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INVESTIGATION AND COMPILATION OF THE THERMODYNAMIC PROPERTIES OF HIGH TEMPERATURE CHEMICAL SPECIES

QUARTERLY TECHNICAL REPORT AFRPL-TR-69-70

(1 October 1968 - 31 December 1968)

January 1969

AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE, CALIFORNIA 93523

(Prepared under Contract Nr. F04611-67-C-0009
The Dow Chemical Company
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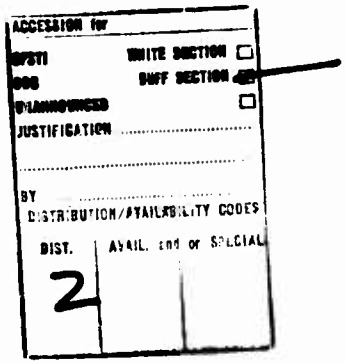

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Dow Report Nr. T0009-4Q-68

AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
EDWARDS, CALIFORNIA
CONTRACT NR. F04611-67-C-0009

THERMAL RESEARCH LABORATORY
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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract Nr. F04611-67-C-0009. The Contract was initiated under Air Force Project Nr. 3148, 'Investigation and Compilation of the Thermodynamic Properties of High Temperature Chemical Species.' The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This is the eighth quarterly report, covering the work performed during 1 October - 31 December 1968. The Dow Report number is T0009-4Q-68.

The work was performed by I. H. Carr, J. Chao, A. T. Hu, G. C. Karris, H. Prophet, A. N. Syverud and D. U. Webb under the technical supervision of D. R. Stull.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

Supplement No. 30 to the JANAF Thermochemical Tables was completed and sent to the printers on December 27, 1968. This Supplement contains the new element calcium and its fluoride, revisions of several ionic species due to a determination of the electron affinity of BO_2, and revisions of several fluorides due to a new table for HF.

A complete description of the measurements used in the simultaneous solution analysis of the interrelated HF heat of formation data is given in the Appendix.

JANAF THERMOCHEMICAL TABLES

Supplement No. 30 to the JANAF Thermochemical Tables was completed, for issue to the panel, and sent to the printers on December 27, 1968. This issue contains 58 tables representing a two-man level of effort. There are 25 new tables including the element calcium and its fluorides, and 33 revised tables. The revised tables include several ionic species, changed because of a reported value for the electron affinity of BO_2, and several fluorides affected by the new HF table.

This supplement brings the total number of species covered to 1072 and the number of tables issued during the present contract to 280. The table of contents for this supplement is shown in Figure 1.

Twenty three thermochemical reactions from the literature are analyzed to obtain new selected values of ΔHf°_{298} for HF(g), HF(50 H_2O), NaF(c), BF_3(g), NF_3(g), CF_4(g), and C_2F_4(polymer). A new method, called simultaneous adjustment, is used in place of the traditional method of sequential adjustment. The selected values are self-consistent and "best" in the least squares sense.

Figure 1

JANAF THERMOCHEMICAL DATA

Supplement No. 30, Issued December 31, 1968

*New Table

APPENDIX

Enthalpies of Formation of Hydrogen Fluoride and Five Closely Related Fluorides

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Introduction

Recent research has provided much data pertinent to the values of ΔHf° for HF(g) and HF(n H_2O). More accurate values for these quantities are desirable in themselves and because they are prime values on which many other fluorides are based. These quantities have remained relatively uncertain despite many calorimetric studies in the period from 1880 to 1950. Subsequent work emphasized important systematic errors, namely, various side reactions involving impurities, corrosion of containers and self-polymerization of HF(g).

The history of values selected from critical analyses (1, 2, (3) of the data may be summarized as follows:

Date and Reference	$\Delta Hf^\circ_{298.15}$		
	HF(g)	HF (50 H_2O)	HF (∞ H_2O)
1936 (1)	-64.0*	-75.56*	-78.2*
	-0.2	-0.10	-0.46
1952 (2)	-64.2	-75.66	-78.66
	-0.6	-0.66	-0.46
1965 (3)	-64.8±0.3	-76.316	-79.50
	-0.34	-0.46	-0.32
1968 (This selection)	-65.14±0.2	-76.78±0.1	-79.82±0.2

* Values correspond to 18°C rather than 25°C.

It is apparent from the differences tabulated between the lines that there has been a continual progression to more negative values. The present selections are no exception. The systematic trend in the values appears to be a reflection of increasing knowledge of the side reactions and increasing emphasis on minimizing them or correcting for them. Therefore, thorough analysis of the chemical reaction is essential for calorimetry involving hydrogen fluoride, fluorine, or, for that matter, almost any fluoride. This criterion is satisfied by several recent and pertinent calorimetric studies which make possible the selection of more reliable values for hydrogen fluoride.

This paper documents the newly selected values of $\Delta Hf^{\circ}_{298.15}$ for HF(g)*, HF(50 H_2O), HF(∞ H_2O)* and five closely related fluorides. First, a new approach to the problem, namely simultaneous adjustment, will be formulated, which will be used instead of the normal sequential adjustment (1, 2, 3). Next will be presented the observations selected for consideration and their resulting simultaneous adjustments. Finally, the results will be discussed and some suggestions offered for future experiments.

Simultaneous Adjustment

The mathematical problem involves the determination of values for several unknowns from an over-determined set of experimental observations of linear combinations of the unknowns. The problem may be formulated as follows: Experimental data are available for a series of reactions (i = 1,2...m) involving a number of species (j = 1,2...n). It is assumed that the data may be reduced to standard heats of reaction, $R_i = \Delta Hr^{\circ}_{298}$, which deviate from the true values by the errors E_i. The heats of formation, $F_j = \Delta Hf^{\circ}_{298}$, are defined by m heat balance equations of the form:

$$\sum_j c_{ij} F_j = R_i + E_i \qquad [1]$$

where c_{ij}, the stoichiometric coefficient for species j in reaction i is taken to be negative for reactants and positive for products. Values for c_{ij} are presumed to be known exactly and a limiting uncertainty interval, $\pm U_i$, is estimated for each observation R_i. We wish to obtain values of F_j' which are "best" approximations for F_j. Of course, neither F_j nor E_i will ever be known exactly; however, the deviations from the approximate solution are given exactly by:

$$E_i' = \left(\sum_j c_{ij} F_j'\right) - R_i. \qquad [2]$$

*The description "(g)" denotes the ideal gas standard state, while "(∞H_2O)" refers to the ionized, aqueous standard state of unit molality, which may be attained by appropriate extrapolation to infinite dilution.

