RI 8096

Bureau of Mines Report of Investigations/1975

Free Energies of Formation of Ferrous and Ferric Fluoride by Electromotive Force Measurements

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8096

Free Energies of Formation of Ferrous and Ferric Fluoride by Electromotive Force Measurements

By Seth C. Schaefer
Albany Metallurgy Research Center, Albany, Oreg.

March 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Thomas S. Kleppe, Secretary
Jack W. Carlson, Assistant Secretary—Energy and Minerals
BUREAU OF MINES
Thomas V. Falkie, Director

This publication has been cataloged as follows:

Schaefer, Seth C

Free energies of formation of ferrous and ferric fluoride by electromotive force measurements, by Seth C. Schaefer. [Washington] U.S. Bureau of Mines [1975]

14 p. illus., tables. (U.S. Bureau of Mines. Report of investigations 8096)

Includes bibliography.

1. Ferrous fluoride. 2. Ferric fluoride. I. U.S. Bureau of Mines. II. Title. (Series)

TN23.U7 no. 8096 622.06173

U.S. Dept. of the Int. Library

CONTENTS

ILLUSTRATIONS

TABLES

FREE ENERGIES OF FORMATION OF FERROUS AND FERRIC FLUORIDE BY ELECTROMOTIVE FORCE MEASUREMENTS

by

Seth C. Schaefer[1]

ABSTRACT

The Bureau of Mines studied the standard free energies[2] of formation of ferrous fluoride (FeF_2) and ferric fluoride (FeF_3) with high-temperature galvanic cells employing calcium fluoride doped with 1 mole-pct yttrium fluoride as the electrolyte.

A free-energy change for the cell reaction

$$Fe(s) + NiF_2(s) = FeF_2(s) + Ni(s) \tag{1}$$

together with the standard free energy of formation of nickel fluoride yields a standard free energy of formation of ferrous fluoride from the elements of

$$\Delta Gf^\circ = -168.74 + 30.63 \times 10^{-3}T \pm 0.41 \text{ kcal/mole } (897\text{-}1{,}098 \text{ K}). \tag{2}$$

Combining the standard free energies of formation of magnesium fluoride, ferric oxide, and magnesium oxide with the free-energy change for the overall cell reaction

$$3MgO(s) + 2FeF_3(s) = 3MgF_2(s) + Fe_2O_3(s) \tag{3}$$

gives a standard free energy of formation of ferric fluoride from the elements as

$$\Delta Gf^\circ = -281.45 + 90.46 \times 10^{-3}T \pm 0.67 \text{ kcal/mole } (880\text{-}935 \text{ K}). \tag{4}$$

Free energies and equilibrium fluorine pressures for the two univariant equilibria of the Fe-F system are tabulated and illustrated.

---

[1] Metallurgist, Thermodynamics Laboratory.

[2] The term free energy refers to the Gibbs free energy or Gibbs function and is designated by the symbol G.

INTRODUCTION

Thermodynamic properties of iron fluoride compounds were investigated by the Bureau of Mines as part of a continuing study to provide fundamental thermochemical data for various phases of metallurgical research. Interest in thermodynamic properties of iron, nickel, and chromium fluorides has been stimulated by molten-salt, breeder-reactor experiments where fluoride salts are used as fuel solvents and reactor coolants (7).[3]

Galvanic cells involving solid CaF_2 electrolytes have been successfully used to obtain Gibbs energy data for fluorides, carbides, borides, and phosphides (11). Extensive investigation of the electrolytic behavior of CaF_2 and CaF_2 doped with YF_3 has determined that conduction is primarily ionic and the transport number of the fluoride ion is essentially unity (6, 16, 18) even under strong reducing conditions. Since the electronic conduction is insignificant, the error from this source is negligible. The method is based on the determination of the difference in chemical potential of fluorine between an electrode of unknown potential consisting of a metal and its coexisting fluoride, two coexisting fluorides, or a metal oxide and its coexisting fluoride of the same metal and a reference electrode of known fluorine potential. The relationship between the open-circuit potential of emf cells and the free-energy change for the actual reaction is as follows:

$$\Delta G(\text{reaction}) = -nFE, \qquad (5)$$

where ΔG is the change in Gibbs free energy for the cell reaction, n is the number of electrochemical equivalents necessary to form 1 mole of fluorine, F is the Faraday constant (23.061 kcal/V equivalent), and E is the emf in volts.

