 20 for the α, β, and liquid forms of nickel.

Solid (α)→Gas (Ni) (273–626°)
$C_p(g) = 5.71,$
$C_p(\alpha) = 4.26 + 6.40 \times 10^{-3} T,$
$\Delta C_p = 1.45 - 6.40 \times 10^{-3} T,$
$\Delta H = 98{,}130 + 1.45\ T - 3.20 \times 10^{-3} T^2,$
$\Delta F^\circ = 98{,}130 - 3.34\ T \log T + 3.20 \times 10^{-3} T^2 - 28.57\ T,$
$\Delta H_{298.1} = 98{,}278;\ \Delta F^\circ_{298.1} = 87{,}433;\ S^\circ_{298.1}(g) = 43.5.$
Solid (β)→Gas (Ni) (626–1,725°)
$C_p(g) = 5.71,$
$C_p(\beta) = 6.99 + 0.905 \times 10^{-3} T,$
$\Delta C_p = -1.28 - 0.905 \times 10^{-3} T,$
$\Delta H = 98{,}670 - 1.28\ T - 0.452 \times 10^{-3} T^2,$
$\Delta F^\circ = 98{,}670 + 2.95\ T \log T + 0.452 \times 10^{-3} T^2 - 45.38\ T,$
$\Delta H_{298.1} = 98{,}248;\ \Delta F^\circ_{298.1} = 87{,}358.$
Liquid→Gas (Ni) (1,725°–   )
$C_p(g) = 5.71,$
$C_p(l) = 8.55,$
$\Delta C_p = -2.84,$
$\Delta H = 95{,}820 - 2.84\ T,$
$\Delta F^\circ = 95{,}820 + 6.54\ T \log T - 54.63\ T,$
B. P. = 3,005°; $\Delta H_{3005} = 87{,}286;\ \Delta S_{3005} = 29.05,$
$\Delta H_{298.1} = 94{,}973;\ \Delta F^\circ_{298.1} = 84{,}359.$

Chloride.—The vapor pressure of nickel chloride was measured by Maier (*232*) (814–1,267°). His two sets of determinations show some divergence, especially at the higher temperatures. The extreme variation in I is 1.11 units if two points are omitted.

Solid→Gas ($NiCl_2$)
$C_p(g) = 14,$
$C_p(s) = 17.07 + 3.12 \times 10^{-3} T,$
$\Delta C_p = -3.07 - 3.12 \times 10^{-3} T,$
$\Delta H = 54{,}700 - 3.07\ T - 1.56 \times 10^{-3} T^2,$
$\Delta F^\circ = 54{,}700 + 7.07\ T \log T + 1.56 \times 10^{-3} T^2 - 67.29\ T,$
S. P. = 1,260°; $\Delta H_{1260} = 48{,}355;\ \Delta S_{1260} = 38.4,$
$\Delta H_{298.1} = 53{,}646;\ \Delta F^\circ_{298.1} = 39{,}995.$

Carbonyl.—Nickel carbonyl, $Ni(CO)_4$ was studied by Anderson (*6*) (238–316°), Dewar and Jones (*84*) (264–303°), and Mittasch (*249*) (275–313°). Anderson's more recent data are given preference over the older values of Dewar and Jones and of Mittasch. Dewar and Jones agree with Anderson at the higher temperatures, but their vapor pressures appear to be too high at the lower temperatures. The results of Mittasch all seem to be low. This substance melts at about 248°, and dissociation becomes apparent around 309°.

Liquid→Gas ($Ni(CO)_4$)

$\Delta H = 7{,}000,$

$\Delta F° = 7{,}000 - 22.18\ T,$

B. P. = 315.6°; $\Delta S_{315.6} = 22.2,$

$\Delta F°_{298.1} = 388.$

NITROGEN

Element.—Several investigators have measured the vapor pressure of nitrogen—Baly (*14*) (77–91°), Cath (*61*) (57–85°), Crommelin (*72, 73*) (81–125°), Dodge and Davis (*87*) (76–122°), Fischer and Alt (*107*) (62–78°), Giauque and Clayton (*120*) (54–79°), Henning and Heuse (*154*) (67–78°), Henning (*153*) (60–80°), Holst and Hamburger (*171*) (69–81°), Olszewski (*265*) (60–79°), Porter and Perry (*290*) (90–122°), Von Siemens (*360*) (56–81°), Verschoyle (*422*) (63–68°), and Wroblewski (*445*) (71–127°). Nitrogen exhibits two crystalline modifications between 15° and the melting point. The heat and free energy of vaporization equations are derived from the thermal data of Giauque and Clayton after correcting, where necessary, for gas imperfection. The specific heat of the liquid is nearly constant, 13.53, and those of the two solid forms may be represented by $C_p(S_I) = 5.42 + 0.09\ T$ and $C_p(S_{II}) = -2.57 + 0.365\ T$. The latter equation is valid from the transition point, 35.61°, down to 15°.

Solid (S_{II})→Gas (N_2) (15–35.61°)

$C_p(g) = 6.95,$

$C_p(S_{II}) = -2.57 + 0.365\ T,$

$\Delta C_p = 9.52 - 0.365\ T,$

$\Delta H = 1{,}652 + 9.52\ T - 0.183\ T^2,$

$\Delta F° = 1{,}652 - 21.92\ T \log T + 0.183\ T^2 + 5.862\ T.$

Solid (S_I)→Gas (N_2) (35.61–63.14°)

$C_p(g) = 6.95,$

$C_p(S_I) = 5.42 + 0.09\ T,$

$\Delta C_p = 1.53 - 0.09\ T,$

$\Delta H = 1{,}707 + 1.53\ T - 0.045\ T^2,$

$\Delta F° = 1{,}707 - 3.52\ T \log T + 0.045\ T^2 - 19.33\ T.$

Liquid→Gas (N_2) (63.14°–   )

$C_p(g) = 6.95,$

$C_p(l) = 13.53,$

$\Delta C_p = -6.58,$

$\Delta H = 1{,}867 - 6.58\ T,$

$\Delta F° = 1{,}867 + 15.15\ T \log T - 52.65\ T.$

The free energy of vaporization equation for the S_{II}-crystalline form may be used to obtain vapor pressures by means of the relationship, $\Delta F° = -R\ T\ ln\ P$, since the pressures are so low that gas imperfection is negligible. The same procedure cannot be followed for the S_I and liquid forms, and so the following vapor-pressure equations are given.

Solid (S_I)→Gas (N_2) (35.61–63.14°)

$$\log P\ (at.) = -\frac{375.1}{T} + 0.769 \log T - 0.0098\ T + 4.269.$$

Liquid→Gas (N_2) (63.14–77.32°)

$$\log P\,(at.) = -\frac{414.4}{T} - 3.311 \log T + 11.613,$$

B. P. = 77.32°.

Nitrous oxide.—Black, Van Praagh, and Topley (*29*) (103–123°), Blue (*30*) (148–186°), Britton (*48*) (192–308°), Burrell and Robertson (*56*) (129–185°), Eucken and Donath (*100*) (135–162°), Kuenen (*216*) (277–309°), Ramsay and Shields (*295*) (183°), and Villard (*423*) (273–293°) have measured the vapor pressure of nitrous oxide, N_2O. Blue has measured the specific heats of solid and liquid, the heat of fusion, and the heat of vaporization. His thermal data, after correction for gas imperfection, were used to obtain free-energy and heat of vaporization equations. The specific heat of the liquid may be taken as 18.57 and that of the solid between 75° and the melting point, 182.3°, as $C_p(s) = 5.16 + 0.047\ T$.

Solid→Gas (N_2O) (75–182.3°)

$C_p(g) = 7.95,$
$C_p(s) = 5.16 + 0.047\ T,$
$\Delta C_p = 2.79 - 0.047\ T,$
$\Delta H = 5{,}809 + 2.79\ T - 0.0235\ T^2,$
$\Delta F^\circ = 5.809 - 6.43\ T \log T + 0.0235\ T^2 - 21.34\ T.$

Liquid→Gas (N_2O) (182.3°–)

$C_p(g) = 7.95,$
$C_p(l) = 18.57,$
$\Delta C_p = -10.62,$
$\Delta H = 5{,}911 - 10.62\ T,$
$\Delta F^\circ = 5{,}911 + 24.46\ T - 87.45\ T.$

The following relationships are suggested for vapor-pressu calculations.

Solid→Gas (N_2O)

$$\log P\,(at.) = -\frac{1{,}294}{T} + 1.405 \log T - 0.0051\ T + 4.800.$$

Liquid→Gas (N_2O)

$$\log P\,(at.) = -\frac{1{,}333}{T} - 5.346 \log T + 19.340,$$

B. P. = 184.6°.

Nitric oxide.—The vapor pressure of nitric oxide, NO, was measured by Adwentowski (*1*) (98–180°), Goldschmidt (*126*) (94–123°), Henglein and Krüger (*150*) (73–125°), Johnston and Giauque (*189*) (94–123°), Mündel (*256*) (74–87°), and Olszewski (*264*, *265*) (96–180°). Again the procedure of obtaining the heat and free-energy equations from thermal data is followed. In this case the thermal measurements of Johnston and Giauque are used. The average specific heat of the liquid in the temperature range of importance for the present purpose is 17.2 and that of the solid is $C_p = 1.80 + 0.068\ T$ between 55° and the melting point, 109.5°.

Solid→Gas (NO) (55–109.5°)

$C_p(g) = 6.95,$
$C_p(s) = 1.80 + 0.068\ T,$
$\Delta C_p = 5.15 - 0.068\ T,$
$\Delta H = 3{,}822 + 5.15\ T - 0.034\ T^2,$
$\Delta F^\circ = 3{,}822 - 11.86\ T \log T + 0.034\ T^2 - 11.39\ T.$

Liquid→Gas (NO) (109.5°-   )

$C_p(g)=6.95,$
$C_p(l)=17.20,$
$\Delta C_p=-10.25,$
$\Delta H=4{,}551-10.25\ T,$
$\Delta F^\circ=4{,}551+23.61\ T\log T-86.66\ T.$

It is necessary to include also a vapor-pressure equation for the liquid. The vapor-pressure relationship for the solid derived from the free-energy equation is satisfactory.

Liquid→Gas (NO) (109.5–121.4°)

$$\log P\ (at.)=-\frac{1{,}014.2}{T}-5.161\log T+19.115,$$

B. P. = 121.4°.

Trioxide.—Vapor-pressure measurements of the oxide, N_2O_3, were attempted by Guye and Drouguinine (*137*) (80–273°). The data are poor, perhaps because of dissociation, and so equations for this substance are not included.

Tetroxide.—Vapor-pressure measurements of nitrogen tetroxide were made by Baume and Robert (*17*) (257-312°), Egerton (*94*) (195-237°), Guye and Drouguinine (*136*) (100–285°), Mittasch, Kusz, and Schlueter (*250*) (276-322°), Ramsay and Young (*299*) (247-277°), Russ (*341*) (193-258°), Scheffer and Treub (*346*) (237-431°), and Scheuer (*351*) (163-288°). For the liquid, the data of Scheffer and Treub, Mittasch, Kusz, and Schlueter, and Ramsay and Young are in agreement, while for the solid those of Egerton and of Scheffer and Treub are the only reliable figures. This substance undergoes dissociation, $N_2O_4=2NO_2$. Lewis and Randall (*226*) have discussed this reaction and have obtained a free-energy equation for it, $\Delta F^\circ=13{,}600-41.6\ T$, where $\Delta F^\circ=-R\ T\ ln\ \frac{P^2_{NO_2}}{P_{N_2O_4}}$ assuming the perfect gas law is obeyed, that is, at low pressures. This free-energy equation has been used to obtain the partial pressures of N_2O_4 from the total vapor pressure of the liquid between 260 and 280°. In this range the total pressure is under 0.6 atmosphere. The dissociation below 220° is not important, so that for practical purposes the total vapor pressure and N_2O_4 partial pressure may be taken as equal below this temperature. In deriving the following equations ΔC_p has been neglected.

Solid→Gas (N_2O_4)

$\Delta H=12{,}580,$
$\Delta F^\circ=12{,}580-44.67\ T,$
$\Delta F^\circ_{298.1}=-836.$

Liquid→Gas (N_2O_4)

$\Delta H=7{,}040,$
$\Delta F^\circ=7{,}040-23.27\ T,$
$P_{(N_2O_4)}=1$ at. at 303°; $\Delta S_{298}=23.3,$
$\Delta F^\circ_{298.1}=103.$

From these results and the free energy of dissociation equation, the following relationships for the formation of NO_2 gas from solid and liquid are derived.

Solid→Gas (NO_2)
$\Delta H = 13{,}090,$
$\Delta F^\circ = 13{,}090 - 43.14\ T,$
$\Delta F^\circ_{298.1} = 230.$

Liquid→Gas (NO_2)
$\Delta H = 10{,}320,$
$\Delta F^\circ = 10{,}320 - 32.44\ T,$
$P(NO_2) = 1$ at. at 318°; $\Delta S_{318} = 32.4,$
$\Delta F^\circ_{298.1} = 650.$

The total vapor pressure of the liquid is given by the following equation:

Liquid→Gas ($N_2O_4 + NO_2$)

$$\log P\ (at.) = -\frac{1{,}746}{T} + 5.939,$$

B. P. = 294.1°.

Pentoxide.—Daniels and Bright (*78*) (258–306°) and Russ and Pokorny (*342*) (243–291°) have measured the vapor pressure of solid nitrogen pentoxide, N_2O_5. The results are in good agreement. If ΔC_p is neglected the following equations are obtained.

Solid→Gas (N_2O_5)
$\Delta H = 13{,}800,$
$\Delta F^\circ = 13{,}800 - 45.22\ T,$
$\Delta F^\circ_{298.1} = 320.$

Nitrosyl chloride.—The vapor pressure of nitrosyl chloride, NOCl, was measured by Briner and Pylkoff (*47*) (204–288°) and Trautz and Gerwig (*414*) (201–268°). The data of the latter authors are adopted, since those of Briner and Pylkoff are very erratic. ΔC_p had been neglected.

Liquid→Gas (NOCl)
$\Delta H = 6{,}140,$
$\Delta F^\circ = 6{,}140 - 23.02\ T,$
B. P. = 266.7°; $\Delta S_{266.7} = 23.0,$
$\Delta F^\circ_{298.1} = -722.$

Ammonia.—Several investigators have studied the vapor pressure of ammonia—Beattie and Lawrence (*21*) (303–405°), Bergstrom (*23*) (195–243°), Blümcke (*31*) (254–337°), Brill (*44*) (193–240°), Burrell and Robertson (*55*, *56*) (159–239°), Cragoe (*70*) (239–323°), Gibbs (*124*) (239°), Henning and Stock (*155*) (193–238°), Holst (*170*) (292–319°), Karwat (*194*) (162–194°), Keyes and Brownlee (*201*) (239–398°), Mündel (*256*) (145–167°), Regnault (*300*) (242–306°), and Stock, Henning, and Kusz (*400*) (196–240°). The results for the liquid are in good agreement up to 6 or 7 atmospheres pressure. A comparison of the higher-pressure results was not made, since they are not suitable for the present purpose. For the solid Karwat's data are the most consistent, and they agree favorably with the average of those of the other investigators who have studied the solid—Brill, Burrell and Robertson, and Mündel. The specific heats of the solid and liquid may be expressed as $C_p(s) = 0.64 + 0.0600\ T$ and $C_p(l) = 18.36$. The first equation is valid for the temperature range 80 to 195.5°, the melting point.

The procedure used in obtaining the heat and free energy of vaporization equations was to compute ΔH_0 from the directly measured heat of vaporization at the boiling point and then to calculate an average value of I for each of the 10 investigations covering all or part of the pertinent liquid range. These 10 average I values have a spread of only 0.11 unit. The equations for the solid were obtained from those for the liquid and thermal data. These latter relationships were checked against the Σ-function plot for the solid and found to correspond within very narrow limits, corresponding to not over 0.03 unit in I, with the data of Harteck.

Liquid→Gas (NH_3)
$C_p(g)=8.36,$
$C_p(l)=18.36,$
$\Delta C_p=-10.00,$
$\Delta H=8{,}037-10.00\ T,$
$\Delta F°=8{,}037+23.0\ T\log T-88.26\ T,$
B. P. = 239.7°; $\Delta H_{239.7}=5{,}640$; $\Delta S_{239.7}=23.53.$

Solid→Gas (NH_3)
$C_p(g)=8.36,$
$C_p(s)=0.64+0.0600\ T,$
$\Delta C_p=7.72-0.0600\ T,$
$\Delta H=7{,}146+7.72\ T-0.0300\ T^2,$
$\Delta F°=7{,}146-17.8\ T\log T+0.0300\ T^2+3.91\ T.$

It should be noted that correction to the ideal state has not been made in this case. The free-energy equations, however, are affected but little by such correction, since the alterations in the heat and entropy nearly compensate each other.

Trifluoride.—The vapor pressure of nitrogen trifluoride, NF_3, was measured by Menzel and Mohry (*244*) (80—143°). This substance melts at 89.5°, but only one result is given for the solid form. The data for the liquid are very consistent, the extreme variation in I being 0.04 unit if Σ-function values are computed ignoring ΔC_p.

Liquid→Gas (NF_3)
$\Delta H=3{,}000,$
$\Delta F°=3{,}000-20.82\ T,$
B. P. = 144.1°; $\Delta S_{144.1}=20.8.$

OSMIUM

Tetroxide.—Ogawa (*262*) (288–404°), Ruff and Tschirch (*336*) (368–408°), Krauss and Wilken (*214*) (273–309°), and Von Wartenberg (*429*) (235–273°) have measured the vapor pressure of osmium tetroxide, OsO_4. This substance is known in two crystalline forms, white and yellow. The results of Krauss and Wilken are not in agreement with the others for either of the two crystalline forms of this substance. On the other hand, Ogawa and Ruff and Tschirch are in fair agreement for the liquid if one determination of the latter investigators is discarded. Ogawa also records a consistent set of data for the white modification. Von Wartenberg's results are all for the yellow form. If the data of Ogawa and Ruff and Tschirch for the liquid state are accepted, it can be shown that Krauss and Wilken's figures for the white modification are thermodynamically impossible and that those for the yellow result in an impossibly high melting point. The conclusion is that the data of Krauss and Wilken are in error both as to magnitude and temperature coefficient, and consequently they are eliminated from the present calculations. ΔC_p also has been ignored.