The established procedure for adjustment of Equation [1] assumes that $E_i' = 0$ for selected heat of reaction (or for a weighted average of selected values), and the heats of formation F_j' are obtained one at a time by use of Equation [2] in some sequential fashion. Inconsistencies arising from multiple determinations or alternate paths are resolved in the selection process by attributing all of the deviations to those observations which are believed to be less accurate. This sequential selection of the variables will be called a sequential adjustment in order to distinguish it from the following alternative.

Simultaneous adjustments of Equation [1] are readily obtained (when $m > n$) by minimization of a suitable function of the weighted deviation E_i'/U_i. Two different minimization criteria appear to be useful: least squares, which minimizes the sum of squares of E_i'/U_i, and least sum, which minimizes the sum of absolute magnitudes of E_i'/U_i. Least squares and least sum correspond, respectively, to the L_2-norm and the L_1-norm of approximation theory (4). The so-called L_∞-norm, which corresponds to minimization of the maximum value of E_i'/U_i, usually does not give acceptable adjustments (5) to Equation [1].

Least squares adjustments tend to distribute the deviations among all of the observations, while least sum adjustments assume at least as many zero deviations as there are variables (5). In the limit, as the simultaneous adjustment is reduced to the stepwise selection of F_j', least squares reduces to selection of the weighted average and least sum reduces to selection of the least uncertain observation.

Simultaneous adjustment may be extended (5) to include the Gibbs energy of formation and the entropy as additional variables. Thermodynamics then requires for each chemical species the linear constraint

$$\Delta Hf^\circ_{298} = \Delta Gf^\circ_{298} + 298.15\ \Delta Sf^\circ_{298}, \qquad [3]$$

where ΔSf°_{298} is the entropy of formation of that species from the

elements in their standard reference states. Linear constraints may be incorporated (6) without changing the adjustment problem. This problem, i.e. the solution of linear systems of algebraic equations, is the subject of many algorithms (7, 8, 9) which have been programmed for digital computers. Least squares adjustments are obtained with these algorithms, but least sum adjustments are usually obtained by the methods of linear programming (10, 11).

Selected Observations

The thermodynamic data considered for possible inclusion in the analysis were those available at the end of 1968. The search included not only HF but also those fluorides having reliable, multiple links to HF. Recent data were concentrated mainly in the latter area. Several reviews (12 - 16) were particularly helpful in screening the related fluorides for reliable and consistent links to HF. Data considered in the previous critical evaluations (1, 2, 3, 17) were newly screened, based on current knowledge. This process led to the selection of five fluorides which warrant consideration in the selection process. These fluorides include NaF(c), BF_3(g), NF_3(g), CF_4(g) and C_2F_4(polymer).

The remainder of this section discusses the selected data for HF and these closely related fluorides. Since the selections are presumably neither definitive nor unique, suggestions of changes for use in future adjustments are welcome. There are several links, for example, which interrelate C_2F_6(g), C_2F_4(g), CHF_3(g), $CClF_3$(g), $CBrF_3$(g) and CF_3I(g) with the selected species. The inconsistencies for C_2F_4(g) and CHF_3(g) appear to be large enough so that these links will contribute little, if any, to a knowledge of HF. Thus, all of these species are subject to a secondary adjustment.

The experimental data for each species are reduced to a chosen standard state for convenience in the subsequent analysis. One exception is HF(n H_2O) which is reduced to HF(50 H_2O). Other

aqueous species in the ionized standard state of unit molality will hereafter be denoted by the description '(aq)". Data for aqueous species are reduced by means of the selected curves of Reference (17) whenever possible. Thermodynamic functions for gaseous and condensed phases are taken from the JANAF Tables (18). Uncertainty intervals for calorimetric data are calculated from $2\bar{s}'_Q$, as recommended by Rossini (19), unless otherwise indicated. In some cases, the interval is increased by an additional contribution for the estimated systematic error. When the overall ΔHr is the sum of two or more independent values, then the overall uncertainty interval is calculated by means of Equation 17 of Rossini (19). The twenty three selected reactions are discussed under the headings R1 through R23.

R1. $0.5\ H_2(g) + 0.5\ F_2(g) \rightarrow HF(50\ H_2O)$ $\Delta Hr^\circ_{298} = -76.68 \pm 0.05$ kcal/gfw
King and Armstrong (2) measured the heats of reaction of fluorine, oxygen and OF_2 with hydrogen by flame calorimetry at 30°C. The oxygen data agree with the accepted ΔHf° for $H_2O(\ell)$ and the fluorine data reduce to the value shown above. This is a very thorough study which serves well to illustrate the importance of side reactions such as corrosion. The latter of the two papers (20) increases the uncertainty to 0.09 kcal/gfw based on estimates of the systematic uncertainty. The smaller value of 0.05 kcal/gfw, exclusive of the systematic uncertainty, has been assigned to weigh this observation more heavily.

R2. $HF(g) \rightarrow H(g) + F(g)$ $\Delta Hr^\circ_{298} = -136.051 \pm 0.3$ kcal/gfw
Johns and Barrow (21) obtained $D_3' = 49310 \pm 100\ cm^{-1}$ from rotational predissociation of the vibrational levels in the UV spectra of HF. From this the value $D_0'' = -135.067 \pm 0.3$ kcal/gfw and the corresponding value at 298.15°K is derived.

R3. $HF(g) + NaOH(aq) \rightarrow NaF(c) + H_2O(\ell)$ $\Delta Hr^\circ_{298} = -28.24 \pm 0.10$ kcal/gfw
Rodenburg and Vanderzee (22) obtained values for the reaction $HF(g) + NaOH(aq) \rightarrow NaF(aq) + H_2O(\ell)$ from calorimetric studies with HF(real gas) at pressures of about 350 and 150 mm Hg. The results are $\Delta Hr^\circ = -27.80 \pm 0.16$ and -28.01 ± 0.10 kcal/gfw, respectively, with preference being given to the latter value on experimental grounds (23). $\Delta Hr^\circ = -28.01 \pm 0.10$ kcal/gfw includes a non-ideality correction of approximately 0.20 ± 0.025 kcal/gfw. Combining this ΔHr° with $-\Delta H^\circ_{soln} = -0.23 \pm 0.01$ kcal/gfw (24) for NaF(c), the selected observation given above is obtained.

