

The enthalpy of formation of FeF_3 by fluorine bomb calorimetry^a

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The energy of combustion of iron in fluorine was measured in a bomb calorimeter. The standard enthalpy of formation of crystalline FeF_3 , $\Delta H_f^\circ(\text{FeF}_3, \text{c}, 298.15 \text{ K})$, was derived to be $-(989.6 \pm 2.2) \text{ kJ mol}^{-1}$.

1. Introduction

The enthalpy of formation of iron (III) fluoride, FeF_3 , beside being of interest in its own right, is an auxiliary quantity needed to determine the enthalpies of formation of iron-containing compounds by fluorine bomb calorimetry. No reliable calorimetric determination of $\Delta H_f^\circ(\text{FeF}_3)$ existed at the time this work was undertaken. Since our research program included studies on several iron-containing compounds, we needed to determine the enthalpy of formation of FeF_3 .

2. Experimental

CALORIMETRIC SYSTEM

The bomb calorimeter, laboratory designation ANL-R-3, employed in this study was of the rotating-bomb type similar to that described by Hubbard, Katz, and Waddington.⁽¹⁾ The single-chambered combustion bomb employed in this study was similar to that described by Rudzitis, Feder, and Hubbard.⁽²⁾ Calorimetric temperatures were measured with a quartz-crystal thermometer (Hewlett-Packard Model 2801-A). The calorimetric system was calibrated by combustion in oxygen of benzoic acid (National Bureau of Standards Sample 39i), whose certified energy of combustion under prescribed conditions is $-(26.434 \pm 0.003) \text{ kJ g}^{-1}$. Four calibration experiments, conducted before the Fe combustions, gave an average value and standard deviation of the mean for $\varepsilon(\text{calor})$, the energy equivalent of the calorimetric system, of $(14070.2 \pm 1.2) \text{ J K}^{-1}$.

MATERIALS

The iron used in the calorimetric experiments was Puratronic[®]-grade, 0.5 mm thick foil (Johnson Matthey Chemicals Ltd., Batch No. W. 1339/A). The foil was cleaned of

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any surface oxidation by treatment with 6 mol kg⁻¹ HCl solution, rinsed with H₂O and acetone, and quickly transferred to a helium-atmosphere glovebox where it was stored for the duration of the experiments. Analysis showed the following mass fractions ($\times 10^6$) of impurities: O, 80; C, 500; N, 113; H, <10; Si, 7; Mg, 2; Ca, 1; and Mn, 1.

Tungsten foils of thickness 0.127 mm and 0.025 mm (Schwarzkopf Development Corporation) were used as auxiliary combustion aids. Five combustions of the 0.127 mm foil in F₂ gave an average value and standard deviation of the mean for the standard energy of combustion of the tungsten sample, $\Delta U_c^\circ/M(\text{sample})$, of $-(9373.3 \pm 2.2) \text{ J g}^{-1}$. Three combustions of the 0.027 mm foil gave $\Delta U_c^\circ/M(\text{sample}) = -(9373.75 \pm 0.63) \text{ J g}^{-1}$. Since these results are in good agreement, the combined average, $-(9373.5 \pm 1.3) \text{ J g}^{-1}$, was used for the energy of combustion of the tungsten sample.

Purified fluorine (99.99 moles per cent F₂) was prepared by distillation of commercial fluorine in a low-temperature still.⁽³⁾