Solid (white)→Gas (OsO_4)
$\Delta H = 11{,}790$,
$\Delta F^\circ = 11{,}790 - 30.89\ T$,
M. P. = 315°; $\Delta F^\circ_{298.1} = 2{,}582$.
Solid (yellow)→Gas (OsO_4)
$\Delta H = 13{,}510$,
$\Delta F^\circ = 13{,}510 - 35.78\ T$,
M. P. = 329°; $\Delta F^\circ_{298.1} = 2{,}844$.
Liquid→Gas (OsO_4)
$\Delta H = 9{,}450$,
$\Delta F^\circ = 9{,}450 - 23.45\ T$,
B. P. = 403°; $\Delta S_{403} = 23.4$,
$\Delta F^\circ_{298.1} = 2{,}460$.

It is seen from these equations that the yellow modification is the more stable solid form. Both varieties have a solid-liquid-gas triple point; and the two solid forms cannot be in equilibrium at any temperature, since the hypothetical transition point is above their individual melting points. The white modification melts at 315°, with a heat of fusion of 2,340 calories per gram formula weight. The heat of fusion of the yellow form is 4,060 calories at 329°. These figures correspond to the entropy of fusion values 7.4 and 12.3 units, respectively.

Hexafluoride.—Ruff and Tschirch (*336*) have reported 476.6° for the boiling point (760 mm) for osmium hexafluoride, OsF_6.

Octafluoride.—The vapor pressure of osmium octafluoride, OsF_8, was measured by Ruff and Tschirch (*336*) (311–321°), and the melting point was reported as 307.5°. Taking ΔC_p as zero, the following equations result.

$\Delta H = 6{,}840$,
$\Delta F^\circ = 6{,}840 - 21.34\ T$,
B. P. = 320.5°; $\Delta S_{593.6} = 21.3$,
$\Delta F^\circ_{298.1} = 479$.

OXYGEN

Element.—Several investigators have measured the vapor pressure of liquid oxygen—Baly (*14*) (77–91°), Bestelmeyer (*26*) (82–91°), Bulle (*53*) (92–136°), Cath (*61*) (62–91°), Crommelin (*72*) (118–154°), Dodge and Davis (*87*) (77–134°), Estreicher (*99*) (62–91°), Henning (*152*) (87–91°), Henning and Heuse (*154*) (68–83°), Keesom, Van der Horst, and Jansen (*196*) (90°), Olszewski (*265*) (62–92°), Onnes and Braak (*268*) (86–91°), Von Siemens (*360*) (57–91°), Stock, Henning, and Kusz (*400*) (88–94°), Travers, Senter, and Jaquerod (*419*, *420*) (77–91°) and Wroblewski (*444*) (89–140°). The data of Cath, Crommelin, Dodge and Davis, Henning, Henning and Heuse, Keesom, Van der Horst, and Jansen, Onnes and Braak, Stock, Henning, and Kusz, and Travers, Senter, and Jaquerod are in good agreement.

Solid oxygen exhibits three polymorphic forms in the temperature range 12 to 54.39°, the melting point. The transitions occur at 23.66 and 43.76°. The thermal data of Giauque and Johnston (*121*), after correcting to the ideal state, are used in obtaining the equations that follow. The specific heats of liquid oxygen and the highest-temperature solid form, S_I, are taken as constants, 12.80 and 11.03 calories per gram formula weight, respectively. The two lower-temperature solid modifications, S_{II} and S_{III}, have specific heats which are represented sufficiently well by $C_P(S_{II}) = -2.55 + 0.310\ T$ and

$C_p(S_{III}) = -3.15 + 0.326\ T$, the latter equation nòt being valid below 12°.

Solid $(S_{III}) \rightarrow$ Gas (O_2) (12–23.66°)
$C_p(g) = 6.95$,
$C_p(S_{III}) = -3.15 + 0.326\ T$,
$\Delta C_p = 10.10 - 0.326\ T$,
$\Delta H = 2{,}080 + 10.10\ T - 0.163\ T^2$,
$\Delta F^\circ = 2{,}080 - 23.26\ T \log T + 0.163\ T^2 + 4.97\ T$.
Solid $(S_{II}) \rightarrow$ Gas (O_2) (23.66–43.76°)
$C_p(g) = 6.95$,
$C_p(S_{II}) = -2.55 + 0.310\ T$,
$\Delta C_p = 9.50 - 0.310\ T$,
$\Delta H = 2{,}068 + 9.50\ T - 0.155\ T^2$,
$\Delta F^\circ = 2{,}068 - 21.88\ T \log T + 0.155\ T^2 + 3.75\ T$.
Solid $(S_I) \rightarrow$ Gas (O_2) (43.76–54.39°)
$C_p(g) = 6.95$,
$C_p(S_I) = 11.03$,
$\Delta C_p = -4.08$,
$\Delta H = 2{,}188 - 4.08\ T$,
$\Delta F^\circ = 2{,}188 + 9.40\ T \log T - 43.54\ T$.
Liquid $\rightarrow$ Gas (O_2) (54.39°–)
$C_p(g) = 6.95$,
$C_p(l) = 12.80$,
$\Delta C_p = -5.85$,
$\Delta H = 2{,}178 - 5.85\ T$,
$\Delta F^\circ = 2{,}178 + 13.47\ T \log T - 50.42\ T$.

The vapor pressure is low enough for the three solid forms that $\Delta F^\circ = -R\ T\ ln\ P$ may be used in conjunction with the free-energy equations to obtain vapor-pressure relationships. For the liquid this is not the case and the following vapor-pressure equation is included.

Liquid $\rightarrow$ Gas (O_2) (54.39–90.13°)

$$\log P\ (at.) = -\frac{483.06}{T} - 2{,}944 \log T + 11.117,$$

B. P. = 90.13°.

Ozone.—Riesenfeld and Beja (*303, 304*) (103–165°), Riesenfeld and Schwab (*305*) (161°), and Spangenberg (*376*) (81–90°) have measured the vapor pressure of zone, O_3. The results of Riesenfeld and his coworkers are consistent. Those of Spangenberg are for pressures below 0.1 mm and are given no weight. ΔC_p has been neglected in obtaining the following equations.

Liquid $\rightarrow$ Gas (O_3)
$\Delta H = 2{,}880$,
$\Delta F^\circ = 2{,}880 - 17.78\ T$,
B. P. = 162°; $\Delta S_{162} = 17.8$.

PHOSPHORUS

Element.—The following investigators have studied the vapor pressure of phosphorus—Bridgeman (*43*) (black, 630–718°, and dense red, 630–717°), Centnerszwer (*63*) (yellow, 293–313°), Hittorff (*166*) (three varieties, 503–803°), Joubert (*192*) (yellow, 278–373°), Macrae and Van Voorhis (*231*) (liquid, 317–423°), Nicolaieff (*259*) (violet, 473°; red, 619°; and black, 763°), Preuner and Brockmöller (*291*) (liquid, 403–563°), Smits and Bokhorst (*369*) (violet and liquid, 563–907°), and Smits, Meyer, and Beck (*373*) (black and violet, 630–853°).

The phosphorus system is quite complex, several solid modifications having been reported, and in the gaseous phase there are present the molecular species, P_4, P_2, and P. However, of the solid forms, the ordinary yellow and the violet are known to be pure crystalline modifications. It is also known that there is a lower-temperature form of yellow phosphorus which is stable below 195°. Evidence also favors the acceptance of the black form as a pure crystalline variety. On the other hand, red phosphorus is a mixture of two crystalline species, a transitional product between yellow and violet, and the various shades of color encountered are presumably due to differences in degree of subdivision of the particles. The polymorphism of phosphorus has been discussed by Mellor (*243*).

The present considerations are confined, therefore, to the higher-temperature yellow, the violet, and the black varieties of solid phosphorus and to liquid phosphorus. Preuner and Brockmöller (*291*) and Stock, Gibson, and Stamm (*399*) have studied the reactions $P_4=2P_2$ and $P_2=2P$. The latter authors claim that dissociation of the P_4-species is not important below 973°. Although the former do not agree with the latter on the order of magnitude of the partial pressures of the gaseous constituents, they do agree that the P_2 and P species are present below 1,000° in amounts that are negligible for the present purpose. Consequently the equations to be given are for the formation of P_4 gas from the given solid or liquid phase. ΔC_p has been neglected, of necessity. The vapor-pressure results given by Smits and Bokhorst (some of which they report as being due to Jolibois), Macrae and Van Voorhis, and Preuner and Brockmöller are in good agreement for the liquid form. The data of Smits and his coworkers are utilized in obtaining the equations for the violet modification. For the black variety there are available the results of Bridgeman and of Smits, Meyer, and Beck. The equations for the yellow variety are in agreement with the data of Centnerszwer.

Solid (yellow)→Gas (P_4)
$\Delta H=13{,}135,$
$\Delta F°=13{,}135-24.59\,T,$
M. P. = 317.3°,
$\Delta F°_{298.1}=5{,}805.$
Solid (violet)→Gas (P_4)
$\Delta H=25{,}600,$
$\Delta F°=25{,}600-37.11\,T,$
S. P. = 690°; $\Delta S_{690}=37.1,$
$\Delta F°_{298.1}=14{,}538.$
Solid (black)→Gas (P_4)
$\Delta H=33{,}100,$
$\Delta F°=33{,}100-45.58\,T,$
S. P. = 726°; $\Delta S_{726}=45.6,$
$\Delta F°_{298.1}=19{,}513.$
Liquid→Gas (P_4)
$\Delta H=12{,}520,$
$\Delta F°=12{,}520-22.65\,T,$
B. P. = 553°; $\Delta S_{553}=22.6,$
$\Delta F°_{298.1}=5{,}768.$

The vapor pressures of the violet and black modifications both exceed 1 atmosphere at temperatures below their melting points. The yellow variety melts at 317.3° with a heat of fusion of 615 calories per gram formula weight of P_4, the entropy of fusion being 1.94 units. The equations given may not be extrapolated to high pressures, and the melting and transition points which formally might be computed are not correct largely because the equations for the liquid were made to fit the lower pressure range where the liquid is in a supercooled condition with respect to the melting point of violet phosphorus. Marked deviation from the experimental data begins around 700° where the pressure is already over 7 atmospheres.

Trioxide.—Van Doormaal and Scheffer (*89*) (329–451°) and Schenck, Banthien, and Mihr (*350*) (293–365°) have determined the vapor pressure of the so-called trioxide, P_4O_6. The results of the latter authors are erratic, and the *ln P* v. $\frac{1}{T}$ plot for the formers' results shows more curvature than is usually encountered. ΔC_p has been neglected, and the equations are based on Van Doormaal and Scheffer's results.

Liquid→Gas (P_4O_6)
$\Delta H = 10{,}380,$
$\Delta F^\circ = 10{,}380 - 23.23T,$
B. P. = 447°; $\Delta S_{447} = 23.2,$
$\Delta F^\circ_{298.1} = 3{,}455.$

Pentoxide.—The oxide, P_4O_{10}, was studied by Hoeflake and Scheffer (*167*) (633–835°) and Smits and Deinum (*370*) (722–973°). The results of these two investigations are in disagreement, and for the present those of Hoeflake and Scheffer are adopted because they give what appear to be more reasonable entropy of vaporization figures. The ordinary metastable form of the solid is considered by the latter authors to be a mixture and not a true crystalline modification. When heated above its normal sublimation point a transformation occurs, and the vapor pressure drops from about 4 atmospheres to nearly zero. On further heating, this substance melts into what is presumably a supercooled liquid, and from the latter crystals of a pure modification separate out on standing. These crystals melt at 842°. The following results are obtained if ΔC_p is neglected. For the usual, metastable variety a vapor-pressure equation only is given.

Solid (α)→Gas (P_4O_{10})
$\Delta H = 37{,}750,$
$\Delta F^\circ = 37{,}750 - 44.20\ T,$
M. P. = 842°,
$\Delta F^\circ_{298.1} = 24{,}574.$

Liquid→Gas (P_4O_{10})
$\Delta H = 20{,}670,$
$\Delta F^\circ = 20{,}670 - 23.91\ T,$
B. P. = 864°; $\Delta S_{864} = 23.9,$
$\Delta F^\circ_{298.1} = 13{,}542.$

Solid (ordinary metastable form)→Gas (P_4O_{10})

$$\log P\ (at.) = -\frac{4{,}940}{T} + 7.823,$$

S. P. = 631°.

Sulphide.—Bodenstein (*32*) has determined the normal boiling point of phosphorus sulphide, P_2S_3, as 781°. This is the only available figure for this substance.

Oxychloride.—The vapor pressure of liquid phosphorus oxychloride, $POCl_3$, was measured by Arii (*9, 12*) (293–378°). If ΔC_p is neglected in calculating Σ, the resulting *I* values vary over a range of 0.06 unit.

Liquid→Gas ($POCl_3$)
$\Delta H = 8{,}380,$
$\Delta F^\circ = 8{,}380 - 22.16\ T,$
B. P. = 378.2°; $\Delta S_{378.2} = 22.2,$
$\Delta F^\circ_{298.1} = 1{,}774.$

Trichloride.—Regnault (*300*) (273–341°) has studied liquid phosphorus trichloride, PCl_3. His measurements are very concordant, giving an extreme variation in I of 0.06 unit.

Liquid → Gas (PCl_3)

$C_p(g) = 18.5$,
$C_p(l) = 28.7$,
$\Delta C_p = -10.2$,
$\Delta H = 10{,}820 - 10.2\ T$,
$\Delta F^\circ = 10{,}820 + 23.5\ T \log T - 90.86\ T$,
B. P. $= 347.3°$; $\Delta H_{347.3} = 7{,}278$; $\Delta S_{347.3} = 21.0$,
$\Delta H_{298.1} = 7{,}779$; $\Delta F^\circ_{298.1} = 1{,}069$.

Phosphene.—The vapor pressure of phosphene, PH_3, was measured by Briner (*45*) (298–325°), Henning and Stock (*155*) (160–179°), Steele and McIntosh (*378*) (167–187°), and Stock, Henning, and Kusz (*400*) (140–186°). The measurements of Briner are for pressures above 38 atmospheres and are not considered here. Of the other three sets, those of Steele and McIntosh appear to be low, and the remainder are in very good agreement. ΔC_p is neglected.

Liquid → Gas (PH_3)

$\Delta H = 3{,}650$,
$\Delta F^\circ = 3{,}650 - 19.67\ T$,
B. P. $= 185.6°$; $\Delta S_{185.6} = 19.7$.

Thiophosphoryl fluoride.—The compound, PSF_3, was studied in the liquid state by Thorpe and Rodger (*408*) (276–294°). Their data are for pressures over 7 atmospheres, and consequently only a vapor-pressure equation is given here. It is not advisable to use this equation at temperatures much higher or lower than the range actually studied.

Liquid → Gas (PSF_3) (276–294°)

$$\log P\,(at.) = -\frac{1{,}150}{T} + 5.030.$$

PLATINUM

Element.—Jones, Langmuir, and Mackay (*191*) (800–4,800°) and Langmuir and Mackay (*221*) (1,000–4,180°) have given vapor-pressure figures for platinum. Their results are calculated from rates of evaporation from filaments. In the more recent paper of the former authors the rate measurements employed are for the temperature range 1,697 to 2,035°. For the present purpose the actual experimental data were utilized. With the value of I in the free-energy equation given below, the individual experimental determinations give ΔH_0 values varying over a range of about 2,800 calories, although if one result is omitted this range is decreased to 980 calories. No systematic trend with the temperature is shown by these values.

Solid → Gas (Pt)

$C_p(g) = 4.97$,
$C_p(s) = 5.92 + 1.16 \times 10^{-3} T$,
$\Delta C_p = -0.95 - 1.16 \times 10^{-3} T$,
$\Delta H = 124{,}690 - 0.95\ T - 0.58 \times 10^{-3} T^2$,
$\Delta F^\circ = 124{,}690 + 2.19\ T \log T + 0.58 \times 10^{-3} T^2 - 38.44\ T$,
$\Delta H_{298.1} = 124{,}355$; $\Delta F^\circ_{298.1} = 114{,}898$; $S^\circ_{298.1}(g) = 41.7$.

Approximate results for the liquid may be obtained from those for the solid assuming the entropy of fusion is 2.3, the average for all the metals whose heats of fusion have been measured, and taking $\Delta C_p = -3.3$.

Liquid→Gas (Pt)

$\Delta C_p = -3.3,$
$\Delta H = 122{,}370 - 3.3\ T,$
$\Delta F^\circ = 122{,}370 + 7.6\ T \log T - 54.03\ T,$
B. P. $= 4{,}680°$; $\Delta H_{4680} = 106{,}926$; $\Delta S_{4680} = 22.8,$
$\Delta H_{298.1} = 121{,}386$; $\Delta F^\circ_{298.1} = 111{,}870.$

POTASSIUM

Element.—The investigators who have studied the vapor pressure of potassium are Edmondson and Egerton (*93*) (372–474°), Fiock and Rodebush (*106*) (679–1,033°), Hackspill (*140*) (537–673°), Hansen (*142*) (940°), Heycock and Lamplough (*161*) (1,035°), Kröner (*215*) (522–672°), Lewis (*227*) (581–714°), Neumann and Völker (*258*) (417–473°), Ruff and Johannsen (*324*) (1,030–1,032°), and Weiler (*435*) (429–628°). A Σ-function plot shows the results of Fiock and Rodebush, Lewis, Kröner, Edmondson and Egerton, and Neumann and Völker to be in agreement. Overstreet (*273*) has computed free-energy values for potassium gas from spectroscopic data which are used here to obtain free energy of vaporization figures. Since diatomic molecules, K_2, are present it is necessary to choose the $\frac{\Delta F^\circ}{T}$ value used in obtaining ΔE°_0 at a low enough temperature that the proportion of K_2 molecules is virtually negligible. Lewis' figures for the ratio of K_2 to K molecules show that this is the case around 500°. Consequently, the result, $\frac{\Delta F^\circ}{T} = -R\ ln\ P = 20.78$ at 500°, taken from the smoothed curve representing the experimental vapor-pressure data, is employed to find $\Delta E^\circ_0 = 21{,}730$ calories. Table 21 summarizes the free-energy calculations.