R4. $HF(50\ H_2O) + NaCl(c) \rightarrow NaF(c) + HCl(aq)$
$\Delta Hr^\circ_{298} = -2.41 \pm 0.07$ kcal/gfw
Coughlin (25) obtained $\Delta Hr^\circ = -1.53 \pm 0.06$ kcal/gfw at 30°C for $NaCl(c) + HF(5.716\ H_2O) \rightarrow NaF(c) + HCl(12.731\ H_2O)$ from combination of five heat of solution measurements involving an acid solution of aluminum. Values (17, 18) of Cp°, ϕ_c and ϕ_L yield a reduction to 25°C of 0.132 kcal/gfw, a reduction to $HF(50\ H_2O)$ of 0.128 ± 0.03 kcal/gfw, and a reduction to HCl(aq) of -1.14 kcal/mol.

R5. $HF(g) + NaCl(c) \rightarrow NaF(c) + HCl(g)$ $\Delta Hr^\circ_{298} = +3.81 \pm 0.25$ kcal/gfw
Hood and Woyski (26) report equilibrium data for this reaction in the range 796-942°K. Second and third law analyses with the latest free energy functions (18) give $\Delta Hr^\circ = 5.91 \pm 0.11$ (second law) and 3.81 kcal/gfw (third law) at 298.15°K. The drift (difference between third and second law values of ΔSr°) is -2.5 ± 0.1 eu, a rather precise value which is probably five times the overall uncertainty in the third law ΔSr°. This suggests a temperature-dependent error in the equilibrium constants; for example, an error in the analyses which determine the partial pressures, or possibly a minor deviation of the condensed phases from their standard states. Attainment of equilibrium is confirmed by consistency of the Kp values, regardless of the direction of approach

to equilibrium. Other aspects of the study appear to be thorough and well documented. It would be desirable to test for similar drifts in comparable studies (26) of $BaCl_2$-BaF_2 and $NiCl_2$-NiF_2, but this was not done because of uncertainties in the free energy functions. Instead, it is noted that the third law ΔHr° is consistent with R3 within about 0.08 kcal/gfw, while the second law value is clearly inconsistent. Such behavior is observed in systems where the equilibrium constants are essentially correct at one extreme in temperature but show minor and increasing error toward the other extreme in temperature. Corrosion is suspected in this case, and the results at the lowest temperature are the most reliable. The individual third law values of ΔHr°, ranging from 3.93 kcal/gfw at 796°K to 3.56 kcal/gfw at 942°K, yield a mean of 3.81 kcal/gfw, which is influenced by the preponderance of points at lower temperatures. This mean is adopted and the uncertainty interval is estimated as ±0.25 kcal/gfw, which exceeds the range of the values and corresponds approximately to the maximum effect arising from uncertainty in the third law ΔSr°.

R6. $0.5\ F_2(g) + NaCl(c) \rightarrow NaF(c) + 0.5\ Cl_2(g)$

$\Delta Hr^\circ_{298} = -39.30 \pm 0.4$ kcal/gfw

Calorimetric data for this reaction at 20°C are reported by von Wartenberg and Fitzner (27). The reduction to 25°C is insignificant. Although the study is old and incompletely documented by current standards, the results are consistent with recent work. An uncertainty of 0.4 kcal/gfw based on 0.28 for the calorimetric experiments is assumed, and an estimate of 0.12 for other contributions.

R7. $HF(50\ H_2O) + NaOH(aq) \rightarrow NaF(c) + H_2O(\ell)$

$\Delta Hr^\circ_{298} = -16.57 \pm 0.05$ kcal/gfw

Kolesov and Skuratov (28) report $\Delta Hn = -16.45 \pm 0.03$ kcal/gfw at 21.5°C for $HF(16\ H_2O) + LiOH(3800\ H_2O) \rightarrow LiF(3800\ H_2O) + H_2O(\ell)$. It appears that this is the only modern determination of ΔHn for

HF with any alkali hydroxide. With auxiliary data from (17, 18), a reduction to 25°C of 0.074 ± 0.02 kcal/gfw is obtained, a reduction to HF(50 H_2O) or 0.036 ± 0.01 kcal/gfw, and a combined reduction to LiOH(aq) and LiF(aq) of 0.001 kcal/gfw. The last mentioned standard states may be considered as OH^-(aq) and F^-(aq), or as NaOH(aq) and NaF(aq), without affecting the ΔHn = -16.34 ± 0.05 kcal/gfw. Combination of this value with $-\Delta H_c^\circ$ = -0.23 ± 0.01 kcal/gfw (24) for NaF(c) gives the selected ΔHr°.

R8. $H^+(aq) + NaF(c) \rightarrow HF(50\ H_2O) + Na^+(aq)$

ΔHr°_{298} = 3.414±0.3 kcal/gfw

This "observation" is a combination of ϕ_L = 3.184 ± 0.3 kcal/gfw (17) for HF(50 H_2O) and ΔH_c°soln = 0.23 ± 0.01 kcal/gfw (24) for NaF(c). Itrepresents the composite of equilibrium and enthalpy data from which the dilution curve (17) was derived. Aqueous HF is a weak electrolyte which ionizes in dilute solutions according to the equilibria (a) $HF = H^+ + F^-$ and (b) $HF + F^- = HF_2^-$. The two ionization reactions make an overall contribution of about 3 kcal/gfw to ϕ_L. Parker (17) used selected values of ΔHa = -3.0 and ΔHb = +0.662 kcal/gfw, along with concentrations based on selected equilibrium data, to calculate ϕ_L in dilute solutions. Recent data suggest that minor changes in these calculations may be desirable. In particular, the calculated dilution curve shows increasing deviations at lower molalities when compared with the new measurements of Cox and Harrop (29). Agreement is satisfactory near HF(1100 H_2O), but near HF(6000 H_2O) the calculated heats of dilution are roughly 240 cal/gfw (or 32%) larger than the observed values. Alternative selections for Ka, Kb, πHa and πHb might reduce this discrepancy considerably. The equilibrium data, both new (30) and old (31), are sufficiently divergent to allow changes in πHa and πHb of perhaps -0.2 and +0.5 kcal/gfw, respectively. Based on this review of the data, the uncertainty of ϕ_L ($50H_2O$) is estimated to be 0.3 kcal/gfw.

