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Fluorine Bomb Calorimetry. XXII.
The Enthalpy of Formation of Aluminum Trifluoride[1]

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The energy of formation of aluminum trifluoride was measured by direct combination of the elements in a bomb calorimeter. The recommended standard enthalpy of formation, $\Delta H_f{}^\circ{}_{298.15}(\mathrm{AlF_3}, \mathrm{c})$, is -360.7 ± 0.3 kcal mole^{-1}. A comparison of results obtained by bomb and reaction calorimetry supports a recently proposed $\Delta H_f{}^\circ(\mathrm{PbF_2}, \mathrm{c})$ value of -161.8 kcal mole^{-1}.

Introduction

This investigation is part of a systematic effort to reduce uncertainties in the thermochemical data for selected metal fluorides by the application of recently developed techniques for calorimetric combustion of metals in fluorine. Several *indirect* determinations of the standard enthalpy of formation of aluminum trifluoride, $\Delta H_f{}^\circ(\mathrm{AlF_3})$, have been carried out by reaction calorimetry[2] and high-temperature equilibrium studies.[3] Domalski and Armstrong[4] recently redetermined this quantity by the *direct* method. Their results did not eliminate the discrepancies among the earlier ones. Because Domalski and Armstrong burned fairly large quantities of Teflon along with aluminum, it was felt that an independent fluorine bomb calorimetric investigation without this source of uncertainty might substantially improve the accuracy of the $\Delta H_f{}^\circ(\mathrm{AlF_3})$ value.

Experimental Section

Materials. Aluminum.—A high-purity, vacuum-zone-refined aluminum ingot was obtained from Materials Research Corp. A part of the ingot was rolled into 5-mil foil, and the rest was converted to filings in a helium-atmosphere glove box. Chemical analysis showed the following significant impurities (in ppm): O, 200; C, 84; N, 17; Si, 21. Spectrochemical analysis showed no significant (<100 ppm) metallic impurities. Aluminum foil and filings were preconditioned by exposure to several atmospheres pressure of fluorine before the bomb combustions; typical weight gains were 0.1 mg g^{-1}.

Fluorine.—Fluorine was purified by distillation.[5] Its impurity content was less than 0.1%.

Aluminum Fluoride.—Powdered, anhydrous $\mathrm{AlF_3}$ was obtained from the A. D. Mackay Co. and contained approximately 0.2% oxygen, as determined by the $\mathrm{KBrF_4}$ method.[6] Repeated autoclaving of this material with chlorine trifluoride at 300° under autogenous pressure effectively removed the oxygen impurity.

Apparatus and Procedure.—The calorimetric system, ANL-R1, has been described previously.[7] The bomb, designated Ni-4B, had an internal volume of 365 ml. It was lined with tamped $\mathrm{AlF_3}$ powder in a manner similar to that described for magnesium combustions.[8] The calorimetric sample was in the form of 5-mil foil which was folded into a basket to contain aluminum filings. Suspension of the basket from a nickel post facilitated ignition by minimizing contact of the basket with the bomb. Combustion was initiated by electrical ignition of a cadmium-foil fuse in contact with the aluminum filings. A minimum initial fluorine pressure of 15 atm was required for satisfactory combustions. After each combustion, the portions of the liner which had come in contact with burning aluminum were removed, and the unburned aluminum was determined by measurement of the hydrogen evolved by acid.[9] The hydrogen evolution and collection system was calibrated by dissolving representative amounts of aluminum. The reaction product was identified by its X-ray powder pattern as rhombohedral $\mathrm{AlF_3}$. No evidence of interaction between $\mathrm{AlF_3}$ and $\mathrm{CdF_2}$ (from the combustion of the cadmium fuse) was found.

Results

Table I gives the results of six combustions in which at least 80% of the aluminum burned. The order of entries in the table and interpretation of symbols are similar to those described in ref 9. For the calculation of item 3, the value of $\mathcal{E}$(calor), 3435.52 ± 0.38 cal deg^{-1}, was obtained from a series of five benzoic acid calibration experiments which immediately followed the aluminum combustions. For the calculation of item 4, the following values were used (cal deg^{-1} mole^{-1}): C_p: Al, 5.82;[10] Ni, 6.23;[10] Cd, 6.21;[10] $\mathrm{AlF_3}$, 17.95;[10] $\mathrm{CdF_2}$, 15.8;[9] and C_v: $\mathrm{F_2}$, 5.50.[11] The contents of the bomb in addition to the sample, fuse, and fluorine were: 390.6 g of nickel, and 295.1, 286.1, 289.6, 272.0, 267.2, or 249.7 g of $\mathrm{AlF_3}$ for the six experiments as listed. For calculation of item 7, $\Delta H_f{}^\circ(\mathrm{CdF_2})$ was taken as -167.4 kcal mole^{-1}.[9] The impurity corrections were made with the assumption that oxygen was present as $\mathrm{Al_2O_3}$, carbon as $\mathrm{Al_4C_3}$, nitrogen as AlN, and silicon was dissolved in its elemental state without a significant heat effect. The following $\Delta H_f{}^\circ$ values were used (in kcal mole^{-1}):

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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TABLE I

RESULTS OF ALUMINUM COMBUSTION EXPERIMENTS[a]