TABLE 21.—*Free energy of vaporization data for potassium*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ - E^\circ_{c,0}}{T}$	$\frac{\Delta F^\circ_v - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−33.337	−9.53	−23.81	72.90	49.09
300	−33.368	−9.56	−23.81	72.43	48.62
400	−34.797	−11.55	−23.25	54.32	31.07
500	−35.906	−13.23	−22.68	43.46	20.78
600	−36.811	−14.62	−22.19	36.22	14.03
700	−37.577	−15.78	−21.80	31.04	9.24
800	−38.240	−16.80	−21.44	27.16	5.72
900	−38.825	−17.70	−21.12	24.14	3.02
1,000	−39.349	−18.50	−20.85	21.73	.88

Solid→Gas (K)

$C_p(g) = 4.97,$
$C_p(s) = 5.24 + 5.55 \times 10^{-3} T,$
$\Delta C_p = -0.27 - 5.55 \times 10^{-3} T,$
$\Delta H = 21{,}848 - 0.27\ T - 2.775 \times 10^{-3} T^2,$
$\Delta F^\circ = 21{,}848 + 0.62\ T \log T + 2.775 \times 10^{-3} T^2 - 26.56\ T,$
$\Delta H_{298.1} = 21{,}521$; $\Delta F^\circ_{298.1} = 14{,}637$; $S^\circ_{298.1}(g) = 38.30.$

Liquid→Gas (K)

$C_p(g)=4.97,$
$C_p(l)=7.70,$
$\Delta C_p=-2.73,$
$\Delta H=21{,}788-2.73\ T,$
$\Delta F°=21{,}788+6.29\ T\log T-39.77\ T,$
$P\ (K)=1\ at.$ at 1,049°; $\Delta H_{1049}=18{,}924$; $\Delta S_{1049}=18.04,$
$\Delta H_{298.1}=20{,}974$; $\Delta F°_{298.1}=14{,}573.$

The boiling point (total vapor pressure=1 at.) is given as 1,035° by Heycock and Lamplough. However, on the Σ-function plot this value seems too low. The following vapor-pressure equation for liquid potassium is representative of the experimental determinations of Fiock and Rodebush, Lewis, Kröner, Neumann and Völker, and Edmondson and Egerton:

Liquid→Gas (K+K₂)

$$\log P\ (at.)=-\frac{4{,}769}{T}-1.375\log T+8.708,$$

B. P.=1,047°.

Hydroxide.—Jackson and Morgan (*179*) (1,063–1,068°) and Von Wartenberg and Albrecht (*430*) (1,443–1,600°) have studied the vapor pressure of liquid KOH. The equations are based on the results of the latter investigators and the assumption that $\Delta C_p=-10$. The extreme deviation in I is 0.18 unit.

Liquid→Gas (KOH)

$\Delta C_p=-10,$
$\Delta H=46{,}850-10\ T,$
$\Delta F°=46{,}850+23.0\ T\log T-102.98\ T,$
B. P.=1,600°; $\Delta H_{1600}=30{,}850$; $\Delta S_{1600}=19.3,$
$\Delta H_{298.1}=43{,}869$; $\Delta F°_{298.1}=33{,}125.$

Bromide.—The vapor pressure of liquid potassium bromide was measured by Fiock and Rodebush (*106*) (1,179–1,336°), Ruff and Mugdan (*333*) (1,361–1,668°), and Von Wartenberg and Albrecht (*430*) (1,368–1,648°). The results of Fiock and Rodebush are the most consistent and correspond to about the mean values of the others. The extreme variation in I is only 0.03 unit when Σ-values are computed on the assumption that $\Delta C_p=-7$.

Liquid→Gas (KBr)

$\Delta C_p=-7,$
$\Delta H=48{,}650-7\ T,$
$\Delta F°=48{,}650+16.1\ T\log T-81.20\ T,$
B. P.=1,656°; $\Delta H_{1656}=37{,}060$; $\Delta S_{1656}=22.4,$
$\Delta H_{298.1}=46{,}563$; $\Delta F°_{298.1}=36{,}320.$

Chloride.—Fiock and Rodebush (*106*) (1,179–1,378°), Greiner and Jellinek (*134*) (1,453°), Hackspill and Grandadam (*141*) (1,071–1,383°), Horiba and Baba (*173*) (973–1,524°), Jackson and Morgan (*179*) (1,074–1,773°), Kordez and Raaz (*212*) (1,684°), Ruff and Mugdan (*333*) (1,393–1,688°), and Von Wartenberg and Albrecht (*430*) (1,389–1,691°) have measured the vapor pressure of liquid potassium chloride. Again, the data of Fiock and Rodebush appear to be by far the best and are adopted for the present purpose. The I values from their data vary over a range of only 0.07 unit. The equations for the solid were derived from those for the liquid and thermal data.

Solid→Gas (KCl)

$C_p(g)=9.0,$
$C_p(s)=10.93+3.76\times10^{-3}T,$
$\Delta C_p=-1.93-3.76\times10^{-3}T,$
$\Delta H=53,770-1.93\ T-1.88\times10^{-3}T^2,$
$\Delta F°=53,770+4.44\ T\log T+1.88\times10^{-3}T^2-51.85\ T,$
$\Delta H_{298.1}=53,028;\ \Delta F°_{298.1}=41,756;\ S_{298.1}(g)=57.6.$

Liquid→Gas (KCl)

$C_p(g)=9.0,$
$C_p(l)=16.0,$
$\Delta C_p=-7.0,$
$\Delta H=50,600-7.0\ T,$
$\Delta F°=50,600+16.1\ T\log T-82.04\ T,$
B. P.=1,680°; $\Delta H_{1680}=38,840;\ \Delta S_{1680}=23.1,$
$\Delta H_{298.1}=48,513;\ \Delta F°_{298.1}=38,020.$

Fluoride.—Ruff, Schmidt, and Mugdan (*339*) (1,551–1,773°) and Von Wartenberg and Schulz (*432*) (1,624–1,776°) have measured the vapor pressure of liquid potassium fluoride. With the exception of the lowest temperature determination of Ruff, Schmidt, and Mugdan the data are in fair agreement, giving an extreme *I* variation of 0.25 unit when ΔC_p is taken as −7.

Liquid→Gas (KF)

$\Delta C_p=-7,$
$\Delta H=53,700-7\ T,$
$\Delta F°=53,700+16.1\ T\log T-82.56\ T,$
B. P.=1,775°; $\Delta H_{1775}=41,275;\ \Delta S_{1775}=23.2,$
$\Delta H_{298.1}=51,613;\ \Delta F°_{298.1}=40,965.$

Iodide.—Liquid potassium iodide was studied by Fiock and Rodebush (*106*) (1,115–1,302°), Greiner and Jellinek (*134*) (1,453°), Ruff and Mugdan (*333*) (1,319–1,590°), and Von Wartenberg and Albrecht (*430*) (1,336–1,606°). The results of Fiock and Rodebush appear to be the most reliable and are used in obtaining the equations. The extreme *I* variation from their data is 0.08 unit, $\Delta C_p=-7$ being assumed.

Liquid→Gas (KI)

$\Delta C_p=-7,$
$\Delta H=45,870-7\ T,$
$\Delta F°=45,870+16.1\ T\log T-80.30\ T$
B. P.=1,597°; $\Delta H_{1597}=34,691;\ \Delta S_{1597}=21.7,$
$\Delta H_{298.1}=43,783;\ \Delta F°_{298.1}=33,809.$

Sulphate.—Jackson and Morgan (*179*) have reported a vapor pressure of potassium sulphate—0.35 mm at 1,402°.

RADON

Element.—The vapor pressure of liquid radon was measured by Gray and Ramsay (*130*) (202–378°), and some results for the solid were determined by Kovarik (*213*) (84–112°). The latter's figures are for pressures below 10^{-6} atmospheres, however, and are not considered here. The following equations result from Gray and Ramsay's lower-pressure results. This substance melts at 202° under its own vapor pressure, 500 mm.

Liquid→Gas (Rn)

$\Delta H=4,010,$
$\Delta F°=4,010-18.98\ T,$
B. P.=211.3°; $\Delta S_{211.3}=19.0.$

RHENIUM

Heptoxide.—Ogawa (*263*) (503–633°) has given vapor-pressure results for solid and liquid rhenium heptoxide, Re_2O_7. His results are quite concordant; and, with ΔC_p neglected, the following equations result:

Solid→Gas (Re_2O_7)

$\Delta H = 33{,}400,$
$\Delta F^\circ = 33{,}400 - 55.40\ T,$
$\Delta F^\circ_{298.1} = 16{,}885.$

Liquid→Gas (Re_2O_7)

$\Delta H = 18{,}060,$
$\Delta F^\circ = 18{,}060 - 28.42\ T,$
B. P. $= 635.5^\circ$; $\Delta S_{908.6} = 28.4,$
$\Delta F^\circ_{298.1} = 9{,}588.$

The equations give 15,340 calories per gram formula weight for the heat of fusion at 569°, the melting point.

Octoxide.—The oxide, Re_2O_8, also was studied by Ogawa (*263*) (373–493°), who found marked decomposition so that equations are not warranted. However, his results indicate a heat of fusion of 3,800 calories at 420°.

Fluoride.—Ruff, Kwasnik, and Ascher (*338*) (273–292°) have reported results for the fluoride, ReF_6. Their results are too erratic to justify any sort of computations.

RUBIDIUM

Element.—The vapor pressure of liquid rubidium was measured by Hackspill (*140*) (523–640°), Scott (*357*) (364–400°), and Ruff and Johannsen (*324*) (970°). The data of Scott, which extrapolate nicely into the higher-temperature values of Hackspill, have been given the most weight. Scott's data show an extreme variation in *I* of 0.44 unit. The equations for the solid are based on those for the liquid and thermal data.

Solid→Gas (Rb)

$C_p(g) = 4.97,$
$C_p(s) = 3.27 + 13.1 \times 10^{-3}T,$
$\Delta C_p = 1.70 - 13.1 \times 10^{-3}T,$
$\Delta H = 20{,}580 + 1.70\ T - 6.55 \times 10^{-3}T^2,$
$\Delta F^\circ = 20{,}580 - 3.92\ T \log T + 6.55 \times 10^{-3}T^2 - 16.50\ T,$
$\Delta H_{298.1} = 20{,}505$; $\Delta F^\circ_{298.1} = 13{,}352$; $\Delta S_{298.1} = 24.0.$

Liquid→Gas (Rb)

$C_p(g) = 4.97,$
$C_p(l) = 7.85,$
$\Delta C_p = -2.88,$
$\Delta H = 20{,}850 - 2.88\ T,$
$\Delta F^\circ = 20{,}850 + 6.63\ T \log T - 41.64\ T,$
B. P. $= 952^\circ$; $\Delta H_{952} = 18{,}108$; $\Delta S_{952} = 19.0,$
$\Delta H_{298.1} = 19{,}991$; $\Delta F^\circ_{298.1} = 13{,}327.$

From the entropy of vaporization of the solid, $\Delta S_{298.1} = 24.0$, and the entropy of the gas, $S^\circ_{298.1} = 40.64$, the value 16.6 is computed for the entropy of solid rubidium at 298.1°. This property has not been directly determined. The figure given here is considered more reliable than the value, 17.2, previously obtained from other considerations (*199*).

Bromide.—Ruff and Mugdan (*333*) (1,323–1,638°) and Von Wartenberg and Schulz (*432*) (1,369–1,631°) have measured vapor pressures of liquid rubidium bromide. The values given by the latter authors are the more consistent and are used here. Taking $\Delta C_p = -7$ in computing Σ-function values, the extreme variation in I is 0.30 unit for their data.

Liquid→Gas (RbBr)

$\Delta C_p = -7,$
$\Delta H = 48{,}500 - 7\,T,$
$\Delta F^\circ = 48{,}500 + 16.1\,T \log T - 81.54\,T,$
B. P. = 1,625°; $\Delta H_{1625} = 37{,}125$; $\Delta S_{1625} = 22.8,$
$\Delta H_{298.1} = 46{,}413$; $\Delta F^\circ_{298.1} = 36{,}069.$

Chloride.—The chloride, RbCl, also was studied by Ruff and Mugdan (*333*) (1,415–1,668°) and Von Wartenberg and Schulz (*432*) (1,434–1,657°), and again the results of the latter authors are the better, the extreme variation in I being 0.12 unit.

Liquid→Gas (RbCl)

$\Delta C_p = -7,$
$\Delta H = 48{,}500 - 7\,T,$
$\Delta F^\circ = 48{,}500 + 16.1\,T \log T - 81.14\,T,$
B. P. = 1,654°; $\Delta H_{1654} = 36{,}922$; $\Delta S_{1654} = 22.3,$
$\Delta H_{298.1} = 46{,}413$; $\Delta F^\circ_{298.1} = 36{,}188.$

Fluoride.—Ruff, Schmidt, and Mugdan (*339*) (1,415–1,673°) and Von Wartenberg and Schulz (*432*) (1,436–1,683°) have measured the vapor pressure of liquid rubidium fluoride. Their results are in fair agreement, those of the latter authors appearing somewhat the better. The I values lie in a range of 0.27 unit.

Liquid→Gas (RbF)

$\Delta C_p = -7,$
$\Delta H = 51{,}280 - 7\,T,$
$\Delta F^\circ = 51{,}280 + 16.1\,T \log T - 82.44\,T,$
B. P. = 1,681°; $\Delta H_{1681} = 39{,}513$; $\Delta S_{1681} = 23.5,$
$\Delta H_{298.1} = 49{,}193$; $\Delta F^\circ_{298.1} = 38{,}581.$

Iodide.—Vapor-pressure measurements of rubidium iodide were made by Ruff and Mugdan (*333*) (1,348–1,598°) and Von Wartenberg and Schulz (*432*) (1,308–1,575°). The results of the latter investigators, which show an extreme I-variation of 0.43 unit, are used for the present purpose.

Liquid→Gas (RbI)

$\Delta C_p = -7,$
$\Delta H = 47{,}000 - 7\,T,$
$\Delta F^\circ = 47{,}000 + 16.1\,T \log T - 81.29\,T,$
B. P. = 1,577°; $\Delta H_{1577} = 35{,}961$; $\Delta S_{1577} = 22.8,$
$\Delta H_{298.1} = 44{,}913$; $\Delta F^\circ_{298.1} = 34{,}643.$

SELENIUM

Element.—The vapor pressure of selenium was measured by Dodd (*86*) (204–467°), Jannek and Meyer (*181*) (473–503°), and Preuner and Brockmöller (*291*) (663–983°). The latter authors have studied also the equilibria in the system $Se_8 = 3Se_2$ between 823 and 1,073°. From their results, $\Delta F^\circ = 59{,}960 - 58.36\,T$ is computed for this reaction. For the present purpose, the vapor pressure results of Preuner and Brockmöller are adopted. Jannek and Meyer's two determinations appear to be erratic and Dodd's figures were obtained on the assumption of Se_2 gas. His results may be recomputed on the assumption of entirely Se_6 gas by multiplying by $\frac{1}{3}\sqrt{3}$. However, it seems safer to use Preuner and Brockmöller's vapor pressure results for the liquid. The partial pressures of Se_6 and Se_2 may be obtained at any temperature from the vapor-pressure and the free-energy change for the reaction $Se_6 = 3Se_2$. This was done at several temperatures and Σ-function plots made for the formation of both Se_6 and Se_2 gases in order to derive the desired equations. The relationships given for the solid were obtained from those for the liquid and thermal data. ΔC_p has been ignored in the computations involving Se_6.

Liquid→**Gas** (Se_6)
$\Delta H = 20{,}600$,
$\Delta F^\circ = 20{,}600 - 20.42\ T$,
$P(Se_6) = 1$ at. at 1,009°; $\Delta S_{1009} = 20.4$,
$\Delta F^\circ_{298.1} = 14{,}513$.
Solid→**Gas** (Se_6)
$\Delta H = 27{,}920$,
$\Delta F^\circ = 27{,}920 - 35.36\ T$.
$\Delta F^\circ_{298.1} = 17{,}359$.
Liquid→**Gas** (Se_2)
$C_p(g) = 9.0$,
$C_p(l) = 16.7$,
$\Delta C_p = -7.7$,
$\Delta H = 33{,}400 - 7.7\ T$,
$\Delta F^\circ = 33{,}400 + 17.7\ T \log T - 85.84\ T$,
$P(Se_2) = 1$ at. at 1,026°; $\Delta H_{1026} = 25{,}492$; $\Delta S_{1026} = 24.8$,
$\Delta H_{298.1} = 31{,}105$; $\Delta F^\circ_{298.1} = 20{,}867$
Solid→**Gas** (Se_2)
$C_p(g) = 9.0$,
$C_p(s) = 9.06 + 11.00 \times 10^{-3} T$,
$\Delta C_p = -0.06 - 11.00 \times 10^{-3} T$,
$\Delta H = 33{,}420 - 0.06\ T - 5.5 \times 10^{-3} T^2$,
$\Delta F^\circ = 33{,}420 + 0.14\ T \log T + 5.5 \times 10^{-3} T^2 - 41.34\ T$,
$\Delta H_{298.1} = 32.913$; $\Delta F^\circ_{298.1} = 21{,}689$.

The total vapor pressure of the liquid is represented by the following equation:

Liquid→**Gas** ($Se_6 + Se_2$)
$\log P\ (at.) = -\frac{5{,}230}{T} + 5.440$,
B. P. = 961°.

Oxide.—Jannek and Meyer (*181*) (293–593°) have measured the vapor pressure of selenium dioxide, SeO_2, in the solid state. The data are peculiar, showing a sharp break at about 500°, and the temperature coefficient of the vapor pressure changes at this temperature in the opposite manner from what would be expected if a transition in the solid occurred. However, utilizing the four highest temperature determinations, the following approximations result:

Solid→Gas (SeO_2)
$\Delta H = 20{,}900$,
$\Delta F^\circ = 20{,}900 - 35.43\ T$,
S. P. = 590°; $\Delta S_{590} = 35.4$,
$\Delta F^\circ_{298.1} = 10{,}338$.

Oxychloride.—Lenher, Smith, and Town (*224*) (357–451°) have studied the vapor pressure of the oxychloride, $SeOCl_2$. This substance tends to decompose, leaving a solution of SeO in $SeOCl_2$, with the consequent lowering of the vapor pressure. The temperature coefficient of the measured values of vapor pressure indicates that this decomposition may be quite serious, and so only an approximate equation for the total measured pressures is included.