R9. $C(graphite) + 2F_2(g) \rightarrow CF_4(g)$ $\Delta Hr^\circ_{298} = -223.05 \pm 0.18$ kcal/gfw
Greenberg and Hubbard (32) report this result from a thorough study of the combustion in fluorine of natural and synthetic graphite.

R10. $C_2F_4(polymer) + O_2(g) + 2H_2O(\ell) \rightarrow 4HF(50\ H_2O) + 2CO_2(g)$
$\Delta Hr^\circ_{298} = -160.62 \pm 0.9$ kcal/gfw
See the following discussion.

R11. $C_2F_4(polymer) + O_2(g) \rightarrow CF_4(g) + CO_2(g)$
$\Delta Hr^\circ_{298} = -118.8 \pm 0.5$ kcal/gfw
Good et al. (33) report the calorimetric combustion of various Teflon-oil mixtures. Reactions R10 and R11 are derived by extrapolation from the observed product ratios of $HF(10\ H_2O)/CF_4$ to the limits of only $HF(10\ H_2O)$ and only $CF_4(g)$. R10 includes a reduction to $HF(50\ H_2O)$ of -0.32 ± 0.08 kcal/gfw.

R12. $C_2F_4(polymer) + 2F_2(g) \rightarrow 2CF_4(g)$
$\Delta Hr^\circ_{298} = -247.85 \pm 0.3$ kcal/gfw
This ΔHr° appears to be a minor adjustment (12) of the earlier data of Domalski and Armstrong (13) who report a value of -247.92 ± 0.07 kcal/gfw. The earlier value is labeled as Reaction R12a. Wood, Lagow and Margrave (34) reported -246.84 kcal/gfw for the same reaction. This is R12b and is reassigned an uncertainty of 0.2 kcal/gfw, since the authors' uncertainties and terminology are inconsistent with (19). No reason is apparent for the discrepancy of 1.0 kcal/gfw between R12 and R12b. Effects due to phase transitions of C_2F_4(polymer) near 20 and 30°C might be involved, but the overall ΔHt for these transitions is only 0.2 kcal/gfw (35).

R13. $C(graphite) + 2F_2(g) \rightarrow CF_4(g)$ $\Delta Hr^\circ_{298} = -222.87 \pm 0.38$ kcal/gfw
Domalski and Armstrong (13) report this result from their combustions in fluorine of graphite-Teflon mixtures.

R14. $CF_4(g) + 2H_2O(\ell) \rightarrow 4HF(50\ H_2O) + CO_2(g)$

$\Delta Hr^\circ_{298} = -41.506 \pm 0.3$ kcal/gfw

Cox, Gundry and Head (36) report calorimetric combustions of mixtures of docosafluorobicyclohexyl ($C_{12}F_{22}$) with benzoic acid. This study, which is analogous to that of Good et al. (33) with Teflon-oil mixtures, yields two reactions having quite different product ratios of $HF(20\ H_2O)/CF_4$. By taking the difference of these two reactions, dividing by 3.3, and adding a reduction to $HF(50\ H_2O)$ of -0.12 ± 0.02 kcal, the above observation is obtained.

R15. $8NF_3(g) + 3C_2N_2(g) \rightarrow 6\ CF_4(g) + 7N_2(g)$

$\Delta Hr^\circ_{298} = -1308.8 \pm 1.3$ kcal/gfw

Walker (37) reported a calorimetric value at 298.15°K of ΔHr° = -218.13 ± 0.15 kcal/gfw for 1/6 of the stoichiometry given above. The uncertainty is reassigned as 0.21 kcal/mol by reference to the original data, since the manuscript (37) is inconsistent in value and terminology with (19). Finally, the observation is multiplied by 6 in order to eliminate stoichiometric coefficients with infinite decimals.

R16. $NF_3(g) + 1.5\ H_2(g) \rightarrow 3HF(50\ H_2O) + 0.5\ N_2(g)$

$\Delta Hr^\circ_{298} = -199.40 \pm 0.22$ kcal/gfw

Sinke (38) reported a calorimetric value at 298.15°K of ΔHr° = -199.49±0.22 kcal/gfw for a final state of $HF(123\ H_2O)$. The reduction to $HF(50\ H_2O)$ is +0.09 ± 0.01 kcal/gfw.

R17. $2NF_3(g) + S(c, rh) \rightarrow SF_6(g) + N_2(g)$

$\Delta Hr^\circ_{298} = -228.26 \pm 0.25$ kcal/gfw

Walker (39) reported a calorimetric value at 298.15°K of ΔHr° = -228.26 ± 0.2 kcal/gfw. The uncertainty is reassigned as 0.25 kcal/gfw by reference to the original data, since the paper (39) is inconsistent in value and terminology with (19).

R18. $NF_3(g) \rightarrow 0.5\ N_2(g) + 1.5\ F_2(g)$ $\Delta Hr^\circ_{298} = 31.44 \pm 0.3$ kcal/gfw
Sinke (40) reported calorimetric data for the explosion of mixtures of hydrogen with 10% excess of NF_3 and with 100% excess of NF_3. The complex final states were not corrected to standard states; instead, the experiments were designed to minimize the corrections. The difference between the two sets of data yields the result given above.

R19. $NF_3(g) + B(c, \beta) \rightarrow BF_3(g) + 0.5\ N_2(g)$
$\Delta Hr^\circ_{298} = -239.46 \pm 1.2$ kcal/gfw
Ludwig and Cooper (41) reported a calorimetric value of $\Delta E_c^\circ/M = -22177$ cal/g after correction for 0.44% impurities in the sample of boron. Using 10.811 for the atomic weight of boron, $\Delta E_c^\circ = -239.76 \pm 1.2$ and $\Delta Hr^\circ = -239.46 \pm 1.2$ kcal/gfw. The amount of unburned boron remaining after combustion averaged 5% as determined by chemical analysis. This analysis was complicated by the retention on the bomb surfaces of some of the $BF_3(g)$, apparently in the form of a metal fluoride - BF_3 adduct which was not identified. It is likely that the metal fluoride in the adduct was formed, at least in part, by corrosion. No correction was made for adduct formation, so the calorimetric result may be biased. Bias may also arise from the impurity correction (cf. R20); however, the existing bias appears to be much smaller than the assigned uncertainty.