OBSERVATIONS AND PROCEDURES

Preliminary experiments established that the Fe foil was not attacked by high-pressure fluorine; therefore, a single-chambered bomb could be used for the combustions. These experiments also established that the ignited Fe sample became molten and alloyed with any nickel bomb parts it touched. The iron fluoride produced in these experiments, which consisted mostly of a melt on top of the unreacted iron, contained a large mole fraction (approximately 20 per cent) of FeF₂ as well as the desired FeF₃. Since this problem was similar to that experienced with the combustion of uranium in F₂,⁽⁴⁾ a combustion procedure identical to that used to solve the problem with uranium was tried and found to be satisfactory for iron. This procedure consisted of using three pieces of tungsten foil attached, one above the other, to a nickel electrode. The Fe was placed on the top (0.127 mm) foil, and during combustion successively burned through the top foil and the two lower (0.025 mm) foils. The tungsten foils, beside providing auxiliary energy, prevented the molten iron from coming into contact with the nickel. In all acceptable combustions, the iron reacted completely producing a finely powdered product which condensed on the bomb surfaces. This powder, although largely FeF₃, still contained some FeF₂.

The calorimetric procedures were as follows. The combustion bomb was taken into the glovebox where the weighed tungsten foils were attached to an electrode by securing them between nickel retaining nuts. A tungsten fuse wire (0.076 mm in diameter) was connected between this post and another electrode. Weighed pieces of the Fe foil were placed on the top tungsten foil. A weighed nickel crucible was placed under the foils. The bomb was assembled, removed from the glovebox, evacuated, charged to 1825 kPa pressure with fluorine, and placed in the calorimeter. After the forerating period, the fuse wire was ignited by discharging through it a 100 μF capacitor charged to 90 V.

Following the combustion, the bomb was removed from the calorimeter, evacuated, and opened. The solid product of the combustions was a pale-green

powder which was distributed over the inside surfaces of the bomb. X-ray diffraction analysis of this powder showed it to be FeF_3 ⁽⁵⁾ with a small amount of FeF_2 . The FeF_2 content of the residue was determined as follows. The solid combustion residue was washed from the bomb surfaces into a solution consisting of a known amount of excess $\text{Ce}(\text{SO}_4)_2$ in $2.5 \text{ mol kg}^{-1} \text{ H}_2\text{SO}_4$ and $0.2 \text{ mol kg}^{-1} \text{ H}_3\text{BO}_3$. The Ce^{4+} in excess of that required to oxidize the Fe^{2+} to Fe^{3+} was back-titrated with standard Fe^{2+} , using Ferroin as an indicator. Preliminary experiments, in which known mixtures of FeF_2 and FeF_3 were used, had established that the F^- ion is complexed by the H_3BO_3 and does not interfere with the titrations.

Pieces of unreacted W foil and wire, which were under the retaining nuts, were collected and weighed. Any spattered droplets of W from the fuse wire were chipped loose from the bomb surfaces and weighed. The Ni crucible did not undergo any detectable change in mass during the combustions.

3. Results

The results of six combustions of iron in fluorine, according to the reaction



are presented in table 1. In the table $\Delta U(\text{FeF}_2)$ is the correction for the hypothetical conversion of FeF_2 to FeF_3 . The other entries in the table have the usual significance.⁽⁶⁾ The corrections to standard states were applied in the usual manner.⁽⁷⁾

The following auxiliary data at 298.15 K were used in the reduction to standard states: for $c_p/\text{J K}^{-1} \text{ g}^{-1}$: Fe, 0.450;⁽⁸⁾ W, 0.132;⁽⁸⁾ Ni, 0.444;⁽⁸⁾ and FeF_3 , 0.806;⁽⁹⁾ for $C_v/\text{J K}^{-1} \text{ mol}^{-1}$, F_2 , 22.99;⁽⁹⁾ and WF_6 , 110.7;⁽⁸⁾ and for the density $\rho/\text{g cm}^{-3}$: Fe, 7.86; W, 19.3; Ni, 8.90; and FeF_3 , 3.18.