Liquid→Gas ($SeOCl_2$)

$$\log P\ (at.) = -\frac{2,907}{T} + 6.588.$$

Hexafluoride.—Solid selenium hexafluoride, SeF_6, was studied by Klemm and Henkel (*206*) (194–226°) and Yost and Clausen (*447*) (185–225°). The melting point is given by the latter authors as 238.5°. The vapor-pressure data are in fair agreement. ΔC_p is ignored.

Solid→Gas (SeF_6)

$\Delta H = 6,350,$
$\Delta F° = 6,350 - 27.94\ T,$
S. P. $= 227.3°$; $\Delta S_{227.3} = 27.9.$

Diethylselenide.—Tanaka and Nagai (*404*) have reported 28 mm as the vapor pressure of diethylselenide, $Se(C_2H_5)_2$, at 298.1°.

SILICON

Element.—Ruff and Konschak (*327*) (2,163–2,433°) and Von Wartenberg (*426*) (1,478–1,588°) have studied the vapor pressure of silicon. The data are too erratic to warrant free-energy calculations, and there is considerable uncertainty concerning the molecular species present in the gas. The following relationship, however, serves for obtaining approximate results for the vapor pressure of liquid silicon:

Liquid→Gas (Si_x)

$$\log P\ (at.) = -\frac{27,620}{T} - 1.27 \log T + 15.12.$$

Oxide.—The vapor pressure of silicon dioxide was measured by Ruff and Schmidt (*335*) (2,057–2,603°). The results obtained are very erratic, and so only an approximate vapor-pressure equation is included.

Liquid→Gas ($(SiO_2)_x$)

$$\log P\ (at.) = -\frac{19,130}{T} + 7.65.$$

Monosilane.—Vapor pressures of the hydride, SiH_4, have been measured by Adwentowski and Drozdowski (*2*) (125–270°) and Stock and Somieski (*392*) (113–161°). The latter authors report the melting point at 88°. The two sets of results are in complete disagreement, and it appears certain that those of Adwentowski and Drozdowski are in error. The data of Stock and Somieski were used in obtaining the following equations, ΔC_p being ignored. With one measurement omitted, the extreme deviation in the I values is 0.14 unit.

Liquid→Gas (SiH_4)

$\Delta H = 2,955,$
$\Delta F° = 2,955 - 18.30\ T,$
B. P. $= 161.5°$; $\Delta S_{161.5} = 18.3.$

Monobrom-monosilane.—Stock and Somieski (*393*) (179–275°) have determined the vapor pressure of monobrom-monosilane, SiH_3Br. The results are very consistent and, taking $\Delta C_p = -4$, the following equations are derived:

Liquid→Gas (SiH_3Br)

$\Delta C_p = -4,$
$\Delta H = 6{,}750 - 4\ T,$
$\Delta F^\circ = 6{,}750 + 9.2\ T \log T - 46.95\ T,$
$B.\ P. = 275.5^\circ;\ \Delta H_{275.5} = 5{,}648;\ \Delta S_{275.5} = 20.5,$
$\Delta H_{298.1} = 5{,}558;\ \Delta F^\circ_{298.1} = -460.$

The above authors find 179.3° for the melting point.

Dibrom-monosilane.—The vapor pressures of this compound, SiH_2Br_2, also were determined by Stock and Somieski (*393*) (208–291°), and 203.0° was reported for the melting point. In the following equations, $\Delta C_p = -6$ is assumed.

Liquid→Gas (SiH_2Br_2)

$\Delta C_p = -6,$
$\Delta H = 8{,}960 - 6\ T,$
$\Delta F^\circ = 8{,}960 + 13.8\ T \log T - 60.90\ T,$
$B.\ P. = 343.6^\circ,\ \Delta H_{343.6} = 6{,}838;\ \Delta S_{343.6} = 19.9,$
$\Delta H_{298.1} = 7{,}111;\ \Delta F^\circ_{298.1} = 925.$

Trichlor-monosilane.—Liquid trichlor-monosilane, $SiHCl_3$, was studied by Stock and Zeidler (*396*) (188–305°), who have given a very consistent set of vapor-pressure determinations and have found 146.6° for the melting point. In this case, ΔC_p is taken as -8.

Liquid→Gas ($SiHCl_3$)

$\Delta C_p = -8,$
$\Delta H = 8{,}800 - 8\ T,$
$\Delta F^\circ = 8{,}800 + 18.4\ T \log T - 74.57\ T,$
$B.\ P. = 304.9^\circ;\ \Delta H_{304.9} = 6{,}361;\ \Delta S_{304.9} = 20.9,$
$\Delta H_{298.1} = 6{,}415;\ \Delta F^\circ_{298.1} = 43.$

Tetrachloride.—The vapor pressure of liquid silicon tetrachloride, $SiCl_4$, was measured by Becker and Meyer (*22*) (273–330°), Regnault (*300*) (247–337°), and Stock, Somieski, and Wintgen (*402*) (203–330°). The results of Regnault and of Stock, Somieski, and Wintgen are in agreement. The latter authors give 204.4° for the melting point.

Liquid→Gas ($SiCl_4$)

$C_p(g) = 22.0,$
$C_p(l) = 32.4,$
$\Delta C_p = -10.4,$
$\Delta H = 10{,}290 - 10.4\ T,$
$\Delta F^\circ = 10{,}290 + 23.95\ T \log T - 91.51\ T,$
$B.\ P. = 329.9^\circ;\ \Delta H_{329.9} = 6{,}859;\ \Delta S_{329.9} = 20.8,$
$\Delta H_{298.1} = 7{,}190;\ \Delta F^\circ_{298.1} = 677.$

Tetrafluoride.—Patnode and Papish (*278*) (148–198°) and Ruff and Ascher (*315*) (140–177°) have measured the vapor pressure of solid silicon tetrafluoride. The data of the former authors are quite erratic but are in approximate agreement with the latter's. ΔC_p has been neglected in this case.

Solid→Gas (SiF_4)

$\Delta H = 6{,}130,$
$\Delta F^\circ = 6{,}130 - 34.38\ T,$
$S.\ P. = 178.3^\circ;\ \Delta S_{178.3} = 34.4.$

Trifluoro-chloro-monosilane.—The vapor pressure of this substance, SiF_3Cl, was measured by Schumb and Gamble (*356*) (187–216°). Their results are very concordant, and the following equations are obtained if ΔC_p is neglected.

Liquid→Gas (SiF_3Cl)
$\Delta H = 4{,}460,$
$\Delta F^\circ = 4{,}460 - 21.97\ T,$
B. P. = 203.0°; $\Delta S_{203.0} = 22.0.$

The above authors give 135° for the melting point.

Difluoro-dichloro-monosilane.—Schumb and Gamble (*356*) (195–257°) also have given a very consistent set of vapor-pressure measurements for the compound, SiF_2Cl_2, in the liquid state. They report the melting point at 129°. Again ΔC_p is neglected.

Liquid→Gas (SiF_2Cl_2)
$\Delta H = 5{,}080,$
$\Delta F^\circ = 5{,}080 - 21.03\ T,$
B. P. = 241.6°; $\Delta S_{241.6} = 21.0,$
$\Delta F^\circ_{298.1} = -1{,}189.$

Disilane.—Stock and Somieski (*392*) (155–258°) and Stock, Somieski, and Wintgen (*402*) (163–258°) have measured the vapor pressure of disilane, Si_2H_6. The results obtained are very concordant, and $\Delta C_p = -4$ has been assumed in deriving the following equations. These investigators find 140.6° for the melting point.

Liquid→Gas (Si_2H_6)
$\Delta C_p = -4,$
$\Delta H = 6{,}140 - 4\ T,$
$\Delta F^\circ = 6{,}140 + 9.2\ T \log T - 45.92\ T,$
B. P. = 258.8°; $\Delta H_{258.8} = 5{,}105$; $\Delta S_{258.8} = 19.7,$
$\Delta H_{298.1} = 4{,}948$; $\Delta F^\circ_{298.1} = -763.$

Hexachloro-disilane.—Martin (*240*) (313–418°) has measured the vapor pressure of this substance, Si_2Cl_6, in the liquid state and reports 272° for the melting point. The data are too erratic to warrant anything but an approximate vapor-pressure equation.

Liquid→Gas (Si_2Cl_6)
$\log P\ (at.) = -\frac{2{,}404}{T} + 5.838,$
B. P. = 412°.

Hexafluoro-disilane.—The vapor pressures of solid and liquid hexafluoro-disilane, Si_2F_6, were measured by Schumb and Gamble (*354*, *355*) (194–270°) and the melting point is given as 254.6°. The vapor-pressure results are consistent. ΔC_p is neglected.

Solid→Gas (Si_2F_6)
$\Delta H = 10{,}400,$
$\Delta F^\circ = 10{,}400 - 40.92\ T,$
S. P. = 254.2°; $\Delta S_{254.2} = 40.9,$
$\Delta F^\circ_{298.1} = -1{,}798.$

Liquid→Gas (Si_2F_6)
$\Delta H = 6{,}500,$
$\Delta F^\circ = 6{,}500 - 25.60\ T,$
$\Delta F^\circ_{298.1} = -1{,}139.$

The solid vaporizes at 1 atmosphere pressure just below the melting point. The heat of fusion deduced from these equations is 3,900 calories per gram formula weight.

Disiloxan.—Stock, Somieski, and Wintgen (*402*) (163–258°) have obtained some very concordant vapor-pressure results for disiloxan $(SiH_3)_2O$. They report 129° for the melting point. In this case, $\Delta C_p = -6$ is assumed.

Liquid→**Gas** ($(SiH_3)_2O$)
$\Delta C_p = -6,$
$\Delta H = 6{,}900 - 6\ T,$
$\Delta F° = 6{,}900 + 13.8\ T \log T - 60.05\ T,$
B. P. = 257.7°; $\Delta H_{257.7} = 5{,}354$; $\Delta S_{257.7} = 20.8,$
$\Delta H_{298.1} = 5{,}111$; $\Delta F°_{298.1} = -822.$

Hexachloro-disiloxan.—This substance, $(SiCl_3)_2O$, also was studied by Stock, Somieski, and Wintgen (*402*) (273–410°). The melting point is given as 240°. $\Delta C_p = -18$ is assumed.

Liquid→**Gas** ($(SiCl_3)_2O$)
$\Delta C_p = -18,$
$\Delta H = 16{,}180 - 18\ T,$
$\Delta F° = 16{,}180 + 41.4\ T \log T - 147.70\ T,$
B. P. = 408.7°; $\Delta H_{408.7} = 8{,}823$; $\Delta S_{408.7} = 21.6,$
$\Delta H_{298.1} = 10{,}814$; $\Delta F°_{298.1} = 2{,}688.$

Trisilane.—The vapor pressure of trisilane, Si_3H_8, was studied by Stock and Somieski (*392*) (203–326°). They give 156° for the melting point. The results are very concordant. In deriving the following equations $\Delta C_p = -6$ is assumed.

Liquid→**Gas** (Si_3H_8)
$\Delta C_p = -6,$
$\Delta H = 8{,}740 - 6\ T,$
$\Delta F° = 8{,}740 + 13.8\ T \log T - 61.48\ T,$
B. P. = 326.2°; $\Delta H_{326.2} = 6{,}783$; $\Delta S_{326.2} = 20.8,$
$\Delta H_{298.1} = 6{,}951$; $\Delta F°_{298.1} = 592.$

Octachloro-trisilane.—Martin (*240*) (373–486°) has measured the vapor pressure of liquid octachloro-trisilane, Si_3Cl_8. The results are in only fair relative agreement and do not warrant more than a simple treatment.

Liquid→**Gas** (Si_3Cl_8)
$\Delta H = 12{,}340,$
$\Delta F° = 12{,}340 - 25.47\ T,$
B. P. = 484.5°; $\Delta S_{484.5} = 25.5,$
$\Delta F°_{298.1} = 4{,}747.$

Trisilosylnitride.—The vapor pressure of this substance, $(SiH_3)_3N$, was measured carefully by Stock and Somieski (*394*) (193–286°) and the melting point found at 167.5°. ΔC_p has been taken as -8 for the present purpose.

Liquid→**Gas** ($(SiH_3)_3N$)
$\Delta C_p = -8,$
$\Delta H = 9{,}420 - 8\ T,$
$\Delta F° = 9{,}420 + 18.4\ T \log T - 75.41\ T,$
B. P. = 321.8°; $\Delta H_{321.8} = 6{,}846$; $\Delta S_{321.8} = 21.3,$
$\Delta H_{298.1} = 7{,}035$; $\Delta F°_{298.1} = 512.$

Tetrasilane.—Stock and Somieski (*392*) (243–298°) have measured the vapor pressure of liquid tetrasilane, Si_4H_{10}, and have given 179.6° for the melting point. The results above 2 mm pressure are fairly consistent.

Liquid→Gas (Si_4H_{10})

$\Delta C_p = -8,$
$\Delta H = 11{,}870 - 8\ T,$
$\Delta F^\circ = 11{,}870 + 18.4\ T \log T - 79.17\ T,$
B. P. = 373°; $\Delta H_{373} = 8{,}886$; $\Delta S_{373} = 23.8,$
$\Delta H_{298.1} = 9{,}485$; $\Delta F_{298.1} = 1{,}841.$

SILVER

Element.—The vapor pressure of silver has been measured by Greenwood (*131, 132, 133*) (1,933-2,268°), Hansen (*142*) (2,313°), Jones, Langmuir, and Mackay (*191*) (1,143-1,234°), Harteck (*144*) (1,196-1,344°), Ruff and Bergdahl (*316*) (1,933-2,213°), and Von Wartenberg (*425, 427*) (1,458-2,373°). The higher temperature measurements, those of Greenwood, Hansen, Ruff and Bergdahl, and Von Wartenberg, are unreliable, the pressures being too high for the assigned temperatures. This matter was discussed by Harteck (*144*). Moreover, the data of Jones, Langmuir, and Mackay and of Harteck for solid silver disagree. For the present purpose, however, Harteck's figures are adopted. The smoothed value, $\frac{\Delta F^\circ}{T} = -R\ln P = 23.12$, at 1,300° from his results was employed in conjunction with the gas free-energy values computed by Overstreet (*273*) to obtain the values of $\frac{\Delta F^\circ}{T}$ given in table 22. The ΔE°_0 value obtained for this substance is 69,004.

TABLE 22.—*Free energy of vaporization data for silver*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_c - E^\circ_{c,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−36.367	−5.54	−30.83	231.48	200.65
400	−37.822	−6.96	−30.86	172.51	141.65
500	−38.931	−8.01	−30.92	138.01	107.09
600	−39.836	−9.07	−30.77	115.01	84.24
700	−40.602	−9.92	−30.68	98.58	67.90
800	−41.265	−10.68	−30.58	86.26	55.68
900	−41.850	−11.37	−30.48	76.67	46.19
1,000	−42.374	−11.99	−30.38	69.00	38.62
1,100	−42.847	−12.56	−30.29	62.73	32.44
1,200	−43.279	−13.10	−30.18	57.50	27.32
1,300	−43.677	−13.72	−29.96	53.08	23.12
1,400	−44.045	−14.35	−29.69	49.29	19.60
1,500	−44.388	−14.49	−29.47	46.00	16.53
1,600	−44.708	−15.46	−29.25	43.13	13.88
1,700	−45.010	−15.97	−29.04	40.59	11.56
1,800	−45.293	−16.45	−28.84	38.34	9.50

The following equations are based on the free energy of vaporization results in table 22 and the entropies of solid and gaseous silver at 298.1°.

Solid→Gas(Ag)

$C_p(g) = 4.97,$
$C_p(s) = 5.60 + 1.50 \times 10^{-3} T,$
$\Delta C_p = -0.63 - 1.50 \times 10^{-3} T,$
$\Delta H = 69{,}377 - 0.63\ T - 0.75 \times 10^{-3} T^2,$
$\Delta F^\circ = 69{,}377 + 1.45\ T \log T + 0.75 \times 10^{-3} T^2 - 35.86\ T,$
$\Delta H_{298.1} = 69{,}122$; $\Delta F^\circ_{298.1} = 59{,}824$; $S^\circ_{298.1}(g) = 41.33.$

Liquid→Gas(Ag)

$C_p(g)=4.97,$
$C_p(l)=8.20,$
$\Delta C_p=-3.23,$
$\Delta H=68{,}744-3.23\ T,$
$\Delta F^\circ=68{,}744+7.44\ T\log T-52.92\ T,$
B. P. $=2{,}485^\circ$; $\Delta H_{2485}=60{,}717$; $\Delta S_{2485}=24.43,$
$\Delta H_{298.1}=67{,}781$; $\Delta F^\circ_{298.1}=58{,}457.$

Bromide.—Jellinek and Rudat (*184*) (1,273–1,473°) have made three vapor-pressure measurements of liquid silver bromide. These few data are insufficient for free-energy calculations, and so only an approximate vapor-pressure equation is included here.

Liquid→Gas(AgBr)

$$\text{Log } P\ (at.)=-\frac{8{,}130}{T}-2.97\log T+13.727.$$

Chloride.—The vapor pressure of liquid silver chloride was measured by Maier (*232*) (1,127–1,429°) and Von Wartenberg and Bosse (*431*) (1,528–1,715°). The data from these two investigations are in marked disagreement. The Σ-function plots, however, give virtually the same value for ΔH_0 but show a considerable temperature displacement. The results of Von Wartenberg and Bosse, which are adopted for the present purpose, give what appears to be a somewhat better value for the entropy of vaporization than do the results of Maier. However, on account of the discrepancy between the two sets of data, no great assurance can be given as to the accuracy of the equations obtained. Thermal data and the equations for the liquid are used in deriving the relationships for the solid.