	Combustion no.					
	3	5	6	7	8	9
1. m', g (% burned)	0.3007_6 (92.2)	0.4274_2 (92.2)	0.5210_0 (93.8)	0.4937_6 (85.3)	0.3782_8 (88.9)	0.5071_7 (89.7)
2. Δt_c, deg	1.21176	1.68917	2.04937	1.95157	1.51632	2.01678
3. $\mathcal{E}$(calor)($-\Delta t_c$), cal	−4163.0	−5803.2	−7040.7	−6704.7	−5209.3	−6928.7
4. $\Delta E_{\text{contents}}$, cal	−128.3	−175.0	−214.0	−196.3	−150.5	−193.0
5. $\Delta E_{\text{ignition}}$, cal	1.8	1.6	1.5	1.7	1.6	1.4
6. ΔE_{gas}, cal	−1.1	−1.7	−1.8	−1.7	−1.3	−1.9
7. ΔE_{fuse}, cal	279.7	277.4	303.9	303.5	314.0	358.9
8. $\Delta E_c°/M$, cal g^{-1}	−13,335.9	−13,337.9	−13,341.8	−13,361.8	−13,338.0	−13,335.4

[a] Mean $\Delta E_c°/M$(sample) = 13,341.8 cal g^{-1}; standard deviation of mean = 4.0 cal g^{-1} or 0.03%; impurity correction = −4.4 cal g^{-1}; $\Delta E_c°/M$(Al) = −13,346.2 cal g^{-1}.

Al_2O_3, −400.4;[12] Al_4C_3, −30.9;[13] AlN, −76.0;[12] SiF_4, −385.4;[14] and CF_4, −222.8.[15] An estimated uncertainty of ±0.4 cal g^{-1} in the impurity correction includes allowances for variations in the analyses and the assigned chemical states of the impurities. A standard enthalpy of formation of −361.0 kcal mole^{-1} was derived for the reaction

$$\mathrm{Al(c)} + {}^3/_2\mathrm{F_2(g)} \longrightarrow \mathrm{AlF_3(c)} \qquad (1)$$

with the reactants and products in their standard states at 25°. An uncertainty interval of ±0.3 kcal mole^{-1}, equal to twice the combined standard deviations of the combustion and calibration experiments plus twice the uncertainty in the impurity corrections, is attached to these values.

Discussion

The comb calorimetric determination of $\Delta H_f°(AlF_3)$ by Domalski and Armstrong[4] yielded a value of −360.4 kcal mole^{-1}. Despite an experimental precision of about ±0.3 kcal mole^{-1}, an uncertainty interval of ±1.6 kcal mole^{-1} was assigned to this value, apparently to encompass the results from indirect determinations. Because of the good agreement between two independent, direct determinations of $\Delta H_f°(AlF_3)$, the value of −360.7 kcal mole^{-1} is recommended as the standard enthalpy for reaction 1. The corresponding $\Delta E_f°$ and $\Delta G_f°$ values are calculated to be −360.8 and −351.7 kcal mole^{-1}, respectively. The uncertainty interval of ±0.3 kcal mole^{-1} encompasses the results of both direct determinations. The entropy values, $S°_{298}$, used to derive $\Delta G_f°$ are (in cal deg^{-1} mole^{-1}):[16] Al, 6.77; F_2, 48.49; and AlF_3, 15.89.

Calorimetric determinations by indirect reaction were based on the reaction

$$\mathrm{Al(c)} + {}^3/_2\mathrm{PbF_2(c)} \longrightarrow \mathrm{AlF_3(c)} + {}^3/_2\mathrm{Pb(c)} \qquad (2)$$

for which enthalpies of −118.53[2a] and −117.7[2b] kcal mole^{-1} have been measured. However, there have been no direct determinations of $\Delta H_f°(PbF_2)$, and most of the indirectly derived values are based on the uncertain enthalpy of formation of aqueous HF. By combining the average enthalpy for reaction 2 with $\Delta H_f°(AlF_3, c)$ = −360.7 ± 0.3 kcal mole^{-1}, one obtains the value $\Delta H_f°(PbF_2, c)$ = − 161.7 ± 0.3 kcal mole^{-1}. The two major current compilations vary markedly in their selected "best" $\Delta H_f°(PbF_2)$ values: −158.7[17] and −161.8[18] kcal mole^{-1}. Clearly, the present work favors the latter value. Furthermore, our reevaluation of all the available information, which includes additional investigations[19–21] not covered by the JANAF tables,[18] but excludes derivations based on $\Delta H_f°(AlF_3)$, also leads to values near −161.8 kcal mole^{-1}. The recommended values for the enthalpies of formation of aluminum trifluoride and lead difluoride are entirely consistent which implicitly shows that the results obtained by direct fluorination are in accord with those obtained by using PbF_2 as a fluorinating agent.

In contrast to the marked consistency of $\Delta H_f°(AlF_3)$ values derived from calorimetric determinations, the value derived from a high-temperature equilibrium study[3] of the reaction

$$\mathrm{AlF_3(c)} + {}^3/_2\mathrm{H_2O(g)} = {}^1/_2\mathrm{Al_2O_3(c)} + 3\mathrm{HF(g)} \qquad (3)$$

is −357.7 ± 0.5 kcal mole^{-1}. A critical reevaluation failed to indicate a possible cause for the discordance. One may, however, question whether the stated stoichiometry is valid near 1000°; interaction between Al_2O_3 and AlF_3 at elevated temperatures has been reported.[22,23]

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