For the calculation of $\Delta U(\text{gas})$, μ in the equation of state $pV = nRT(1 - \mu p)$ and $(\partial U/\partial p)_T$ were estimated by the method of Hirschfelder *et al.*⁽¹⁰⁾ from the

TABLE 1. Results of Fe combustions

$m(\text{Fe reacted})/\text{g}$	0.20296	0.20380	0.20094	0.20058	0.20348	0.19902
$m(\text{W reacted})/\text{g}$	2.10165	2.00157	2.01283	2.13617	1.96355	2.06630
$m(\text{FeF}_2 \text{ formed})/\text{g}$	0.01363	0.01670	0.02005	0.01065	0.03732	0.01346
$\Delta\theta_c/\text{K}$	1.64822	1.58226	1.58513	1.66895	1.55193	1.61979
$e(\text{calor})(-\Delta\theta_c)/\text{J}$	-23190.8	-22262.7	-22303.1	-23482.5	-21836.0	-22790.8
$\Delta U(\text{contents})/\text{J}$	-57.6	-55.3	-55.4	-58.4	-54.3	-56.7
$\Delta U(\text{gas})/\text{J}$	0.8	0.7	0.8	0.9	0.7	0.8
$\Delta U(\text{ignition})/\text{J}$	0.4	0.4	0.4	0.4	0.4	0.4
$\Delta U(\text{W})/\text{J}$	19699.8	18761.7	18867.3	20023.4	18405.3	19368.5
$\Delta U(\text{FeF}_2)/\text{J}$	-41.0	-50.3	-60.4	-32.1	-112.4	-40.5
$\{\Delta U_c^\circ/M(\text{sample})\}/\text{J g}^{-1}$	-17680.3	-17691.4	-17669.0	-17690.2	-17674.0	-17678.1
$\langle \Delta U_c^\circ/M(\text{sample}) \rangle = -(17680.5 \pm 3.6) \text{ J g}^{-1} \text{ }^a$						
Impurity correction = $(26.5 \pm 3.1) \text{ J g}^{-1} \text{ }^a$						
$\Delta U_c^\circ/M(\text{Fe}) = -(17654 \pm 40) \text{ J g}^{-1} \text{ }^b$						

^a \pm Standard deviation of the mean.

^b \pm Uncertainty interval.

intermolecular force constants for F_2 ,⁽¹¹⁾ and WF_6 .⁽¹²⁾ The volume of the empty bomb was 0.3059 dm^3 .

For calculation of $\Delta U(\text{FeF}_2)$ the energy of combustion of FeF_2 in fluorine to form FeF_3 was taken to be $-282.6 \text{ kJ mol}^{-1}$ based on $\Delta H_f^\circ(\text{FeF}_2, \text{c}) = -705.8 \text{ kJ mol}^{-1}$.⁽⁹⁾

The thermal correction for the impurities in the sample is based on the assumption that the C, O, N, and Si impurities were initially present as Fe_3C , Fe_3O_4 , Fe_4N , and FeSi , respectively, and formed CF_4 , O_2 , N_2 , and SiF_4 , respectively, during combustion. The metallic impurities were such that no thermal correction was required. The dominant contribution to the impurity correction is from the carbon, for which the correction is 31.0 J g^{-1} .

The derived results for the combustion of iron in fluorine to form FeF_3 are given in table 2. The molar mass of Fe was taken to be $55.847 \text{ g mol}^{-1}$. The entropies,

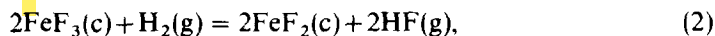
TABLE 2. Derived results at 298.15 K

$\Delta U_c^\circ(\text{Fe}, \text{c}) = \Delta U_f^\circ(\text{FeF}_3, \text{c}) = -(985.9 \pm 2.2) \text{ kJ mol}^{-1}$
$\Delta H_c^\circ(\text{Fe}, \text{c}) = \Delta H_f^\circ(\text{FeF}_3, \text{c}) = -(989.6 \pm 2.2) \text{ kJ mol}^{-1}$
$\Delta S_f^\circ(\text{FeF}_3, \text{c}) = -(233.1 \pm 8.4) \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta G_f^\circ(\text{FeF}_3, \text{c}) = -(920.1 \pm 3.3) \text{ kJ mol}^{-1}$