Liquid→Gas(AgCl)

$C_p(g)=9.0,$
$C_p(l)=14.05,$
$\Delta C_p=-5.05,$
$\Delta H=51{,}800-5.05\ T,$
$\Delta F^\circ=51{,}800+11.63\ T\log T-66.16\ T,$
B. P. $=1{,}837^\circ$; $\Delta H_{1837}=42{,}523$; $\Delta S_{1837}=23.2,$
$\Delta H_{298.1}=50{,}295$; $\Delta F^\circ_{298.1}=40{,}043.$

Solid→Gas(AgCl)

$C_p(g)=9.0,$
$C_p(s)=9.60+9.29\times10^{-3}T,$
$\Delta C_p=-0.60-9.29\times10^{-3}T,$
$\Delta H=54{,}180-0.60\ T-4.64\times10^{-3}T^2,$
$\Delta F^\circ=54{,}180+1.38\ T\log T+4.64\times10^{-3}T^2-43.47\ T,$
$\Delta H_{298.1}=53{,}589$; $\Delta F^\circ_{298.1}=42{,}652.$

Iodide.—Jellinek and Rudat (*184*) (1,173–1,473°) have measured the vapor pressure of liquid silver iodide at four different temperatures. Three of the results are relatively consistent. Such meager data hardly suffice for obtaining the desired equations. However, the following relationships are included, with the understanding that they are only approximations.

Liquid→Gas(AgI)

$\Delta C_p=-7,$
$\Delta H=46{,}900-7\ T,$
$\Delta F^\circ=46{,}900+16.1\ T\log T-78.69\ T,$
B. P. $=1{,}779^\circ$; $\Delta H_{1779}=34{,}447$; $\Delta S_{1779}=19.4,$
$\Delta H_{298.1}=44{,}813$; $\Delta F^\circ_{298.1}=35{,}319.$

SODIUM

Element.—Several investigators have measured vapor pressures of sodium—Edmondson and Egerton (*93*) (495–571°), Gebhardt (*115*) (653–843°), Haber and Zisch (*139*) (746–838°), Hackspill (*140*) (623–670°), Hansen (*142*) (1,015°), Heycock and Lamplough (*161*) (1,156°), Ladenberg and Thiel (*217*) (495–1,156°), Lewis (*227*) (630–763°), Rodebush and De Vries (*308*) (454–870°), Rodebush and Henry (*311*) (536–670°), Rodebush and Walters (*312*) (924–1,118°), Ruff and Johannsen (*324*) (1,151°), Thiel (*405*) (614–772°), Von Wartenberg (*428*) (713°), and Weiler (*435*) (519–591°). Ladenberg and Thiel have given partial pressures of both the monatomic and diatomic molecules, and Lewis reports the ratio of the number of diatomic molecules to that of the monatomic at several temperatures. The vapor-pressure results, except those of Gebhardt, Hansen, and Von Wartenberg, are in good agreement. Ladenberg and Thiel and Lewis agree in order of magnitude only on the proportion of diatomic molecules present in the equilibrium vapor. A smooth curve representing Ladenberg and Thiel's results shows 1 percent diatomic molecules at 500° and about 8 percent at 800°.

Overstreet (*273*) has computed free-energy values for monatomic sodium gas at temperatures between 298.1 and 3,000°. At 500°, the experimental vapor-pressure results, after allowing for 1 percent of diatomic molecules, give $\frac{\Delta F^\circ}{T} = -R \ ln \ P = 28.06$ for the monatomic gas. This figure, Overstreet's $\frac{F^\circ - E^\circ_0}{T}$ values for the gas, and the corresponding results for the liquid determine ΔE°_0 as 26,020 calories. Table 23 summarizes the free energy of vaporization calculations.

TABLE 23.—*Free energy of vaporization data for sodium*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_l - E^\circ_{l,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−31.756	−6.99	−24.77	87.29	62.52
350	(−32.50)	−7.85	−24.65	74.34	49.69
400	−33.216	−8.72	−24.50	65.05	40.55
500	−34.325	−10.34	−23.98	52.04	28.06
600	−35.230	−11.67	−23.56	43.37	19.81
700	−35.996	−12.80	−23.20	37.17	13.97
800	−36.659	−13.79	−22.87	32.52	9.65
900	−37.244	−14.65	−22.59	28.91	6.32
1000	−37.768	−15.43	−22.34	26.02	3.68

The equations representing these data follow. The entropies of solid and gas at 298.1° were utilized in obtaining the I values, and the ΔH_0 figures were computed from the latter and the Σ-equation values.

Solid→Gas (Na)

$C_p(g) = 4.97,$

$C_p(s) = 5.01 + 5.36 \times 10^{-3} T,$

$\Delta C_p = -0.04 - 5.36 \times 10^{-3} T,$

$\Delta H = 26{,}199 - 0.04\ T - 2.68 \times 10^{-3} T^2,$

$\Delta F^\circ = 26{,}199 + 0.09\ T \log T + 2.68 \times 10^{-3} T^2 - 26.38\ T,$

$\Delta H_{298.1} = 25{,}949;\ \Delta F^\circ_{298.1} = 18{,}639;\ S^\circ_{298.1} = 36.72.$

Liquid→Gas (Na)

$C_p(g) = 4.97,$
$C_p(l) = 7.50,$
$\Delta C_p = -2.53,$
$\Delta H = 26{,}124 - 2.53\ T,$
$\Delta F° = 26{,}124 + 5{,}83\ T \log T - 39.93\ T,$
$P(\text{Na}) = 1$ at. at 1187°; $\Delta H_{1187} = 23{,}121$; $\Delta S_{1187} = 19.48,$
$\Delta H_{298.1} = 25{,}370$; $\Delta F°_{298.1} = 18{,}521.$

The total vapor pressure of liquid sodium is represented by the following equation. For the solid, the vapor-pressure expression corresponding to the given free-energy equation is entirely satisfactory, since the proportion of diatomic gas is negligible at any temperature where the solid exists.

Liquid→Gas (Na+Na$_2$)

$$\log P\ (at.) = -\frac{5.775}{T} - 1.274 \log T + 8.868.$$

Hydroxide.—The vapor pressure of liquid sodium hydroxide was measured by Von Wartenberg and Albrecht (*430*) (1,283–1,675°). The results are erratic and warrant no more than a simple vapor-pressure relationship.

Liquid→Gas (NaOH)

$$\log P\ (at.) = -\frac{7{,}519}{T} + 4.553,$$

B. P. = 1,651°.

Bromide.—The vapor pressure of liquid sodium bromide has been measured by Ruff and Mugdan (*333*) (1,338–1,683°) and Von Wartenberg and Albrecht (*430*) (1,411–1,667°). The data are in fair agreement, those of the latter authors being the more consistent. However, the average I values for the two sets, computed on the assumption that $\Delta C_p = -7$, differ by only 0.03 unit.

Liquid→Gas (NaBr)

$\Delta C_p = -7,$
$\Delta H = 49{,}600 - 7\ T,$
$\Delta F° = 49{,}600 + 16.1\ T \log T - 81.65\ T,$
B. P. = 1,665°; $\Delta H_{1665} = 37{,}945$; $\Delta S_{1665} = 22.8,$
$\Delta H_{298.1} = 47{,}513$; $\Delta F°_{298.1} = 37{,}136.$

Chloride.—Fiock and Rodebush (*106*) (1,249–1,429°), Greiner and Jellinek (*134*) (1,453°), Hackspill and Grandadam (*141*) (1,093–1,396°), Horiba and Baba (*173*) (1,073–1,514°), Kordez and Raaz (*212*) (1,703°), Maier (*232*) (1,020–1,420°), Ruff and Mugdan (*333*) (1,433–1,723°), and Von Wartenberg and Albrecht (*430*) (1,429–1,703°) have measured the vapor pressure of liquid sodium chloride. The results of Fiock and Rodebush, which are by far the most concordant and near the mean of all the determinations, show an extreme deviation in I of only 0.04 unit. Thermal data are available for deriving equations for the solid from those for the liquid.

Liquid→Gas (NaCl)

$C_p(g)=9.0,$
$C_p(l)=15.9,$
$\Delta C_p=-6.9,$
$\Delta H=52{,}800-6.9\ T,$
$\Delta F°=52{,}800+15.9\ T\log T-81.89\ T,$
B. P. = 1,738°; $\Delta H_{1738}=40{,}808$; $\Delta S_{1738}=23.5,$
$\Delta H_{298.1}=50{,}743$; $\Delta F°_{298.1}=40{,}117.$

Solid→Gas (NaCl)

$C_p(g)=9.0,$
$C_p(s)=10.79+4.20\times10^{-3}T,$
$\Delta C_p=-1.79-4.20\times10^{-3}T,$
$\Delta H=56{,}960-1.79\ T-2.10\times10^{-3}T^2,$
$\Delta F°=56{,}960+4.12\ T\log T+2.10\times10^{-3}T^2-52.32\ T,$
$\Delta H_{298.1}=56{,}240$; $\Delta F°_{298.1}=44{,}589$; $S°_{298.1}(g)=46.4.$

Fluoride.—Ruff, Schmidt, and Mugdan (*339*) (1,699–1,974°) and Von Wartenberg and Schulz (*432*) (1,669–1,830°) have made vapor-pressure measurements of liquid sodium fluoride. Taking $\Delta C_p=-7$, the average I values of the two sets of data differ by 0.05 unit.

Liquid→Gas (NaF)

$\Delta C_p=-7,$
$\Delta H=67{,}100-7\ T,$
$\Delta F°=67{,}100+16.1\ T\log T-87.00\ T,$
B. P. = 1,977°; $\Delta H_{1977}=53{,}261$; $\Delta S_{1977}=26.9,$
$\Delta H_{298.1}=65{,}013$; $\Delta F°_{298.1}=53{,}041.$

Iodide.—The vapor pressure of liquid sodium iodide was measured by Greiner and Jellinek (*134*) (1,453°), Ruff and Mugdan (*333*) (1,339–1,568°), and Von Wartenberg and Schulz (*432*) (1,336–1,580°). The data are concordant, the average I values lying in a range of 0.02 unit.

Liquid→Gas (NaI)

$\Delta C_p=-7,$
$\Delta H=49{,}200-7\ T,$
$\Delta F°=49{,}200+16.1\ T\log T-82.68\ T,$
B. P. = 1,577°; $\Delta H_{1577}=38{,}161$; $\Delta S_{1577}=24.2,$
$\Delta H_{298.1}=47{,}113$; $\Delta F°_{298.1}=36{,}429.$

Cyanide.—Ingold (*176*) (1,078–1,626°) has made a very concordant set of vapor-pressure measurements of liquid sodium cyanide, NaCN. If ΔC_p is neglected, the extreme variation in I is 0.23 unit.

Liquid→Gas (NaCN)

$\Delta H=37{,}280,$
$\Delta F°=37{,}280-21.06\ T,$
B. P. = 1,770°; $\Delta S_{1770}=21.1,$
$\Delta F°_{298.1}=31{,}002.$

STRONTIUM

Element.—The vapor pressure of liquid strontium has been studied by Hartmann and Schneider (*146*) (1,199–1,379°) and Ruff and Hartmann (*322*) (1,217–1,411°). The results of the first-mentioned authors are very consistent, giving an extreme variation in I of 0.17 unit, and may be considered as superseding the earlier ones of Ruff and Hartmann.

Liquid→Gas (Sr)

$C_p(g)=4.97,$
$C_p(l)=7.50,$
$\Delta C_p=-2.53,$
$\Delta H=37,800-2.53\ T,$
$\Delta F°=37,800+5.83\ T \log T-41.58\ T,$
B. P. = 1,657°; $\Delta H_{1657}=33,608$; $\Delta S_{1657}=20.3,$
$\Delta H_{298.1}=37,046$; $\Delta F°_{298.1}=29,705.$

Oxide.—Claasen and Veenemans (*64*) have given a vapor-pressure equation for strontium oxide based on measurements between 1,500–1,650°. As this is the only quantitative information available, their equation is included after changing from millimeters to atmospheres.

Solid→Gas (SrO)

$$\log P\ (at.)=-\frac{30,700}{T}+10.24.$$

SULPHUR

Element.—The vapor pressure of sulphur has been measured by Barus (*16*) (479–719°), Bodenstein (*32*) (647–718°), Brown and Muir (*49*) (323°), Gruener (*136*) (322–394°), Matthies (*241*) (483–653°), Preuner and Schupp (*292*) (373–723°), Regnault (*300*) (660–827°), Ruff and Graf (*320*, *321*) (351–485°), and West and Menzies (*439*) (376–816°). Above about 380° the data, except those of Barus and of Matthies, are in good agreement. The figures of West and Menzies are especially concordant.

The sulphur system is complicated by the coexistence of two molecular species in the liquid, S_8 and S_6, commonly designated Sλ and Sμ, respectively, and the presence of the constituents, S_8, S_6, S_2, and at high temperatures, S, in the vapor phase. Preuner and Schupp (*292*) (523–1,123°) have studied equilibria in the gaseous reactions, $3S_8=4S_6$ and $S_6=3S_2$. Lewis and Randall (*226*) have investigated the sulphur data and have obtained equations from which the heat and free energy of formation of the several gaseous species from the solid and liquid forms may be obtained. A recalculation of these quantities by the present author gave results very little different from those of Lewis and Randall; and it seems inadvisable to replace their equations, which are already in use, by slightly different ones which give virtually the same results. For completeness, their equations pertaining to the rhombic variety of crystalline sulphur, which they have adopted as the standard form, are repeated here. The results are expressed per mole of the gas indicated.

Solid (rhombic)→Gas (S_8)

$\Delta H=20,000,$
$\Delta F°=20,000-33.6\ T,$
$\Delta F°_{298.1}=10,000.$

Solid (rhombic)→Gas (S_6)

$\Delta H=22,600,$
$\Delta F°=22,600-35.9\ T,$
$\Delta F°_{298.1}=11,900.$

Solid (rhombic)→Gas (S_2)

$\Delta H=30,580-1.74\ T-0.0042\ T^2,$
$\Delta F°=30,580+4.01\ T \log T+0.0042\ T^2-52.4\ T,$
$\Delta H_{298.1}=29,690$; $\Delta F°_{298.1}=18,280$; $S°_{298.1}(g)=53.3.$

The total vapor pressure of liquid sulphur, the greatest weight being given to the results of West and Menzies, may be represented by the following empirical equation:

Liquid→Gas ($S_8+S_6+S_2$)

$$\log P\ (at.) = -\frac{4{,}940}{T} - 4.08 \times 10^{-3} T + 9.811,$$

B. P. = 717.7°.

Dioxide.—The vapor pressure of sulphur dioxide was measured by Bergstrom (*23*) (183–268°), Blümcke (*31*) (263–318°), Briner and Cardoso (*46*) (345–430°), Burrell and Robertson (*56*) (178–262°), Cardoso and Fiorentino (*59*) (273–431°), Gibbs (*124*) (263°), Henning and Stock (*155*) (211–262°), Maass and Maass (*229*) (274–296°), Mund (*255*) (289–293°), Regnault (*300*) (242–322°), Scheuer (*351*) (91–285°), Steele and Bagster (*377*) (200–237°), and Stock, Henning, and Kusz (*400*) (216–263°). For the liquid seven of the sets of data are in fair agreement, those of Bergstrom, Blümcke, Burrell and Robertson, Gibbs, Henning and Stock, Regnault, and Stock, Henning, and Kusz. Neglecting ΔC_p, the seven corresponding I values lie in a range of 0.17 unit. The equations for the solid depend upon rather scanty data, seven determinations in all, obtained by Bergstrom and Burrell and Robertson.

Liquid→Gas (SO_2)

$\Delta H = 6{,}400,$
$\Delta F° = 6{,}400 - 24.33\ T,$
B. P. = 263.1°; $\Delta S_{298.1} = 24.3,$
$\Delta F°_{298.1} = -853.$

Solid→Gas (SO_2)

$\Delta H = 8{,}460,$
$\Delta F° = 8{,}460 - 34.63\ T,$
$\Delta F°_{298.1} = -1{,}863.$

A heat of fusion of 2,060 calories per gram formula weight at the melting point, 200°, is indicated by these equations.

Trioxide.—Berthoud (*25*) (297–492°), Grau and Roth (*129*) (287–318°), and Smits and Shoenmaker (*371*, *372*) (273–364°) have measured vapor pressures of sulphur trioxide. These results are in fair agreement. The latter authors, however, have contributed by far the most extensive information, having studied the icelike, the low-melting-asbestoslike, the high-melting-asbestoslike, and the equilibrium liquid forms. The three crystalline modifications are distinguished by α, β, and γ in the order named, and ΔC_p has been neglected in the following equations.

Solid (α)→Gas (SO_3)

$\Delta H = 12{,}250,$
$\Delta F° = 12{,}250 - 39.17\ T,$
$\Delta F°_{298.1} = 573.$

Solid (β)→Gas (SO_3)

$\Delta H = 13{,}080,$
$\Delta F° = 13{,}080 - 41.53\ T,$
$\Delta F°_{298.1} = 700.$

Solid (γ)→Gas (SO_3)

$\Delta H = 16{,}500,$
$\Delta F° = 16{,}500 - 50.89\ T,$
$\Delta F°_{298.1} = 1{,}330.$

Liquid→Gas (SO_3)
$\Delta H = 10{,}190,$
$\Delta F = 10{,}190 - 32.07\ T,$
B. P. = 317.9°; $\Delta S_{317.9} = 32.1,$
$\Delta F^{\circ}_{298.1} = 630.$

All three crystalline forms have a solid-liquid-gas triple point, and the α and β forms are unstable with respect to the γ throughout their range of existence. The α form melts at 290° with a heat of fusion of 2,060 calories per gram formula weight of SO_3. The heat of fusion of the β-modification is 2,890 calories at 305.5° and that of the γ-variety is 6,310 calories at 335.3°

Thionyl bromide.—The vapor pressure of liquid thionyl bromide, $SOBr_2$, was measured by Mayes and Partington (*242*) (318–411°), who report 221° for the melting point. If ΔC_p is neglected, the extreme variation in the I values from these data is 0.15 unit.

Liquid→Gas ($SOBr_2$)
$\Delta H = 9{,}920,$
$\Delta F^{\circ} = 9{,}920 - 24.04\ T,$
B. P. = 412.6°; $\Delta S_{412.6} = 24.0,$
$\Delta F^{\circ}_{298.1} = 2{,}754.$

Thionyl chloride.—Arii (*11, 12*) (293–348°) has measured the vapor pressure of liquid thionyl chloride, $SOCl_2$. With ΔC_p taken as zero, the variation in the I values is only 0.03, which shows the high relative accuracy of these measurements.