R20. $1.5\ F_2(g) + B(c, \beta) \rightarrow BF_3(g)$ $\Delta Hr^\circ_{298} = -271.6 \pm 0.9$ kcal/gfw
Wise et al. (43) reported the calorimetric result $\Delta Hr^\circ = -270.10 \pm 0.24$ kcal/(10.82g B), based on correction for 0.62% impurities in the sample of boron. Reanalysis (42) of the sample with more reliable techniques showed the presence of 1.32% impurities. This made ΔHr° more negative by 1.5 kcal/gfw and increased the uncertainty by more than a factor of three. Here is a pointed example of bias caused by side reactions due to impurities. Calorimetric combustions in fluorine have also been reported by

Gross et al. (44), but their boron (the zone-refined sample) was not analyzed for C, N, O and N. The calorimetric result, ΔHr°_{298} = -270.58 + 0.3 kcal/(10.811g B), becomes -270.9 ± ? depending on whether the correction for CHON impurities is estimated from (42) or (45). Since such estimates may give only lower limits to the correction, the data of Gross et al. (44) are not considered.

R21. 1.5 $F_2(g)$ + B(C, β) → $BF_3(g)$ ΔHr°_{298} = -271.65±0.22 kcal/gfw
Johnson et al. (42) remeasured the heat of combustion in fluorine using two different experimental techniques with a zone-refined sample of boron. The sample contained 0.13% impurities (O, C, N and H), for which the corrections amounted to about 0.12% of ΔE°_{c}. Experimental determination of the isotopic ratio in the sample gave an atomic weight of 10.805 ± 0.004 which was used in calculating ΔHr°. This value remains essentially unchanged in terms of the accepted atomic weight of 10.811 for natural boron.

R22. 1.5 $F_2(g)$ + B(c, β) → $BF_3(g)$ ΔHr°_{298} = -271.03±0.51 kcal/gfw
Domalski and Armstrong (45) report the combustion in fluorine of pelleted mixtures of boron and Teflon. The boron contributed roughly 35% of the energy. Corrections for impurities in the boron (0.12% metallic impurities and 0.20% C, O and N) amounted to about 0.24% of ΔE°_{c} (boron). Experimental determination of the isotopic ratio gave 10.812 ± 0.005; thus, the accepted atomic weight of 10.811 was used in calculating ΔHr°. The authors' estimate of the overall experimental uncertainty is accepted instead of a value based only on random error (19).

R23. 3HF(50 H_2O) + B(c, β) + 0.75 $O_2(g)$ → $BF_3(g)$ + 1.5 $H_2O(\ell)$
ΔHr°_{298} = -142.77±0.5 kcal/gfw
Gunn (46) reported ΔHr°_{298} = -28.29 ± 0.07 kcal/gfw for the reaction $BF_3(g)$ + 15.67 HF(3.747 H_2O) → [solution], while Good and Mansson (47) reported ΔHr°_{298} = -173.406 ± 0.2 kcal/gfw for B(c, β) + 0.75 $O_2(g)$ + 18.57 HF(3.065 H_2O) → [solution] +

1.5 $H_2O(\ell)$, where the resulting solutions have the same composition. A reduction to HF(3.747 H_2O) of +1.624 kcal/gfw with an estimated uncertainty of 10 to 25%, or roughly 0.2 to 0.4 kcal/gfw, is applied to the latter reaction. The difference between the two reactions and a reduction to HF(50 H_2O) of +0.717 ± 0.1 kcal/gfw are used to obtain the result given above. The overall uncertainty is estimated as 0.3 to 0.5 kcal/gfw, depending on the choice of uncertainty for reduction to HF(3.747 H_2O).

Input Data

The computer program (48) is a generalized version which allows ΔHf°_{298}, ΔGf°_{298} and S°_{298} as variables; however, only ΔHf°_{298} is involved in this study. The program performs two functions: it edits the observations and then obtains the least squares adjustment. Editing consists of transforming the observations from the form given previously into the system of linear equations ready for solution.

The input to the program consists of (i) species with variables, (ii) species with fixed values, (iii) observations, and (iv) constraints, if any. There are seven variables in this study, namely, the values of ΔHf°_{298} for HF(g), HF(50 H_2O), NaF(c), BF_3(g), NF_3(g), CF_4(g) and C_2F_4(polymer). Species with fixed values of ΔHf°_{298} are listed in Table I. These include nine elements or ions in their standard reference states and eleven compounds with assumed fixed enthalpies of formation. The twenty three observations, each consisting of the reaction, enthalpy of reaction, and uncertainty, are summarized* in Table II. The last six columns in the table indicate variations in the observations which were used in six preliminary adjustments. No constraints are involved.

The edited observations, shown in Table III, summarize the relationships among the variables for the final adjustment (HF-7). All "fixed" species have been removed by substitution of their heats of formation and uncertainties. All uncertainties are assumed to be independent and are combined by use of Equation 17 of Rossini (19). The resulting values of R_i+U_i, involving only variables, provide the most direct comparison among the observations. Table III is also the most concise representation of the input data. It is the starting point for both sequential and simultaneous adjustments.

*Table II is an example of a catalog of observed thermochemical processes. Armstrong (12) has suggested the value of such catalogs. They summarize the input data used for adjustment, either sequential or simultaneous.

Results of the Simultaneous Adjustments

Results of the final adjustment (HF-7) and six preliminary adjustments (HF-1 through HF-6) are given in Table IV. Also shown is the least sum adjustment of HF-7. Below each least squares value of ΔHf°_{298} is the corresponding standard error (54) based on the overall consistency rather than the internal consistency of each observation. This point will be emphasized in the discussion.