The states for the solid phases involved in the present investigation are metals saturated with fluorides, fluorides saturated with metals, fluorides saturated with oxides, and oxides saturated with fluorides. Intersolubility of the various two-phase electrode mixtures was determined to be negligible by parametric methods. Consequently, no appreciable error would be introduced in the free energies for the cell reactions by assuming unit activity for the reactants and products involved in the various cell reactions.

Thermodynamic data for FeF_2 and FeF_3 reported in various compilations (3-4, 13, 19) include enthalpy ($\Delta Hf^{\circ}_{298.15}$) and free energy ($\Delta Gf^{\circ}_{298.15}$) of formation deduced by thermodynamic analyses of equilibrium data, low-temperature heat capacity data, and estimated high-temperature heat capacity data. Uncertainties in the enthalpy ($\Delta HF^{\circ}_{298.15}$) values of (168.7 ± 10 and -249 ± 3 kcal/mole of FeF_2 and FeF_3 (3), respectively, are exemplary of the inadequacies which characterize existing thermodynamic data for fluoride compounds. Free energies of formation of FeF_2 obtained from recent emf measurements (1, 9, 11-12, 17) are included in the discussion.

---

[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

ACKNOWLEDGMENTS

The author expresses appreciation to the members of the analytical and spectrochemistry groups at the Albany Metallurgy Research Center of the Bureau of Mines for their X-ray emission and chemical analyses of the numerous samples used in this study.

EXPERIMENTAL WORK

Materials

High-purity metals and reagents obtained commercially, were used without further purification. X-ray emission and chemical analyses are presented in table 1. Commercial, ultra-high-purity argon was passed through magnesium perchlorate (anhydrone) drying agent and was purified of residual oxygen by passing over hot titanium-zirconium chips to provide an inert atmosphere in the cells used to determine the free energy of formation of FeF_2. Commercial argon, containing approximately 80 ppm of oxygen, was required to provide a stabilizing atmosphere for cells employed in the determination of the free energy of formation of FeF_3. Single crystals of CaF_2, doped with approximately 1 mole-pct yttrium fluoride, were used as the electrolyte. Platinum foil connected to nickel wire provided electrical contact between the external circuit and the cell electrodes. High-density, recrystallized alumina was used for cell construction. Ascarite was used in the gas-stream exit to adsorb volatile fluorides.

TABLE 1. - Analyses of reagents

Reagent	Element[1]	Wt-pct or major component	Reagent	Element[1]	Wt-pct or major component
Ni	Co	0.049	FeF_3	Al	<0.01
	Fe	.019		Cu	<.01
	Si	<.003		Mn	.20
	C	.0285		Ni	.01
	S	.0040		Fe	(2)
	Ni	>99.8965	AlF_3	Ca	<.03
Fe	N	.000025		Mg	<.001
	C	.000011		Ti	<.01
	S	.000050		Al	(2)
	O	1.39	MgO	Si	<.03
	Ni	.036		Mg	(2)
	Cu	<.0003	MgF_2	Ag	<.01
	Fe	>98.573614		Si	<.10
Al	Ga	.055		Mg	(2)
	Mo	.013	Fe_2O_3	Mn	.05
	Si	.015		Mo	<.03
	Al	99.917		Si	<.01
NiF_2	Ag	.030		Fe	(2)
	Al	<.010			
	Co	.032			
	Cu	.021			
	Mg	<.001			
	Si	<.010			
	Ti	<.003			
	Ni	(2)			

[1] Impurities not detected by spectrochemical analyses except as noted in table were: Ag, Al, As, B, Ba, Be, Bi, Ca, Cb, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hf, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Sb, Si, Sn, Ta, Ti, V, W, Zn, Zr.

[2] Major component.