Liquid→Gas ($SOCl_2$)
$\Delta H = 7{,}600,$
$\Delta F^{\circ} = 7{,}600 - 21.81\ T,$
B. P. = 348.5°; $\Delta S_{348.5} = 21.8,$
$\Delta F^{\circ}_{298.1} = 1{,}096.$

Sulphuryl chloride.—Trautz (*412*) (273–343°) has made very concordant vapor-pressure measurements of liquid sulphuryl chloride, SO_2Cl_2. Neglecting ΔC_p, his results give an extreme variation in I of only 0.07 unit.

Liquid→Gas (SO_2Cl_2)
$\Delta H = 7{,}760,$
$\Delta F^{\circ} = 7{,}760 - 22.67\ T,$
B. P. = 342.3°; $\Delta S_{342.3} = 22.7,$
$\Delta F^{\circ}_{298.1} = 1{,}002.$

Sulphur chloride.—The vapor pressure of liquid sulphur chloride, S_2Cl_2, was measured by Harvey and Schuette (*147*) (273–411°) and Trautz, Rick, and Acker (*416*) (310–410°). The results are in good agreement, the I values having an extreme deviation of 0.10 unit if $\Delta C_p = -14$ is assumed.

Liquid→Gas (S_2Cl_2)
$\Delta C_p = -14,$
$\Delta H = 14{,}470 - 14\ T,$
$\Delta F^{\circ} = 14{,}470 + 32.2\ T \log T - 119.39\ T,$
B. P. = 411°; $\Delta H_{411} = 8{,}716$; $\Delta S_{411} = 21.2,$
$\Delta H_{298.1} = 10{,}297$; $\Delta F^{\circ}_{298.1} = 2{,}631.$

Hexafluoride.—Klemm and Henkel (*206*) (174–208°) have measured the vapor pressure of solid sulphur hexafluoride, SF_6. They report 223° for the melting point. The vapor-pressure measurements are concordant, the extreme variation in I being 0.07 unit if ΔC_p is ignored.

Solid→Gas (SF_6)

$\Delta H = 5{,}600,$
$\Delta F^\circ = 5{,}600 - 26.72\ T,$
S. P. $= 209.6^\circ$; $\Delta S_{209.6} = 26.7.$

TANTALUM

Pentafluoride.—The only tantalum compound whose vapor pressure has been measured is the pentafluoride, TaF_5, studied in the liquid state by Ruff and Schiller (*334*) (456–502°). The data are erratic and have a too small temperature coefficient. However, a simple vapor-pressure equation is included which may be used in rough calculations.

Liquid→Gas (TaF_5)

$\log P\ (at.) = -\frac{1{,}776}{T} + 3.510,$
B. P. $= 503^\circ$.

TELLURIUM

Element.—Doolan and Partington (*88*) (771–944°) have measured the vapor pressure of liquid tellurium at three temperatures by a dynamic method. They assume the gas is entirely Te_2 molecules, but this assumption is not borne out by analogy with selenium and sulphur. The following equation, of doubtful significance, represents the data which they have reported.

Liquid→Gas (Te_2)

$\log P\ (at.) = -\frac{6{,}820}{T} - 3.02 \log T + 14.466$ (?).

Tetrachloride.—The vapor pressure of liquid tellurium tetrachloride was measured by Simons (*364*) (506–666°), who claims the gas is composed of $TeCl_4$ molecules. Assuming that $\Delta C_p = -18$, his results show an extreme variation in I of 0.40 unit. The solid form melts at 487°.

Liquid→Gas ($TeCl_4$)

$\Delta C_p = -18,$
$\Delta H = 28{,}800 - 18\ T,$
$\Delta F^\circ = 28{,}800 + 41.5\ T \log T - 160.46\ T,$
B. P. $= 665^\circ$; $\Delta H_{665} = 16{,}830$; $\Delta S_{665} = 25.3,$
$\Delta H_{298.1} = 23{,}434;$
$\Delta F^\circ_{298.1} = 11{,}578.$

The entropy of vaporization value is high for a substance of this type.

Hexafluoride.—Klemm and Henkel (*206*) (194–241°) and Yost and Clausen (*447*) (194–233°) have studied the vapor pressure of solid tellurium hexafluoride, TeF_6. The melting points obtained in these investigations differ by 0.2°, the average being 235.4°. The vapor-pressure results show considerable disagreement, and those of Yost and Clausen are undoubtedly the better. Neglecting ΔC_p, their individual-point I values lie in a range of 0.20 unit if one determination is discarded.

Solid→Gas (TeF_6)

$\Delta H = 6{,}700,$
$\Delta F^\circ = 6{,}700 - 28.57\ T,$
S. P. $= 234.5^\circ$; $\Delta S_{234.5} = 28.6.$

THALLIUM

Element.—The vapor pressure of liquid thallium was measured by Gibson (*125*) (1,223–1,473°), Leitgebel (*223*) (1,730°), and Von Wartenberg (*425*) (907–1,579°). The data of Gibson and of Von Wartenberg disagree both in magnitude and temperature coefficient. The normal boiling-point temperature measured by Leitgebel appears to be reliable, however, since his determinations of the boiling points of lead, zinc, cadmium, and magnesium are very satisfactory. Consequently, in this case, the *I* values were obtained from the entropies of gas and solid at 298.1° and thermal data. Leitgebel's boiling-point measurement was used in fixing ΔH_0 for the liquid.

Solid (α)→Gas (Tl)

$C_p(g)=4.97,$
$C_p(\alpha)=5.32+3.85\times10^{-3}T,$
$\Delta C_p=-0.35-3.85\times10^{-3}T,$
$\Delta H=43{,}050-0.35\ T-1.92\times10^{-3}T^2,$
$\Delta F^\circ=43{,}050+0.81\ T\log T+1.92\times10^{-3}T^2-31.22\ T,$
$\Delta H_{298.1}=42{,}775;\ \Delta F^\circ_{298.1}=34{,}511;\ S^\circ_{298.1}(g)=43.23.$

Solid (β)→Gas (Tl)

$C_p(g)=4.97,$
$C_p(\beta)=8.12,$
$\Delta C_p=-3.15,$
$\Delta H=43{,}870-3.15\ T,$
$\Delta F^\circ=43{,}870+7.25\ T\log T-49.28\ T,$
$\Delta H_{298.1}=42{,}931;\ \Delta F^\circ_{298.1}=34{,}528.$

Liquid→Gas (Tl)

$C_p(g)=4.97,$
$C_p(l)=7.12,$
$\Delta C_p=-2.15,$
$\Delta H=42{,}530-2.15\ T,$
$\Delta F^\circ=42{,}530+4.95\ T\log T-40.61\ T,$
B. P. = 1,730°; $\Delta H_{1730}=38{,}810;\ \Delta S_{1730}=22.4,$
$\Delta H_{298.1}=41{,}889;\ \Delta F^\circ_{298.1}=34{,}075.$

Bromide.—The vapor pressure of thallous bromide was measured by Volmer (*424*) (603–753°) and Von Wartenberg and Bosse (*431*) (907–1,090°). For the liquid range the average *I* values from the two sets of data differ by only 0.14 unit. The equations for the solid are based on those for the liquid and thermal data since the vapor-pressure measurements of the solid and liquid disagree with the directly measured heat of fusion.

Liquid→Gas (TlBr)

$C_p(g)=9.0,$
$C_p(l)=16.0,$
$\Delta C_p=-7.0,$
$\Delta H=31{,}440-7.0\ T,$
$\Delta F^\circ=31{,}440+16.1\ T\log T-77.70\ T,$
B. P. = 1,092°; $\Delta H_{1365}=23{,}796;\ \Delta S_{1365}=21.8.$

Solid→Gas (TlBr)

$C_p(g)=9.0,$
$C_p(s)=12.53+1.00\times10^{-3}T,$
$\Delta C_p=-3.53-1.00\times10^{-3}T,$
$\Delta H=35{,}160-3.53\ T-0.50\times10^{-3}T^2,$
$\Delta F^\circ=35{,}160+8.13\ T\log T+0.50\times10^{-3}T^2-60.31\ T,$
$\Delta H_{298.1}=34{,}064;\ \Delta F^\circ_{298.1}=23{,}223;\ S^\circ_{298.1}(g)=63.2.$

Chloride.—Volmer (*424*) (593–743°) and Von Wartenberg and Bosse (*431*) (938–1,080°) have measured also the vapor pressure of thallous chloride. Volmer's results for the liquid, which cover only a narrow temperature range, show a somewhat too high temperature coefficient. However, the extrapolation of Von Wartenberg's data to the temperatures of Volmer's results agrees with the latter's figures in magnitude. The vapor-pressure measurements on solid and liquid agree with the directly determined heat of fusion.

Liquid→Gas (TlCl)

$C_p(g)=9.0,$
$C_p(l)=14.2,$
$\Delta C_p=-5.2,$
$\Delta H=30{,}040-5.2\ T,$
$\Delta F^\circ=30{,}040+12.0\ T\log T-64.22\ T,$
B. P. $=1{,}080^\circ$; $\Delta H_{1080}=24{,}424$; $\Delta S_{1080}=22.6,$
$\Delta H_{298.1}=28{,}490$; $\Delta F^\circ_{298.1}=19{,}747.$

Solid→Gas (TlCl)

$C_p(g)=9.0,$
$C_p(s)=12.56+0.88\times10^{-3}T,$
$\Delta C_p=-3.56-0.88\times10^{-3}T.$
$\Delta H=33{,}370-3.56\ T-0.44\times10^{-3}T^2,$
$\Delta F^\circ=33{,}370+8.20\ T\log T+0.44\times10^{-3}T^2-58.47\ T,$
$\Delta H_{298.1}=32{,}270$; $\Delta F^\circ_{298.1}=22{,}027$; $S^\circ_{298.1}(g)=59.2.$

Iodide.—Another substance whose vapor pressure was measured by Volmer (*424*) (603–753°) and Von Wartenberg and Bosse (*431*) (966–1,093°) is thallous iodide. Their results are in fair agreement. The extreme deviations in the *I* values are 0.25 unit for the solid and 0.65 for the liquid.

Liquid→Gas (TlI)

$C_p(g)=9.0,$
$C_p(l)=16.0,$
$\Delta C_p=-7.0,$
$\Delta H=32{,}700-7.0\ T,$
$\Delta F^\circ=32{,}700+16.1\ T\log T-78.77\ T,$
B. P. $=1{,}096^\circ$; $\Delta H_{1096}=25{,}028$; $\Delta S_{1096}=22.8,$
$\Delta H_{298.1}=30{,}613$; $\Delta F^\circ_{298.1}=21{,}095.$

Solid→Gas (TlI)

$C_p(g)=9.0,$
$C_p(s)=12.05+2.73\times10^{-3}T,$
$\Delta C_p=-3.05-2.73\times10^{-3},T,$
$\Delta H=33{,}700-3.05\ T-1.36\times10^{-3}T^2,$
$\Delta F^\circ=33{,}700+7.02\ T\log T+1.36\times10^{-3}T^2-55.23\ T,$
$\Delta H_{298.1}=32{,}670$; $\Delta F^\circ_{298.1}=22{,}535$; $S^\circ_{298.1}(g)=63.9.$

From these equations, the heat of fusion at the melting point, 713°, is 3,125 calories per gram formula weight.

TIN

Element.—The vapor pressure of tin has been measured by Greenwood (*131, 132, 133*) (2,243–2,543°), Harteck (*144*) (1,264–1,434°), Ruff and Bergdahl (*316*) (2,243–2,278°), and Von Wartenberg (*425, 427*) (1,403–2,473°). The measurements of Harteck depend on the assumption that the gas is composed of Sn_4 molecules. The other results, which are for higher temperatures, are directly measured, but the molecular constituents of the gas are unknown. These latter results cannot be reconciled with the assumption of a pure monatomic, diatomic, or tetratomic gas. To test the first two cases, *I* values were obtained from entropy calculations and applied to Σ-function values to obtain ΔH_0 figures. In each case a large trend, about 3,000 calories or

5 percent, in the individual ΔH_0 values resulted for the temperature range covered by the experiments. Harteck's results cannot be brought into even approximate agreement with the higher temperature values by extrapolation, from which fact it is clear that if Harteck had tetratonic gas the others did not. It appears that the reasonable procedure in this instance is to give equations for the formation of Sn_4 gas from liquid tin based on Harteck's measurements and for the higher temperatures to set down only a vapor-pressure relationship of very doubtful accuracy, representing the measurements in the temperature range 2,243 to 2,543°.

Liquid→Gas (Sn_4)

$\Delta H = 68{,}000,$
$\Delta F^\circ = 68{,}000 - 20.32\ T,$
$\Delta F^\circ_{298.1} = 61{,}943.$

Liquid→Gas (Sn_x) (2,243–2,543°)

$$\log P\ (at.) = -\frac{16{,}630}{T} + 6.542.$$

Stannous chloride.—Maier (*232*) (645–914°) has measured the vapor pressure of liquid stannous chloride, $SnCl_2$. Σ-function values were computed on the assumption that $\Delta C_p = -10$. If two determinations are omitted the *I* values lie in a range of 0.27 unit.

Liquid→Gas ($SnCl_2$)

$\Delta C_p = -10,$
$\Delta H = 29{,}700 - 10\ T,$
$\Delta F^\circ = 29{,}700 + 23.0\ T \log T - 101.06\ T,$
B. P. = 896°; $\Delta H_{896} = 20{,}740$; $\Delta S_{896} = 23.2,$
$\Delta H_{298.1} = 26{,}719$; $\Delta F^\circ_{298.1} = 16{,}539.$

Stannic chloride.—The vapor pressure of stannic chloride was measured by Mündel (*256*) (220–243°), Wertheimer (*438*) (303–592°), and Young (*449, 452*) (263–594°). The three sets of data for the liquid are in good agreement.

Liquid→Gas ($SnCl_4$)

$C_p(g) = 24.5,$
$C_p(l) = 38.4,$
$\Delta C_p = -13.9,$
$\Delta H = 13{,}690 - 13.9\ T,$
$\Delta F^\circ = 13{,}690 + 32.0\ T \log T - 118.22\ T,$
B. P. = 386°; $\Delta H_{386} = 8{,}325$; $\Delta S_{386} = 21.6,$
$\Delta H_{298.1} = 9{,}546$; $\Delta F^\circ_{298.1} = 2{,}053.$

Hydride.—Liquid stannic hydride, SnH_4, was studied by Paneth, Haken, and Rabinowitsch (*275*) (125–224°). The melting point is given as 123.3°. Their results show an extreme variation in *I* of 0.35 unit when Σ-function values are computed with ΔC_p neglected.

Liquid→Gas (SnH_4)

$\Delta H = 4{,}420,$
$\Delta F^\circ = 4{,}420 - 20.02\ T,$
B. P. = 220.8°; $\Delta S_{220.8} = 20.0,$
$\Delta F^\circ_{298.1} = -1{,}548.$

Tetramethyl.—The vapor pressure of tin tetramethyl, $Sn(CH_3)_4$, was investigated by Bullard and Haussmann (*52*) (273–354°) and Tanaka and Nagai (*404*) (298–308°). Assuming that $\Delta C_p = -10$, the results give an extreme deviation in *I* values of only 0.06 unit.

Liquid→Gas ($Sn(CH_3)_4$)

$\Delta C_p = -10,$
$\Delta H = 10{,}830 - 10\ T,$
$\Delta F^\circ = 10{,}830 + 23.0\ T \log T - 89.37\ T,$
$\text{B. P.} = 351.4^\circ;\ \Delta H_{351.4} = 7{,}316;\ \Delta S_{351.4} = 20.8,$
$\Delta H_{298.1} = 7{,}849;\ \Delta F^\circ_{298.1} = 1{,}154.$

Trimethyl-ethyl.—The vapor pressure of trimethyl-ethyl tin, $Sn(CH_3)_3 \cdot C_2H_5$, was measured by Bullard and Haussmann (*52*) (273–384°) with the same high relative accuracy as for the previous compound, the extreme variation in I being 0.22 if $\Delta C_p = -12$ is assumed.

Liquid→Gas ($Sn(CH_3)_3 \cdot C_2H_5$)

$\Delta C_p = -12,$
$\Delta H = 12{,}630 - 12\ T,$
$\Delta F^\circ = 12{,}630 + 27.6\ T \log T - 104.36\ T,$
$\text{B. P.} = 381.4^\circ;\ \Delta H_{381.4} = 8{,}053;\ \Delta S_{381.4} = 21.1,$
$\Delta H_{298.1} = 9{,}053;\ \Delta F^\circ_{298.1} = 1{,}878.$

Trimethyl-propyl.—Another substance whose vapor pressure was measured by Bullard and Haussmann (*52*) (286–405°) is trimethyl-propyl tin, $Sn(CH_3)_3 \cdot C_3H_7$. In this case, if $\Delta C_p = -14$ is assumed, the individual I values lie in a range of 0.10 unit.

Liquid→Gas ($Sn(CH_3)_3 \cdot C_3H_7$)

$\Delta C_p = -14,$
$\Delta H = 14{,}190 - 14\ T,$
$\Delta F^\circ = 14{,}190 + 32.2\ T \log T - 119.04\ T,$
$\text{B. P.} = 404.2^\circ;\ \Delta H_{404.2} = 8{,}531;\ \Delta S_{404.2} = 21.1,$
$\Delta H_{298.1} = 10{,}017;\ \Delta F^\circ_{298.1} = 2{,}455.$

TITANIUM

Tetrachloride.—Arii (*10, 12*) (293–408°) has measured the vapor pressure of liquid titanium tetrachloride. His results are quite consistent, showing a spread of only 0.19 unit in the individual point I values.

Liquid→Gas ($TiCl_4$)

$C_p(g) = 24.5,$
$C_p(l) = 36.0,$
$\Delta C_p = -11.5$
$\Delta H = 13{,}050 - 11.5\ T$
$\Delta F^\circ = 13{,}050 + 26.5\ T \log T - 101.10\ T$
$\text{B. P.} = 409^\circ;\ \Delta H_{409} = 8{,}346;\ \Delta S_{409} = 20.4$
$\Delta H_{298.1} = 9{,}622;\ \Delta F^\circ_{298.1} = 2{,}459.$

TUNGSTEN

Element.—Jones, Langmuir, and Mackay (*191*) (1,200–6,970°), Langmuir (*219*) (2,000–5,110°), and Zwikker (*454*) (1,500–3,400°) have given vapor-pressure results for tungsten obtained from rates of evaporation of filaments. The values given by Jones, Langmuir, and Mackay and Zwikker are in fair agreement between 2,400 and 3,400°, and the following equations are obtained for the solid.