The preliminary adjustments represent various stages in the review of the input data as noted in Table II. All preliminary adjustments used our tentative estimate of 0.05 kcal/gfw for the uncertainty of R3 rather than the proper value (23) of 0.10 kcal/gfw. The effect of this change is insignificant (cf. HF-7 and HF-6 in Table IV). Adjustments prior to HF-6 do not include R7, the heat of neutralization from Kolesov and Skuratov (28). Inclusion of this observation (cf. HF-7 and HF-4) changes the values of both HF(g) and NaF(c) by about +0.07 kcal/gfw and reduces the standard error of the latter from 0.11 to 0.07. Other changes are insignificant. It is noted in R12 that the Teflon combustions of Wood et al. (34) and Armstrong (12, 13) differ by 1 kcal/gfw or twice the sum of their uncertainties. When the value of Wood is substituted for that of Armstrong (cf. HF-5 and HF-4), C_2F_4 (polymer) is changed by +0.7 kcal/gfw and CF_4(g) by +0.08 kcal/gfw. Adjustments prior to HF-4 use 0.3 rather than 0.5 kcal/gfw as the estimated uncertainty for R23. The only significant effect of this is to shift BF_3(g) from -271.42 to -271.29 kcal/gfw. Adjustments HF-3 and HF-2 indicate the effects of different combinations of R12, R12a and R12b. Omission of R6 and R19 has negligible effect (cf. HF-2 and HF-1), since these observations are relatively consistent but uncertain.

Not listed in Table IV are several other adjustments in which ϕ_L for HF(50 H_2O) was changed by ±0.2 kcal/gfw and the uncertainty was reduced from 0.3 to 0.2 kcal/gfw. These results are not significantly different from those already tabulated.

Discussion

There is an excellent precedent for use of the simultaneous method in adjustments. The fundamental constants of physics and chemistry, formerly treated via sequential adjustment by Birge (55), have been obtained for over two decades by simultaneous adjustment with the criterion of least squares (56, 57, 58). Experience derived from these studies of the physical constants will serve as the basis of the following discussion.

The species with fixed values in Table I correspond roughly to the "auxiliary constants" of physics (58). In this classification are included standard reference states, which are zero by definition, and experimental values of relatively high precision. Since some of these experimental values have uncertainties comparable with the data to be analyzed, both the fixed values and their uncertainties are substituted into the observations.

Error assignments must be expressed on as comparable a basis as possible, since they are to be used in weighting the observations. Assignments for the HF system are based on the random uncertainty supplemented in some cases by estimates of the systematic uncertainty. Reliable estimates of the latter appear to be particularly important in the present system due to the common occurrence of side reactions. It must be emphasized that the observations are usually a combination of at least three measurements including an energy calibration, an energy determination, and an analysis of the amount of chemical reaction.

Cohen and DuMond (58) stress the importance of over-determination in testing the observations. They suggest that consistency of the data as a whole is the ultimate test and that this test becomes more searching with each new path of measurement. It is this sort of testing which revealed the bias in early data for HF and prompted the new data analyzed herein. Over-determination in this system remains extensive even after elimination of those experiments which are probably biased. The selected observations include only two variables which are

involved in as few as three different experiments. The remainder are involved in from five to eight experiments.

Birge's ratio test may be used as a measure of the overall consistency of the data. Cohen and DuMond (58) note that this ratio consists of the quotient of the external or a posteriori error with the internal or a priori error. The a priori error is derived from the uncertainties of the individual observations, while the a posteriori error is based on their deviations from the adjustment. When the ratio is close to one, there is no strong evidence of the presence of systematic error. The ratio is evaluated from:

$$(\text{Birge's ratio})^2 = (\text{Chi})^2/(m-n) \qquad [4]$$

and

$$(\text{Chi})^2 = \sum_{i=1}^{m} (E_i'/U_i)^2, \qquad [5]$$

where E_i'/U_i is the weighted deviation or normalized residual.

Results of the ratio test are summarized in Table V. It may be concluded that there is no strong evidence of systematic error in HF-7, HF-6 and HF-4. Larger ratio values in the other adjustments suggest the possibility of systematic errors or underestimates of the a priori uncertainties. Sharp increases in the ratio occur with the inclusion of R12a and R12b due to their mutual inconsistency. In such cases, Cohen and DuMond (58) recommend the rejection of one or both observations upon location of a physical cause of unreliability in the experiment. Thus R12b is rejected without a probable physical cause, since our estimate of the uncertainty is based on inadequate information. Likewise, R12a is replaced with R12, which involves the later (and presumably more reliable) estimate of the uncertainty.

Individual deviations of the observations from the final adjustments by least squares and least sum are shown in the last four columns of Table III. Note that least sum assigns zero deviations to seven observations: R3, R7, R9, R12, R14, R18 and R20.

These same observations in least squares have small but non-zero deviations, the largest magnitude being 0.18 kcal/gfw for R20.

The largest weighted deviations are -2.21 (R16), +2.04 (R1), +1.87 (R17) and + 1.55 (R23). Most of the inconsistency is concentrated in these four observations. R1 is the direct measurement of HF(50 H_2O). R16, R17 and R23 are quite sensitive to HF(50 H_2O) and they tend toward a more negative value than the direct measurement. The strain would be partially relieved by increasing the uncertainty of R1 to 0.09 kcal/gfw, which includes a reasonable estimate for systematic uncertainty (20). Lack of comparable estimates for R16, R17 and R23 makes this undesirable.

Sequential adjustments of the observations are not attempted in this paper. Interested readers may use Table III to make their own adjustments. No two individuals will get the same answers, since the number of possible paths to each variable is quite large.

As stated by DuMond and Cohen (58), simultaneous adjustment is the logical approach in situations where there is considerable over-determination. However, least squares is not the only logical criterion in a particular situation. Least sum considers all of the data, yet provides a logical means of selecting a preferred subset just sufficient to determine the constants. DuMond and Cohen (58) imply, to the contrary, that such a selection must ignore all of the other data. Least sum is also less sensitive to outlying observations than is least squares. It is true that a least sum adjustment is not necessarily unique. There may be multiple solutions in a particular case, but this has not appeared in our systems. It is not likely in cases with considerable over-determination. We conclude that least sum is complementary with least squares and that the two should be used together whenever practical.

There is little reason to prefer one criterion over the other in the HF system. The only significant difference is that least sum agrees slightly better with the direct determinations of BF_3(g). Preference for least sum could be based on the

likelihood of outlying observations in this system. The difference is so small, however, that the least squares adjustment is preferred.

The selected values are summarized in Table VI, along with overall uncertainties estimated from twice the standard errors of the least squares adjustment. The user should be warned that the simple formula for propagation of errors (19) is only the first approximation when two or more of the selected values are combined in calculation of a third quantity. Correlation of errors is likely among some of the selected values; giving rise to additional terms, which may be either positive or negative, in the general formula for propagation of errors (58, 59). Interpretation of the derived uncertainties is further complicated by the input data being weighted in some cases by inclusion of reasonable bounds for the systematic error.