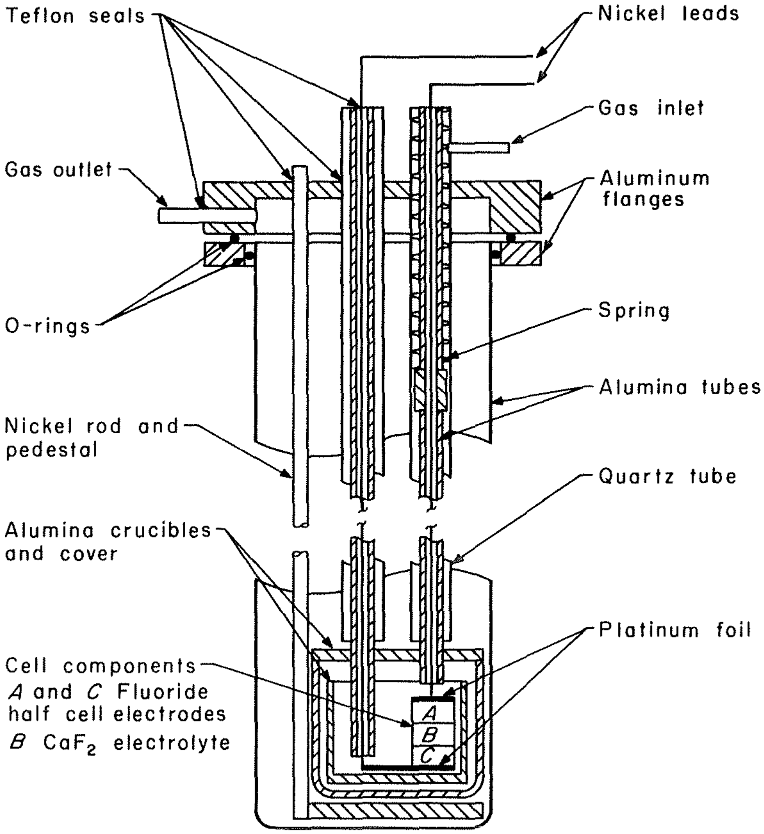

FIGURE 1. - High-temperature galvanic cell.

Apparatus and Procedure

Internal arrangement of the cell components is shown in figure 1. The cell was contained in two high-density, recrystallized, alumina crucibles with dimensions approximately 18 mm OD by 26 mm in height and 31 mm OD by 42 mm in height. The cell assembly was enclosed in a closed-end alumina tube 73 mm OD by 559 mm in length. Platinum foil, connected to nickel wire, was used to contact the cell electrodes with the external circuit. Alumina insulation tubes sheathed the nickel leads. A slight pressure was applied to the assembled cell components by a spring-loaded electrode holder shown in figure 1. An air-cooled aluminum head with teflon fittings to seal the electrode leads, pedestal rod, and thermocouple protection tube was fitted to the top of the tube. The assembled cell was heated in a 51 mm ID by 305 mm in length vertical resistance furnace. Power was supplied by a silicon-controller-rectifier power supply. A temperature gradient of ±2.1 K existed over a 15-mm zone. Temperature was maintained to ±0.5 K by an Electromax[4] current-limiting controller. Electrode samples were positioned in the uniform temperature zone. Sample temperatures were measured with a platinum versus platinum-10 pct rhodium thermocouple that was protected by a 7-mm-OD quartz tube and was positioned near the vicinity of the cell. The thermocouple was standardized against the melting points of ice and gold using the International Practical Temperature Scale of 1968.

Ferrous fluoride (FeF_2) was prepared by blending and annealing stoichiometric quantities of Fe and FeF_3, in purified argon at 1,025 K for approximately 30 hours. X-ray diffraction analyses identified only FeF_2 in the homogenized sample. Attempts to prepare Fe_2F_5 by similar techniques were not successful. X-ray diffraction analyses showed FeF_2 and FeF_3 in the annealed sample indicating that Fe_2F_5, which has been reported (2) to exist at 453 K, is not stable at these elevated temperatures.

---

[4] Reference to specific manufacturers and brands of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

Electrodes were prepared by blending and compacting metal, metal-fluoride powder mixtures in ratios between 1:1 and 3:1. Metal-fluoride to metal oxide ratios were varied in mixtures ranging between 1:1 and 2:1. An increase in the metal-fluoride content of these mixtures improved the cell performance by decreasing the internal resistance of the cells. Pellets having dimensions of 6 or 12 mm OD by 3 mm in thickness were formed in a steel die under pressures of 25,000 to 35,000 psi. Compacts consisting of Fe or Ni and their coexisting fluorides (FeF_2 or NiF_2) were sintered in purified argon at 1,025 K for approximately 30 hours. Commercial argon, containing approximately 80 ppm of oxygen, provided a stabilizing atmosphere for sintering compacts consisting of FeF_3 or MgF_2 and their coexisting oxides (Fe_2O_3 or MgO). The surfaces of the sintered compacts were polished flat and fitted against the flat faces of the CaF_2 single crystal which had dimensions of 7 or 12 mm OD by 3 mm in thickness. Assembled cells were purged and operated in purified or commercial argon. A positive pressure of approximately 20 mm of Hg and a flow rate of 20 ml/min was maintained during the experiments. Cells were heated to 900 K and permitted to stabilize for 12 hours. Emf measurements were made with a Keithley model 630 high-input-impedance potentiometric electrometer, thereby reducing current flow to an absolute minimum and avoiding polarization of the emf source. Measurements were completed during the first day, following a preliminary 12-hour stabilization period. Potential measurements were made at each temperature after they became constant with time. Reversibility of the cell was checked by approaching equilibrium from above and below a specified temperature. Cell response to temperature was rapid for metal, metal-fluoride cells and normally stabilized in approximately one-half hour after a steady-state temperature had been attained. Cells employing metal-fluoride, metal-oxide electrodes were sluggish and required several hours to equilibrate following each 20 to 30 degree temperature change. Internal resistance for the metal-fluoride, metal-oxide type of cell was extremely high and consequently special shielding precautions were required to minimize spurious electric field effects in the high-impedance circuit. Preliminary tests were conducted for each type of cell to determine operating parameters such as temperature and electrode composition.