Solid→Gas (W)

$C_p(g) = 4.97,$
$C_p(s) = 5.65 + 0.866 \times 10^{-3} T,$
$\Delta C_p = -0.68 - 0.866 \times 10^{-3} T,$
$\Delta H = 202{,}900 - 0.68\ T - 0.433 \times 10^{-3} T^2,$
$\Delta F^\circ = 202{,}900 + 1.57\ T \log T + 0.433 \times 10^{-3} T^2 - 42.23\ T,$
$\Delta H_{298.1} = 202{,}659;\ \Delta F^\circ_{298.1} = 191{,}507;\ S^\circ_{298.1}(g) = 45.4.$

Approximate relationships for the liquid may be obtained from those for the solid and an assumed value for the entropy of fusion, 2.3 units, at the melting point, 3,660°.

Liquid→Gas (W)

$\Delta C_p = -4.0,$
$\Delta H = 200{,}830 - 4.0\,T,$
$\Delta F^\circ = 200{,}830 + 9.2\,T \log T - 67.27\,T,$
B. P. $= 6{,}203°$; $\Delta H_{6203} = 176{,}018$; $\Delta S_{6203} = 28.4,$
$\Delta H_{298.1} = 199{,}638$; $\Delta F^\circ_{298.1} = 187{,}563.$

Hexafluoride.—Ruff and Ascher (*315*) (218–288°) have measured the vapor pressures of solid and liquid tungsten hexafluoride, WF_6. The data are quite concordant. In obtaining the following equations, −12 and −26 have been assumed for ΔC_p for the vaporization of solid and liquid, respectively.

Solid→Gas (WF_6)

$\Delta C_p = -12,$
$\Delta H = 11{,}880 - 12\,T,$
$\Delta F^\circ = 11{,}880 + 27.6\,T \log T - 109.32\,T,$
$\Delta H_{298.1} = 8{,}303$; $\Delta F^\circ_{298.1} = -350.$

Liquid→Gas (WF_6)

$\Delta C_p = -26,$
$\Delta H = 13{,}900 - 26\,T,$
$\Delta F^\circ = 13{,}900 + 59.9\,T \log T - 195.40\,T,$
B. P. $= 290.4°$; $\Delta H_{290.4} = 6{,}350$; $\Delta S_{290.4} = 21.9,$
$\Delta H_{298.1} = 6{,}149$; $\Delta F^\circ_{298.1} = -166.$

These equations indicate a heat of fusion value, 1,800 calories per gram formula weight at the melting point, 272.7°.

URANIUM

Hexafluoride.—Ruff and Heinzelmann (*323*) (310–330°) have made a few vapor-pressure determinations of solid uranium fluoride, UF_6. The following equations can be considered only as rough approximations, since the data are not particularly consistent and only a small temperature range was studied.

Solid→Gas (UF_6)

$\Delta C_p = -16,$
$\Delta H = 15{,}250 - 16\,T,$
$\Delta F^\circ = 15{,}250 + 36.8\,T \log T - 139.00\,T,$
S. P. $= 328.8°$; $\Delta H_{328.8} = 9{,}989$; $\Delta S_{328.8} = 30.4,$
$\Delta H_{298.1} = 10{,}480$; $\Delta F^\circ_{298.1} = 958.$

XENON

Element.—The vapor pressure of xenon was measured by Allen and Moore (*3*) (156–166°), Heuse and Otto (*160*) (160–166°), Patterson, Cripps, and Whytlow-Gray (*279*) (253–283°), Peters and Weil (*283*) (95–164°), and Ramsay and Travers (*296*) (183–288°). Allen and Moore report 161.6° for the melting point. The following equations are in good agreement with the experimental data.

Solid→Gas (Xe)

$\Delta H = 3{,}850,$
$\Delta F^\circ = 3{,}850 - 23.42\,T.$

Liquid→Gas (Xe)

$\Delta H = 3{,}110,$
$\Delta F^\circ = 3{,}110 - 18.84\,T,$
B. P. $= 165.1°$; $\Delta S_{165.1} = 18.8.$

The heat of fusion is 740 calories per gram formula weight at 161.6°.

ZINC

Element.—Several investigators have measured the vapor pressure of zinc—Barus (*16*) (948–1,206°), Braune (*38*) (767–995°), Burmeister and Jellinek (*54*) (973°), Egerton (*95*) (573–606°), Greenwood (*132*, *133*) (1,393–1,783°), Hansen (*142*) (1,193°), Heycock and Lamplough (*161*) (1,179°), Jenkins (*186*) (898–1,255°), Leitgebel (*223*) (1,180°), Rodebush and Dixon (*309*) (857–960°), and Ruff and Bergdahl (*316*) (926–1,198°). For the liquid range, the results of Braune, Heycock, and Lamplough, Leitgebel, and Rodebush and Dixon are in good agreement, while those of Jenkins are not far different. The data of Barus, Burmeister and Jellinek, and Ruff and Bergdahl are considered erratic. Greenwood's results are for pressures above 6 atmospheres and agree reasonably well with the lower-pressure data. Egerton has reported a very consistent set of measurements for the solid.

Overstreet (*273*) has computed free-energy values for zinc gas between 298.1 and 3,000°. His figures and the smoothed value, $\frac{\Delta F^\circ}{T} = -R \ln p = 4.245$ at 1,000°, taken from the experimental results for the liquid, are used in computing the $\frac{\Delta F^\circ}{T}$ values given in table 24. The value for ΔE°_0 is 31,060 calories.

TABLE 24.—*Free energy of vaporization data for zinc*

T	$\frac{F^\circ - E^\circ_0}{T}$	$\frac{F^\circ_l - E^\circ_{l,0}}{T}$	$\frac{\Delta F^\circ - \Delta E^\circ_0}{T}$	$\frac{\Delta E^\circ_0}{T}$	$\frac{\Delta F^\circ}{T}$
298.1	−33.493	−5.43	−28.06	104.19	76.13
400	−34.953	−6.82	−28.13	77.65	49.52
500	−36.062	−7.96	−28.10	62.12	34.02
600	−36.967	−8.94	−28.03	51.77	23.74
700	−37.733	−9.82	−27.91	44.37	16.46
800	−38.396	−10.90	−27.50	38.82	11.32
900	−38.981	−11.84	−27.14	34.51	7.37
1,000	−39.505	−12.68	−26.82	31.06	4.24
1,100	−39.978	−13.43	−26.55	28.24	1.69
1,200	−40.410	−14.14	−26.27	25.88	−.39
1,300	−40.808	−14.79	−26.02	23.89	−2.13
1,400	−41.176	−15.38	−25.80	22.19	−3.61
1,500	−41.519	−15.94	−25.58	20.71	−4.87
1,600	−41.839	−16.47	−25.37	19.41	−5.96
1,700	−42.141	−16.96	−25.18	18.27	−6.91
1,800	−42.424	−17.42	−25.00	17.26	−7.74

In obtaining the equations, the I value for the solid was found from the entropies of solid and gas at 298.1° and the ΔH_0 from the I value and Σ-function results. The individual ΔH_0 values for the solid show an extreme difference of only 7 calories. The ΔH_0 for the liquid was obtained from that of the solid and thermal data. The I values, computed from the Σ-function results and ΔH_0, show an extreme variation of only 0.01 unit for the liquid range considered in table 24.

Solid→Gas (Zn)

$C_p(g) = 4.97,$
$C_p(s) = 5.25 + 2.70 \times 10^{-3}T,$
$\Delta C_p = -0.28 - 2.70 \times 10^{-3}T,$
$\Delta H = 31{,}392 - 0.28\ T - 1.35 \times 10^{-3}T^2,$
$\Delta F^\circ = 31{,}392 + 0.64\ T \log T + 1.35 \times 10^{-3}T^2 - 31.17\ T,$
$\Delta H_{298.1} = 31{,}189;\ \Delta F^\circ_{298.1} = 22{,}692;\ S^\circ_{298.1}(g) = 38.46.$

Liquid→Gas (Zn)

$C_p(g)=4.97,$
$C_p(l)=7.59+0.55\times10^{-3}T,$
$\Delta C_p= -2.62-0.55\times10^{-3}T,$
$\Delta H=30{,}902-2.62\ T-0.275\times10^{-3}T^2,$
$\Delta F^\circ=30{,}902+6.03\ T\log T+0.275\times10^{-3}T^2-45.03\ T,$
B. P. $=1{,}180^\circ$; $\Delta H_{1180}=27{,}427$; $\Delta S_{1180}=23.24,$
$\Delta H_{298.1}=30{,}097$; $\Delta F^\circ_{298.1}=21{,}951.$

The corresponding vapor-pressure equations for both solid and liquid fit the reliable experimental data virtually exactly. In fact, of all the metals considered here, zinc is outstanding in the exactness of the coherence of the available data—specific heats of solid and liquid, heat of fusion, vapor pressures of solid and liquid, theoretical gas entropy, and spectroscopically determined free-energy values for the gas.

Chloride.—Jellinek and Koop (*183*) (873–973°) and Maier (*232*) (727–1,013°) have measured the vapor pressure of liquid zinc chloride. The results are not in agreement, and the more extensive investigation of Maier is considered the more reliable. Assuming that $\Delta C_p= -10$, the extreme variation in I from his results is 0.51 unit.

Liquid→Gas ($ZnCl_2$)

$\Delta C_p= -10,$
$\Delta H=38{,}760-10\ T,$
$\Delta F^\circ=38{,}760+23.0\ T\log T-107.63\ T,$
B. P. $=1{,}005^\circ$; $\Delta H_{1005}=28{,}710$; $\Delta S_{1005}=28.6,$
$\Delta H_{298.1}=35{,}779$; $\Delta F^\circ_{298.1}=23{,}640.$

Zinc ethyl.—Hein and Schramm (*148*) (299–358°) have made very consistent vapor-pressure measurements of liquid zinc ethyl, $Zn(C_2H_5)_2$. Neglecting ΔC_p, the I values lie in a range of 0.11 unit.

Liquid→Gas ($Zn(C_2H_5)_2$)

$\Delta H=8{,}960,$
$\Delta F^\circ=8{,}960-22.92\ T,$
B. P. $=391^\circ$; $\Delta S_{391}=22.9,$
$\Delta F^\circ_{298.1}=2{,}128.$

ZIRCONIUM

Bromide.—Rahlfs and Fischer (*294*) (538–633°) have studied the vapor pressure of solid zirconium bromide, $ZrBr_4$. They report that the gas contains only normal molecules and find 723° for the melting point. This substance, however, sublimes at 1 atmosphere pressure at 630°. The extreme deviation in the I values is 0.30 unit.

Solid→Gas ($ZrBr_4$)

$C_p(g)=22,$
$C_p(s)=25.5+15.1\times10^{-3}T,$
$\Delta C_p= -3.5-15.1\times10^{-3}T,$
$\Delta H=31{,}000-3.5T-7.55\times10^{-3}T^2,$
$\Delta F^\circ=31{,}000+8.06\ T\log T+7.55\times10^{-3}T^2-76.53\ T,$
S. P. $=630^\circ$; $\Delta H_{630}=25{,}798$; $\Delta S_{630}=41.0,$
$\Delta H_{298.1}=29{,}286$; $\Delta F^\circ_{298.1}=14{,}802.$

Chloride.—Rahlfs and Fischer (*294*) (535–607°) also studied solid zirconium chloride. Again normal molecules are reported, and the melting point is given as 710°. The I values lie in a range of 0.36 unit.

Solid→Gas ($ZrCl_4$)

$C_p(g)=22,$
$C_p(s)=25.2+16.3\times10^{-3}T,$
$\Delta C_p=-3.2-16.3\times10^{-3}T,$
$\Delta H=30{,}200-3.2\ T-8.15\times10^{-3}T^2,$
$\Delta F°=30{,}200+7.37\ T\log T+8.15\times10^{-3}T^2-75.39\ T,$
S. P.$=604°$; $\Delta H_{604}=25{,}294$; $\Delta S_{604}=41.9,$
$\Delta H_{298.1}=28{,}522$; $\Delta F°_{298.1}=13{,}886.$

Iodide.—Another substance whose vapor pressure was measured by Rahlfs and Fischer (*294*) (558–671°) is zirconium iodide. Normal molecules were found, and the melting point is given as 772°. The *I* values vary over a range of 0.12 unit if two determinations are discarded.

Solid→Gas (ZrI_4)

$C_p(g)=22,$
$C_p(s)=26.3+12.3\times10^{-3}T,$
$\Delta C_p=-4.3-12.3\times10^{-3}T,$
$\Delta H=35{,}100-4.3\ T-6.15\times10^{-3}T^2,$
$\Delta F°=35{,}100+9.90\ T\log T+6.15\times10^{-3}T^2-82.39\ T,$
S. P.$=704°$; $\Delta H_{704}=29{,}025$; $\Delta S_{704}=41.2,$
$\Delta H_{298.1}=33{,}271$; $\Delta F°_{298.1}=18{,}389.$

VAPOR-PRESSURE TABLE

In the following table vapor-pressure results are summarized for the substances discussed in the previous section of this bulletin. For each substance, where it is possible, the temperatures at which the vapor pressures are 0.0001, 0.001, 0.01, 0.1, 0.25, 0.5, and 1.0 atmosphere, respectively, are tabulated. These values were read from smoothed curves obtained from the free energy of vaporization and vapor-pressure equations previously derived. The letters *s*, *l*, α, β, γ, etc., have the same significance as in the last section.

Substance	Pressure, atmosphere						
	0.0001	0.001	0.01	0.1	0.25	0.5	1.0
Aluminum:							
Al (*l*)	1,383	1,536	1,734	1,986	2,110	2,213	2,329
Al_2O_3	(*s*)	(*l*)2,395	2,624	2,901	3,030	3,137	3,250
Al_2Br_6	326.2	351.0(*s*)	(*l*)385.3	441.0	470.9	497.5	529.5
Al_2Cl_6 (*s*)	349.9	369.9	393.6	421.2	432.4	442.1	453.3
Al_2I_6	417.4	446.9(*s*)	(*l*)490.4	557.5	592.4	623.0	658.6
Antimony:							
Sb (*l*)	1,032	1,145	1,286	1,469	1,566	1,632	1,713
Sb_4O_6	778	841(α)	(β)920(β)	(*l*)1,183	1,346	1,501	1,698
$SbCl_3$	292.0	318.7(*s*)	(*l*)352.3	408.3	437.0	462.9	492.1
$SbCl_5$	(*s*)	(*l*)291.6	329.2	379.6	Decomposes		
Argon:							
A	47.2	53.0	61.0	71.6	77.2	81.8(*s*)	(*l*)87.3
Arsenic:							
As (*s*)	561	636	701	772	820	851	883
As_4O_6	450	482(α)	(β)526(β)	(*l*)592.3	640.9	682.0	730.3
$AsCl_3$	----------	(*s*)	(*l*)276.0	322.6	347.3	369.2	396.1
AsF_3	140.3	153.0	168.1	186.5(*s*)	(*l*)196.5	207.9	220.3
Barium:							
Ba	----------	(*s*)	(*l*)1,394	1,539	1,668	1,782	1,911
BaO	1,973	2,192(*s*)	(*l*)	----------	----------	----------	----------
Beryllium:							
$BeBr_2$ (*s*)	513	556.5	606	670	699	722.5	747
$BeCl_2$	514.5	558	611.5	678.5(*s*)	(*l*)707	733	760
BeI_2 (*s*)	504	550.5	606.5	674	706.5	733	760
Bismuth:							
Bi (*l*)	1,167	1,281	1,394	1,537	1,598	1,640	1,698
$BiBr_3$	----------	(*s*)	(*l*)546	622	663	696	732.9
$BiCl_3$	----------	(*s*)	(*l*)529.5	605	643	676.5	714