Values of ΔHf°_{298} for HF(n H_2O) should be obtained from that for HF(50 H_2O) using differences taken from the dilution curve of Parker (17). Additional error should be small, except for n > 1000. The values selected for HF(50 H_2O) and NaF(c) imply that ϕ_L for HF(50 H_2O) is about 0.15 ± 0.2 kcal/gfw less positive than tabulated by Parker (17). This difference arises partly from the heat of neutralization (28) and partly from other data.

The analysis reveals some paths which should receive further attention. Since NaF is so closely linked with HF(aq), it is most surprising that good, modern data are not available for the heat of neutralization of NaOH with HF or for the heat of dilution of NaF. Parker's estimate (17) for the latter is reasonable, but it should be verified by experimental data. New measurements of the heat of dilution of HF are also desirable in dilute solutions, and would be an accurate way of testing the calculated ϕ_L curve (cf. earlier discussion for R8). It has already been stressed that links such as R16 are very sensitive for testing the enthalpy of formation of HF(50 H_2O). Other links would add to the test. Finally, a thorough analysis of the data for HF(real gas) could

remove the non-ideality corrections as a source of uncertainty for HF(g).

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TABLE I

Species with Fixed Values of ΔHf°_{298}

Species	ΔHf°_{298}, kcal/gfw		Reference
B(c, β)	0.0	± 0.0	Defined
C(graphite)	0.0	± 0.0	Defined
$Cl_2(g)$	0.0	± 0.0	Defined
$CO_2(g)$	-94.051	± 0.030	(3)
$C_2N_2(g)$	73.8[illegible]	± 0.43	(3)
F(g)	18.86	± 0.3	(18, 49)
$F_2(g)$	0.0	± 0.0	Defined
H(g)	52.095	± 0.002	(3)
HCl(g)	-22.062	± 0.02	(3)
HCl(aq)	-39.932	± 0.02	(49, 50, 51)
$H^+(aq)$	0.0	± 0.0	Defined
$H_2(g)$	0.0	± 0.0	Defined
$H_2O(\ell)$	-68.315	± 0.01	(3)
$N_2(g)$	0.0	± 0.0	Defined
NaCl(c)	-98.32	± 0.06	(49, 52)
NaOH(aq)	-112.44	± 0.04	(49, 52)
$Na^+(aq)$	-57.47	± 0.04	(49, 52)
$O_2(g)$	0.0	± 0.0	Defined
S(c, rh)	0.0	± 0.0	Defined
$SF_6(g)$	-291.77	± 0.24	(53)

TABLE II

Observations Used for Simultaneous Adjustments

No.	Reaction	Adjustment No. →	$\Delta H_{f,298}^{\circ}$, kcal/gfw HF-7	HF-6	HF-5	HF-4	HF-3	HF-2	HF-1
1.	0.5 $H_2(g)$+0.5 $F_2(g)$ → HF(50 H_2O)		-76.68±0.05						
2.	HF(g) → H(g) + F(g)		136.051±0.3						
3.	HF(g)+NaOH(aq) → NaF(c) + $H_2O(\ell)$		-28.24±0.10	±0.05	±0.05	±0.05	±0.05	±0.05	±0.05
4.	HF(50 H_2O)+NaCl(c) → NaF(c)+HCl(aq)		-2.41±0.07						
5.	HF(g)+NaCl(c) → NaF(c) + HCl(g)		3.81±0.25						
6.	0.5 $F_2(g)$+NaCl(c) → NaF(c)+0.5 $Cl_2(g)$		-39.30±0.4						omit
7.	HF(50 H_2O)+NaOH(aq) → NaF(c)+$H_2O(\ell)$		-16.57±0.05		omit	omit	omit	omit	omit
8.	H^+(aq)+NaF(c) → HF(50 H_2O)+Na^+(aq)		3.414±0.3						
9.	C(graph)+2$F_2(g)$ → $CF_4(g)$		-223.05±0.18						
10.	C_2F_4(polymer)+$O_2(g)$+2$H_2O(\ell)$ → 4HF(50 H_2O)+2$CO_2(g)$		-160.62±0.9						
11.	C_2F_4(polymer)+$O_2(g)$ → $CF_4(g)$+$CO_2(g)$		-118.8±0.5						
12.	C_2F_4(polymer)+2$F_2(g)$ → 2$CF_4(g)$		-247.85±0.3		12b		12,12b*	12a,12b	12a,12b
13.	C(graph)+2$F_2(g)$ → $CF_4(g)$		-222.87±0.38						
14.	$CF_4(g)$+2$H_2O(\ell)$ → 4HF(50 H_2O)+$CO_2(g)$		-41.506±0.3						
15.	8$NF_3(g)$+3$C_2N_2(g)$ → 6$CF_4(g)$+7$N_2(g)$		-1308.8±1.3						
16.	$NF_3(g)$+1.5 $H_2(g)$ → 2HF(50 H_2O)+0.5$N_2(g)$		-199.4±0.22						
17.	2$NF_3(g)$+S(c, rh) → $SF_6(g)$+$N_2(g)$		-228.26±0.25						
18.	$NF_3(g)$ → 0.5 $N_2(g)$+1.5 $F_2(g)$		31.44±0.3						
19.	$NF_3(g)$+B(c, β) → $BF_3(g)$+0.5$N_2(g)$		-239.46±1.2						omit
20.	1.5 $F_2(g)$+B(c, β) → $BF_3(g)$		-271.6±0.9						
21.	1.5 $F_2(g)$+B(c, β) → $BF_3(g)$		-271.65±0.22						
22.	1.5 $F_2(g)$+B(c, β) → $BF_3(g)$		-271.03±0.51						
23.	3HF(50 H_2O)+B(c, β)+0.75 $O_2(g)$ → $BF_3(g)$+1.5 $H_2O(\ell)$		-142.77±0.5				±0.3	±0.3	±0.3

*Uncertainty for Reaction 12b in HF-3 is assigned as 0.4 rather than 0.2 kcal/gfw.