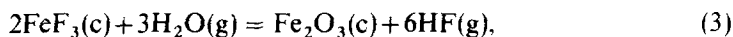
$S^\circ(298.15 \text{ K})$, of Fe ,⁽⁹⁾ F_2 ,⁽⁹⁾ and FeF_3 ⁽⁹⁾ were taken to be (27.32 ± 0.13) , (202.69 ± 0.04) , and $(98.3 \pm 8.4) \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The uncertainties are uncertainty intervals⁽¹³⁾ equal to twice the final overall standard deviation. The overall uncertainty of $\pm 40 \text{ J g}^{-1}$ includes major contributions from the following sources: the tungsten auxiliary an uncertainty of $\pm 27 \text{ J g}^{-1}$; the estimated uncertainty of $\pm 21 \text{ kJ mol}^{-1}$ in the enthalpy of formation of FeF_2 , $\pm 21 \text{ J g}^{-1}$; the analytical uncertainty on the FeF_2 analysis, $\pm 14 \text{ J g}^{-1}$; the contributions from impurities, $\pm 6 \text{ J g}^{-1}$; and the experimental standard deviation, $\pm 7 \text{ J g}^{-1}$.

4. Discussion

The value derived in this study for $\Delta H_f^\circ(\text{FeF}_3, \text{c}, 298.15 \text{ K})$, $-(989.6 \pm 2.2) \text{ kJ mol}^{-1}$, differs significantly from that selected in the JANAF Thermochemical Tables,⁽⁹⁾ and from that reported in the e.m.f. studies of Schaefer.⁽¹⁴⁾ The JANAF selection is based on earlier equilibrium results. Jellinek and Rudat⁽¹⁵⁾ measured equilibrium pressures for the reaction:



from which JANAF derived values for $\Delta H_f^\circ(\text{FeF}_3)$ of -1056 and $-1043 \text{ kJ mol}^{-1}$ by the third- and second-law methods, respectively. Domange⁽¹⁶⁾ measured equilibrium pressures for the reaction:

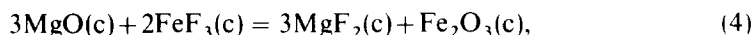


from which JANAF derived $\Delta H_f^\circ(\text{FeF}_3) = -993 \text{ kJ mol}^{-1}$ by the third-law method.

This latter result we note is in good agreement with our result. JANAF, however, selected the value:

$$\Delta H_f^\circ(\text{FeF}_3, \text{c}) = -(1042 \pm 13) \text{ kJ mol}^{-1}.$$

Schaefer⁽¹⁴⁾ reported e.m.f. measurements on the reaction:



from which he derived $\Delta H_f^\circ(\text{FeF}_3, 298.15 \text{ K}) = -1039 \text{ kJ mol}^{-1}$ by the third-law method. Schaefer did not report a second-law value. Since agreement between $\Delta H^\circ(298.15 \text{ K})$ values derived by the second- and third-law methods is often used as an argument for the reliability of equilibrium and e.m.f. results, we calculated a second-law value from his data for comparison purposes. The value was $-1185 \text{ kJ mol}^{-1}$. The large difference, 146 kJ mol^{-1} , between the second- and third-law values derived from Schaefer's e.m.f.'s suggests that these results are significantly in error.

After the present work was completed, we became aware of a value for $\Delta H_f^\circ(\text{FeF}_3, \text{c})$ which was reported by Pervov *et al.*⁽¹⁷⁾ This result, $-(990.8 \pm 2.1) \text{ kJ mol}^{-1}$, also based on fluorine bomb calorimetry, was reported only in an abstract. As a result, we do not have full knowledge of the experimental procedures. The value, however, is in excellent agreement with our result; we, therefore, feel that $\Delta H_f^\circ(\text{FeF}_3, \text{c})$ has now been firmly established by fluorine bomb calorimetry.

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