Substance	Pressure, atmosphere						
	0.0001	0.001	0.01	0.1	0.25	0.5	1.0
Boron:							
BBr_3	(s)	(l)228.6	258.5	300.3	322.3	342.0	364.1
BCl_3	(s)	(l)179.1	202.5	235.2	252.9	268.3	285.6
BF_3	106.5	116.3	129.8(s)	(l)147.1	156.2	163.6	172.2
B_2H_6	(s)	(l)108.1	124.7	147.8	159.3	169.4	180.7
B_4H_{10} (l)	159.1	179.3	206.1	239.8	257.6	272.8	289
B_5H_9	----------	(s)	(l)238.0	277.0	296.1	312.2	331
B_5H_{11}	----------	(l)219.6	249.0	287.5	306.5	322.8	339.9
$B_{10}H_{14}$	307.3	331.3	356.4(s)	(l)408.6	434.6	Decomposes	
B_2H_5Br	(s)	(l)177.0	203.0	239.0	256.1	271.7	289.2
$B_3N_3H_6$	----------	(s)	(l)233.5	271.5	290.1	306.0	328.5
Bromine:							
Br_2	202.8	221.8	244.7(s)	(l)278.8	296.6	312.4	331.1
BrF_5	182.0	200.8(s)	(l)227.2	262.8	281.4	297.2	313.5
Cadmium:							
Cd	580(s)	(l)657	744	867	927.5	981	1,038
CdO (s)	1,143	1,257	1,403	1,588	1,677	1,752	1,832
$CdCl_2$	----------	(s)	(l)914	1,050	1,117	1,177	1,240
CdI_2	610(s)	(l)678	771	896	958	1,011	1,069
Calcium:							
Ca	961	1,075(s)	(l)1,231	1,448	1,554	1,653	1,760
CaO	2,518	2,771(s)	(l)	----------	----------	----------	----------
Carbon:							
C (s)	3,530	3,820	4,170	4,590	4,780	4,940	5,100
CO	45.25	50.40	56.95(S_{II})	(S_I)65.95(S_I)	(l)71.25	76.15	81.61
CO_2 (s)	128.2	136.3	151.3	170.1	179.1	186.6	194.6
COS	(s)	(l)137.6	157.7	184.8	198.1	208.8	220.9
CS_2 (l)	173.3	196.3	224.3	263.0	282.0	299.2	319.6
C_3S_2	(s)	(l)282.7	322.2	374.8	Polymerizes		
CSSe (l)	200.1	222.5	253.0	294.3	316.2	336.1	358.5
$COCl_2$ (l)	151.4	171.2	196.7	231.7	249.1	264.6	281.1
CH_4	59.0	66.6	76.4	89.8(S_I)	(l)97.2	103.9	111.7
CCl_4	----------	----------	(s)	(l)289.7	310.6	328.7	350.2
CF_4	----------	(s)	(l)101.7	119.6	128.8	136.7	145.2
$(CN)_2$	157.7	173.6	193.3	218.2	230.3	240.0(s)	(l)252
CNBr	212.6	234.4	259.6	291.1	305.6	317.7(s)	(l)
CNCl	175.6	193.8	216.1	244.4	257.8(s)	(l)269.3	286
CNF (s)	122.7	135.7	152.1	173.0	182.8	191.1	200.3
CNI (s)	268.6	294.5	326.0	365.0	382.7	397.9	414
Cesium:							
Cs (l)	476	544	634	762	830	893	963
CsBr	(s)	(l)1,007	1,139	1,318	1,408	1,488	1,573
CsCl	(s)	(l)1,003	1,137	1,315	1,406	1,484	1,573
CsF	(s)	(l)970	1,099	1,273	1,360	1,438	1,524
CsI (l)	895	997	1,128	1,302	1,392	1,468	1,553
Chlorine:							
Cl_2	138.6	153.0	169.4(s)	(l)196.8	211.2	224.1	238.4
Cl_2O	(s)	(l)171.9	196.5	228.9	245.2	259.3	275.1
ClO_2	----------	(s)	(l)208.1	240.5	255.8	268.8	284.0
Cl_2O_7 (l)	200.0	224.3	255.2	295.8	316.1	333.5	351.7
ClF	----------	(s)	(l)122.0	149.5	158.1	165.0	172.4
ClF_3	----------	(s)	(l)197.5	232.9	251.0	266.7	284.4
Chromium:							
Cr	1,693(s)	(l)1,867	2,086	2,370	2,507	2,624	2,755
CrO_2Cl_2 (l)	227.6	251.2	282.1	325.2	346.7	368.2	390.0
Cobalt:							
$CoCl_2$	Melting point unknown			(l)1,093	1,173	1,243	1,323
Columbium:							
CbF_5	----------	(s)	(l)363	413	443	469	498
Copper:							
Cu (l)	1,685	1,875	2,117	2,435	2,588	2,723	2,868
Cu_2Br_2	(s)	(l)831	968	1,186	1,316	1,450	1,628
Cu_2Cl_2 (l)	708	808	951	1,157	1,340	1,502	1,763
CuI	----------	(s)	(l)908	1,128	1,281	1,419	1,609
Fluorine:							
F_2	----------	(s)	(l)57.65	68.70	74.28	79.21	84.98
F_2O (l)	68.0	77.1	88.9	104.9	113.3	120.5	128.3
Gallium:							
Ga (l)	1,451	1,603	1,793	2,034	2,139	2,235	2,344
Germanium:							
GeH_4	----------	(s)	(l)125.2	149.0	160.9	172.0	184.0
$GeBr_4$	----------	(s)	(l)334	378	408	432	462
$GeCl_4$	(s)	(l)228	254	294	316	335	357
$GeHCl_3$ (l)	208	229	256	294	313	330	348
$Ge(CH_3)_4$	(s)	(l)197	224	261.5	280.5	297.5	317
Ge_2H_6	(s)	(l)181.5	209	247	267	285	304.5
Ge_3H_8 (l)	206.7	232.5	267.0	313.5	337.9	360.0	383.7
Gold:							
Au (l)	1,896	2,112	2,388	2,742	2,919	3,080	3,239
Helium:							
He (l)	0.95	1.18	1.66	2.58	3.08	3.56	4.22

Substance	Pressure, atmosphere						
	0.0001	0.001	0.01	0.1	0.25	0.5	1.0
Hydrogen:							
H_2 (ordinary)	7.84	9.33	11.41(*s*)	(*l*)14.60	16.49	18.26	20.45
H_2 (para)			(*s*)	(*l*)14.47	16.34	18.08	20.28
H_2O	231.0	252.9(*s*)	(*l*)280.4	319.2	338.7	355.2	373.1
H^2H^2O		(*s*)	(*l*)283.2	321.5	340.6	356.8	374.5
H_2O_2	(*s*)	(*l*)284.5	318.5	365	388	408.5	431
H_2S	(s_{II})	(s_I)136.7	154.1	177.4(s_I)	(*l*)188.8	199.9	212.8
H_2S_2 (*l*)	205	227	254	290	307	321	337
HBr		131.5	148.8	171.9	183.4(s_I)	(*l*)193.0	206.4
HCl	107.1	119.3	134.9	155.6(s_I)	(*l*)166.6	176.6	188.1
HF		(*s*)	(*l*)203.5	239.8	258.4	274.8	292.6
HI	130.4	146.4	167.6	196.9	211.4(s_I)	(*l*)223.6	237.8
HCN	181.2	199.6	222.3	251.1(*s*)	(*l*)266.0	281.7	298.8
H_2Se					(*s*)	(*l*)217.7	231.8
H_2Te	157.3	174.2	195.2	222.6(*s*)	(*l*)239.3	254.6	270.9
Iodine:							
I_2	281.7	308.2	340.8	382.9(*s*)	(*l*)408	430	456
IF_7 (*s*)	165.2	183.5	207.0	237.2	251.4	263.8	277.1
Iron:							
Fe (*l*)	1,837	2,033	2,277	2,569	2,730	2,865	3,008
$FeCl_2$				(*l*)1,094	1,166	1,229	1,299
Fe_2Cl_6	445	462	503	540	556	570(*s*)	(*l*)592
$Fe(CO)_5$		(*s*)	(*l*)273	317	339.5	357.5	378
Krypton:							
Kr	64.7	73.0	84.2	99.2	108.8	113.5(*s*)	(*l*)121
Lead:							
Pb (*l*)	1,088	1,226	1,408	1,657	1,784	1,895	2,017
PbO	1,095(*s*)	(*l*)1,201	1,339	1,514	1,599	1,670	1,745
PbS	1,023	1,113	1,224	1,363(*s*)	(*l*)1,430	1,489	1,554
$PbBr_2$	709(*s*)	(*l*)776	870	998	1,066	1,125	1,187
$PbCl_2$	739(*s*)	(*l*)810	906	1,037	1,102	1,161	1,227
PbF_2		(*s*)	(*l*)1,159	1,329	1,413	1,487	1,566
PbI_2 (*l*)	674	743	832	956	1,019	1,076	1,145
Lithium:							
Li (*l*)	865	980	1,131	1,337	1,444	1,539	1,645
LiBr (*l*)	901	1,006	1,141	1,321	1,414	1,494	1,583
LiCl (*l*)	936	1,042	1,184	1,375	1,470	1,556	1,655
LiF (*l*)	1,181	1,304	1,462	1,669	1,770	1,857	1,954
LiI (*l*)	894	985	1,099	1,245	1,318	1,379	1,444
Magnesium:							
Mg	789	881(*s*)	(*l*)998	1,159	1,236	1,303	1,380
$MgCl_2$	(*s*)	(*l*)1,036	1,180	1,385	1,490	1,583	1,691
Manganese:							
Mn	1,388(γ)	(*l*)1,542	1,749	2,023	2,165	2,292	2,424
$MnCl_2$		(*s*)	(*l*)1,034	1,206	1,296	1,376	1,463
Mercury:							
Hg (*l*)	351.0	393.9	449.2	524.4	563.0	594.6	630
$HgBr_2$	371	405	444	501(*s*)	(*l*)533	561	592
$HgCl_2$	369	404	447	501	527	546(*s*)	(*l*)577
HgI_2	389(α)	(β)425	470(β)	(*l*)527	561	594	627
Molybdenum:							
Mo (*l*)	3,000	3,330	3,750	4,300	4,560	4,810	5,077
MoO_3	934	999	1,074(*s*)	1,207	1,283	1,350	1,424
MoF_6	183.5	203.5	229	260.5	276	289(*s*)	(*l*)309
Neon:							
Ne	13.79	15.66	18.17	21.64	23.43(*s*)	(*l*)25.01	27.15
Nickel:							
Ni (*l*)	1,859	2,055	2,298	2,594	2,730	2,868	3,006
$NiCl_2$ (*s*)	862	934	1,021	1,126	1,175	1,216	1,260
$Ni(CO)_4$			(*s*)	(*l*)261.6	280.8	297.2	315.6
Nitrogen:							
N_2	41.20	46.31	53.05	62.20(s_I)	(*l*)67.27	71.90	77.32
N_2O	116.6	128.1	142.4	160.3	169.0	176.2(*s*)	(*l*)184.6
NO	77.3	84.7	93.8	106.3(*s*)	(*l*)110.6	115.7	121.4
N_2O_4	200	215.5	234	255.5(*s*)	(*l*)267.1	280.0	294.1
N_2O_5	217.4	234.2	253.8	277.3	288.0	296.4(*s*)	(*l*)305.5
NOCl			(*s*)	(*l*)222.6	237.9	251.7	266.7
NH_3	147.3	161.4	179.0(*s*)	(*l*)202.0	215.1	226.8	239.7
NF_3		(*s*)	(*l*)100.2	118.3	127.2	135.4	144.1
Osmium:							
OsO_4 (yellow)	250	273	300.5(*s*)	(*l*)337.5	360.5	380.5	403
OsO_4 (white)	240	264	294.5(*s*)	(*l*)337.5	360.5	380.5	403
OsF_8						(*s*)	(*l*)320.5
Oxygen:							
O_2	47.52	53.38(s_I)	(*l*)61.70	72.50	78.86	84.29	90.13
O_3 (*l*)	80.0	91.4	107.0	128.9	139.9	150.6	162.0
Phosphorus:							
P (white)	303.5(*s*)	(*l*)344.5	394	460.5	498	531.5	553
P (violet)	462	504	554	614.5	642.5	673	690
P (black)	518.5	558.5	605	660	685.5	706.5	728
P_4O_6 (*l*)	280	301	330.5	372.5	400	425	446
P_4O_{10} (stable)	604	652	708	774	804	828(*s*)	(*l*)866

Substance	Pressure, atmosphere						
	0.0001	0.001	0.01	0.1	0.25	0.5	1.0
Phosphorus—Contd.							
P_4O_{10} (metastable)	418	457	508	560	586	608	631
$POCl_3$			(s)	(l)313.6	336.7	356.0	378.2
PCl_3 (l)	190.9	218.4	247.5	287.9	305.8	327.2	347.3
PH_3			(s)	(l)150.6	162.7	173.7	185.6
Platinum:							
Pt (l)	2,640	2,960	3,360	3,910	4,180	4,430	4,680
Potassium:							
K (l)	534	605	702	838	911	977	1,047
KOH (l)	875	978	1,116	1,308	1,409	1,500	1,600
KBr	(s)	(l)1,063	1,193	1,382	1,479	1,565	1,656
KCl	977(s)	(l)1,079	1,221	1,409	1,506	1,590	1,680
KF	(s)	(l)1,142	1,291	1,490	1,591	1,677	1,775
KI	(s)	(l)1,004	1,142	1,326	1,420	1,505	1,597
Radon:							
Rn			(s)	(l)170.1	184.5	197.0	211.3
Rhenium:							
Re_2O_7	453.5	483.5	517	557.5(s)	(l)580	607	635.5
Rubidium:							
Rb (l)	496	561	650	770	834	890	952
RbBr	(s)	(l)1,039	1,176	1,360	1,454	1,535	1,625
RbCl	(s)	(l)1,050	1,190	1,379	1,475	1,562	1,654
RbF	(s)	(l)1,185	1,225	1,415	1,508	1,590	1,681
RbI	(s)	(l)1,007	1,140	1,319	1,410	1,491	1,577
Selenium:							
Se (l)	555	620	703	813	865	907	953
SeO_2 (s)	389	425	469	523	548	568	590
$SeOCl_2$	(s)	(l)304	340	384.5	406	423	441
SeF_6 (s)	137.4	152.4	171.5	196.4	207.3	217.1	227.3
Silicon:							
Si (l)	1,845	1,980	2,140	2,330	2,420	2,490	2,560
SiO_2		(s)	(l)1,980	2,210	2,320	2,410	2,500
SiH_4	(s)	(l)92.4	107.8	129.3	140.4	150.5	161.6
SiH_3Br		(s)	(l)192.3	226.0	243.2	258.6	275.5
SiH_2Br_2	(s)	(l)209.2	239.4	281.1	302.6	322.6	343.6
$SiHCl_3$ (l)	169.8	189.8	215.9	251.4	269.6	286.4	304.9
$SiCl_4$	(s)	(l)206.7	234.5	272.6	292.1	309.1	329.9
SiF_4 (s)	116.4	127.4	140.9	157.3	165.2	171.6	178.3
SiF_3Cl		(s)	(l)143.5	168.1	180.7	190.9	203.0
SiF_2Cl_2 (l)	129.2	146.1	168.3	198.1	213.7	227.2	241.8
Si_2H_6	(s)	(l)155.7	178.6	210.8	227.3	241.6	258.8
Si_2Cl_6		(s)	(l)307	352	373.5	392	412
Si_2F_6 (s)	175.9	190.3	207.7	228.7	238.2	246.0	254.2
$(SiH_3)_2O$ (l)	142.1	159.0	181.8	212.7	228.5	242.6	257.7
$(SiCl_3)_2O$ (l)	240.3	264.6	297.6	341.8	364.2	384.5	408.7
Si_3H_8 (l)	180.0	201.3	230.1	268.8	289.3	307.2	326.3
Si_3Cl_8 (l)	282.2	315.0	356.5	411.2	437.5	460.5	484.5
$(SiH_3)_3N$ (l)	180.5	201.5	228.8	266.5	284.5	300.5	321.8
Si_4H_{10} (l)	218	242	273	314	335	353	373
Silver:							
Ag (l)	1,442	1,607	1,816	2,098	2,236	2,354	2,485
AgCl (l)	1,054	1,168	1,324	1,540	1,645	1,733	1,837
AgI (l)	956	1,076	1,233	1,450	1,564	1,665	1,779
Sodium:							
Na (l)	622	702	807	952	1,027	1,092	1,165
NaOH (l)	880	996	1,148	1,354	1,459	1,552	1,651
NaBr	(s)	(l)1,064	1,205	1,393	1,489	1,572	1,665
NaCl	1,016(s)	(l)1,123	1,269	1,465	1,563	1,646	1,738
NaF	(s)	(l)1,332	1,491	1,699	1,799	1,884	1,977
NaI	(s)	(l)1,026	1,158	1,332	1,418	1,493	1,577
NaCN (l)	949	1,072	1,234	1,454	1,565	1,666	1,770
Strontium:							
Sr		(s)	(l)1,150	1,354	1,460	1,552	1,657
SrO	2,160	2,320	2,510(s)	(l)			
Sulphur:							
S (l)	406.6	450.3	507.2	587.1	629.4	669.1	717.7
SO_2	159.8	174.9	194.7(s)	(l)222.0	236.7	249.6	263.1
$SO_3(\alpha)$	213.7	231.6	253.5	280.1(s)	(l)292.6	304.6	317.9
$SO_3(\beta)$	218.9	236.8	258.0	284.1	295.9	304.9(s)	(l)317.9
$SO_3(\gamma)$ (s)	239.1	255.7	274.9	297.9	308.3	316.4	324.7
$SOBr_2$ (l)	234.4	262.6	299.1	347.0	370.3	390.6	412.6
$SOCl_2$ (l)	189.6	213.8	245.8	288.4	309.6	328.0	348.5
SO_2Cl_2		(s)	(l)244.0	285.0	306.2	322.9	342.3
S_2Cl_2 (l)	236.5	262	296.5	341	365.5	386.5	411
SF_6 (s)	124.6	138.5	156.0	179.0	189.5	199.5	209.6
Tantalum:							
TaF_5			(s)	(l)392	430	468.5	508
Tellurium:							
Te	(s)	(l)783	906	1,083	1,178	1,264	1,360
$TeCl_4$		(s)	(l) 500	548	601.5	631	665
TeF_6 (s)	143.0	158.4	177.6	202.1	213.6	225.8	234.5

Substance	Pressure, atmosphere						
	0.0001	0.001	0.01	0.1	0.25	0.5	1.0
Thallium:							
Tl (*l*)	965	1,082	1,235	1,439	1,542	1,633	1,730
TlBr	634	695(*s*)	(*l*)781	908	973	1,028	1,092
TlCl	623	686(*s*)	(*l*)777	900	964	1,017	1,080
TlI	636	702(*s*)	(*l*)793	919	982	1,034	1,096
Tin:							
Sn				(*l*)2,205	2,329	2,436	2,543
$SnCl_2$ (*l*)	523	581	654	752	804	847	896
$SnCl_4$	(*s*)	(*l*)247	278.5	321.5	343	363.5	386
SnH_4	(*s*)	(*l*)131.0	151.6	179.7	194.2	206.8	220.8
$Sn(CH_3)_4$	Melting point unknown.			(*l*)290.2	311.6	330.2	351.4
$Sn(CH_3)_3 . C_2H_5$	do.			(*l*)316.0	338.4	358.4	381.4
$Sn(CH_3)_3 . C_3H_7$	do.		(*l*)290.8	336.0	359.6	380.1	404.2
Titanium:							
$TiCl_4$	(*s*)	(*l*)255.5	290	337	361.5	383.5	409
Tungsten:							
W (*l*)	3,820	4,210	4,710	5,350	5,660	5,920	6,200
WF_6	182.4	199.4	220.9	248.8	262.3(*s*)	(*l*)273.2	290.4
Uranium:							
UF_6 (*s*)	213.0	231.9	255.9	286.8	301.5	314.5	328.8
Xenon:							
Xe	92.3	103.6	118.1	137.6	147.2	155.2(*s*)	(*l*)165.1
Zinc:							
Zn	672(*s*)	(*l*)750	852	990	1,067	1,115	1,180
$ZnCl_2$	(*s*)	(*l*)693	770	870	919	960	1,005
$Zn(C_2H_5)_2$	(*s*)	(*l*)245	279.5	326	349.5	369.5	391
Zirconium:							
$ZrBr_4$ (*s*)	442	476.5	517.5	568	590.5	609.5	630
$ZrCl_4$ (*s*)	426.5	459.5	498.5	546	567.5	585.5	604
ZrI_4 (*s*)	496	533	579	634	660.5	681.5	704

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