TABLE III. Relationships among the Variables as Obtained from the Input for the Final Adjustment(HF-7)

i	Relationships among the ΔHf°_{298} Variables	$R_i \pm U_i$ kcal/gfw	Dev.* Least Squares	Dev./U_i Least Squares	Dev.* Least Sum	Dev./U_i Least Sum
1.	HF(50 H_2O)	-76.680±0.050	0.102	2.035	0.104	2.075
2.	-HF(g)	65.096±0.424	-0.040	-0.094	-0.018	-0.042
3.	NaF(c) - HF(g)	-72.365±0.108	0.015	0.135	0.0	0.0
4.	NaF(c) - HF(50 H_2O)	-60.798±0.094	-0.064	-0.680	-0.103	-1.096
5.	NaF(c) - HF(g)	-72.448±0.258	-0.068	-0.265	-0.083	-0.322
6.	NaF(c)	-137.620±0.404	-0.104	-0.258	-0.141	-0.350
7.	NaF(c) - HF(50 H_2O)	-60.695±0.065	0.039	0.600	0.0	0.0
8.	-[NaF(c) - HF(50 H_2O)]	60.884±0.303	0.150	0.496	0.189	0.624
9.	CF_4(g)	-223.050±0.180	-0.015	-0.083	0.0	0.0
10.	4 x HF(50 H_2O) - C_2F_4(polymer)	-109.148±0.902	-0.239	-0.265	-0.263	-0.292
11.	CF_4(g) - C_2F_4(polymer)	-24.749±0.501	0.068	0.136	0.051	0.102
12.	2 x CF_4(g) - C_2F_4(polymer)	-247.850±0.300	0.002	0.007	0.0	0.0
13.	CF_4(g)	-222.870±0.380	0.165	0.434	0.180	0.474
14.	4 x HF(50 H_2O) - CF_4(g)	-84.085±0.302	0.007	0.023	0.0	0.0
15.	6 x CF_4(g) - 8 x NF_3(g)	-1087.280±1.831	-0.516	-0.282	-0.500	-0.273
16.	3 x HF(50 H_2O) - NF_3(g)	-199.400±0.220	-0.486	-2.207	-0.489	-2.222
17.	-2 x NF_3(g)	63.510±0.347	0.648	1.871	0.630	1.816
18.	-NF_3(g)	31.440±0.300	0.009	0.030	0.0	0.0
19.	BF_3(g) - NF_3(g)	-239.460±1.200	0.529	0.441	0.700	0.583
20.	BF_3(g)	-271.600±0.900	-0.180	-0.200	0.0	0.0
21.	BF_3(g)	-271.650±0.220	-0.230	-1.045	-0.050	-0.227
22.	BF_3(g)	-271.030±0.510	0.390	0.765	0.570	1.118
23.	BF_3(g) - 3 x HF(50 H_2O)	-40.297±0.500	0.777	1.554	0.952	1.904
		Sum of absolute values =		13.906		13.517
		Sum of squares =		18.436		20.013

*Dev. = E_i' = observed value minus calculated value in kcal/gfw.

TABLE IV

Values of ΔHf°_{298} from the Simultaneous Adjustments

Species	Least Sum kcal/gfw HF-7	Least Squares* kcal/gfw HF-7	HF-6	HF-5	HF-4	HF-3	HF-2	HF-1
HF(g)	-65.114	-65.136	-65.144	-65.209	-65.210	-65.224	-65.224	-65.223
		0.122	0.094	0.132	0.119	0.138	0.188	0.204
HF(50 H_2O)	-76.784	-76.782	-76.782	-76.779	-76.781	-76.795	-76.796	-76.796
		0.040	0.040	0.045	0.040	0.046	0.062	0.067
NaF(c)	-137.479	-137.516	-137.515	-137.581	-137.583	-137.596	-137.597	-137.596
		0.068	0.068	0.111	0.100	0.116	0.158	0.173
BF_3(g)	-271.600	-271.420	-271.420	-271.419	-271.420	-271.285	-271.286	-271.293
		0.195	0.195	0.218	0.196	0.210	0.285	0.307
NF_3(g)	-31.440	-31.431	-31.431	-31.414	-31.430	-31.437	-31.442	-31.438
		0.124	0.124	0.138	0.125	0.145	0.197	0.211
CF_4(g)	-223.050	-223.035	-223.035	-222.949	-223.034	-223.020	-223.044	-223.043
		0.140	0.140	0.155	0.141	0.164	0.219	0.234
C_2F_4(polymer)	-198.250	-198.218	-198.218	-198.900	-198.216	-198.476	-198.284	-198.283
		0.351	0.351	0.354	0.353	0.388	0.447	0.478

*The number immediately below ΔHf°_{298} is the standard error (54) as based on the overall consistency of the least squares adjustment.

TABLE V

Statistical Summary of the Simultaneous Adjustments

Adjustment No.	Unknowns n	Observations* m	Degrees of Freedom(m-n)	$(Chi)^2$	Birge's Ratio**
HF-7	7	23	16	18.44	1.073
(Least Sum)	7	23	16	(20.01)	(1.118)
HF-6	7	23	16	18.45	1.074
HF-5	7	22	15	21.46	1.196
HF-4	7	22	15	17.46	1.079
HF-3	7	23	16	25.37	1.259
HF-2	7	23	16	46.77	1.710
HF-1	7	21	14	46.66	1.826

* Changes in the observations are shown in Table II.

**See Equations 4 and 5.

TABLE VI

Selected Values of ΔHf°_{298}

Species	ΔHf°_{298}, kcal/gfw
HF(g)	-65.14±0.2
HF(50 H_2O)	-76.78±0.1
HF(∞ H_2O)	-79.82±0.2
NaF(c)	-137.52±0.15
BF_3(g)	-271.42±0.4
NF_3(g)	-31.43±0.3
CF_4(g)	-223.04±0.3
C_2F_4(polymer)	-198.2 ±0.7

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13 ABSTRACT

Supplement No. 30 to the JANAF Thermochemical Tables was completed and sent to the printers on December 27, 1968. This Supplement contains the new element calcium and its fluoride, revisions of several ionic species due to a determination of the electron affinity of BO_2, and revisions of several fluorides due to a new table for HF.

A complete description of the measurements used in the simultaneous solution analysis of the interrelated HF heat of formation data is given in the Appendix.

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KEY WORDS	LINK A		LINK B		LINK C	
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Exhaust Species						
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