Results and Discussion

A preliminary experiment was designed to calibrate and test the apparatus by measuring the open-circuit potential for the cell

$$\mathrm{Al, AlF_3 \ // \ CaF_2 \ // \ NiF_2, Ni} \qquad \text{(I)}$$

with the overall reaction

$$\mathrm{2Al(s) + 3NiF_2(s) = 3Ni(s) + 2AlF_3(s).} \qquad (6)$$

At 900 K a free energy of formation (ΔGf°) or -123.73 kcal/mole of NiF_2, deduced from these measurements, compares favorably with -123.63 kcal/mole derived from various calorimetric data (10).

The free energy of formation ($\Delta Gf°$) of ferrous fluoride was determined by measuring the open-circuit potential for cells of the type

$$\text{Fe, FeF}_2 \ // \ \text{CaF}_2 \ // \ \text{NiF}_2\text{, Ni} \qquad \text{(II)}$$

with the overall cell reaction

$$\text{Fe(s)} + \text{NiF}_2\text{(s)} = \text{Ni(s)} + \text{FeF}_2\text{(s)}.$$

Results of these measurements are reported in table 2. A standard free energy of formation ($\Delta Gf°$) of FeF_2 can be derived from the following relationship:

$$\Delta G°\text{(cell reaction)} = -nFE = \Delta Gf°(\text{FeF}_2) - \Delta Gf°(\text{NiF}_2). \qquad (7)$$

Potential measurements for the cell reaction together with a standard error of estimate may be expressed by the least-squares equation

$$E = 272.1337 + 0.11996T \pm 1.65 \ (897 - 1{,}098 \text{ K}), \qquad (8)$$

where E is expressed in millivolts and the standard error of estimate is

$$\frac{1}{n}\left[n\Sigma y^2 - (\Sigma y)^2 - \frac{(n\Sigma xy - \Sigma x\Sigma y)^2}{n\Sigma x^2 - (\Sigma x)^2}\right]^{1/2}.$$

Smooth emf data derived from the foregoing linear equation are given in column 4 of table 2. Representative emf versus temperature data are illustrated in figure 2. The corresponding standard free-energy change for the cell reaction is

$$\Delta G°\text{(cell reaction)} = -12.551 - 5.53 \times 10^{-3}T \pm 0.076 \text{ kcal/mole}$$

$$(897 - 1{,}098 \text{ K}). \qquad (9)$$

TABLE 2. - Electromotive force of cell Ni, Pt, Fe + FeF_2 // CaF_2 // NiF_2 + Ni, Ni

Experiment number[1]	Temp, K	E, mv	
		Measured[2]	Calculated[3]
5	897.5	381.48±0.115	379.80
6	898.7	382.47± .036	379.94
4	923.2	384.06± .007	382.88
7	948.1	384.76± .062	385.87
11	958.6	385.72± .023	387.13
3	972.1	387.90± .043	388.75
1	973.2	388.02± .038	388.88
8	1,004.9	390.77± .059	392.68
10	1,005.1	391.10± .055	392.70
12	1,005.8	391.66± .027	392.79
2	1,019.7	393.89± .013	394.46
15	1,051.0	396.95± .019	398.21
13	1,052.5	398.92± .014	398.39
9	1,052.9	399.33± .007	398.44
14	1,098.7	407.80± .117	403.93

[1] Chronological order of measurements.

[2] Average of two measurements taken at 1-hour intervals and corrected for a Seebeck effect at the electrodes.

[3] Calculated from linear equation $E = 272.1337 \pm 0.11996T \pm 1.65$.

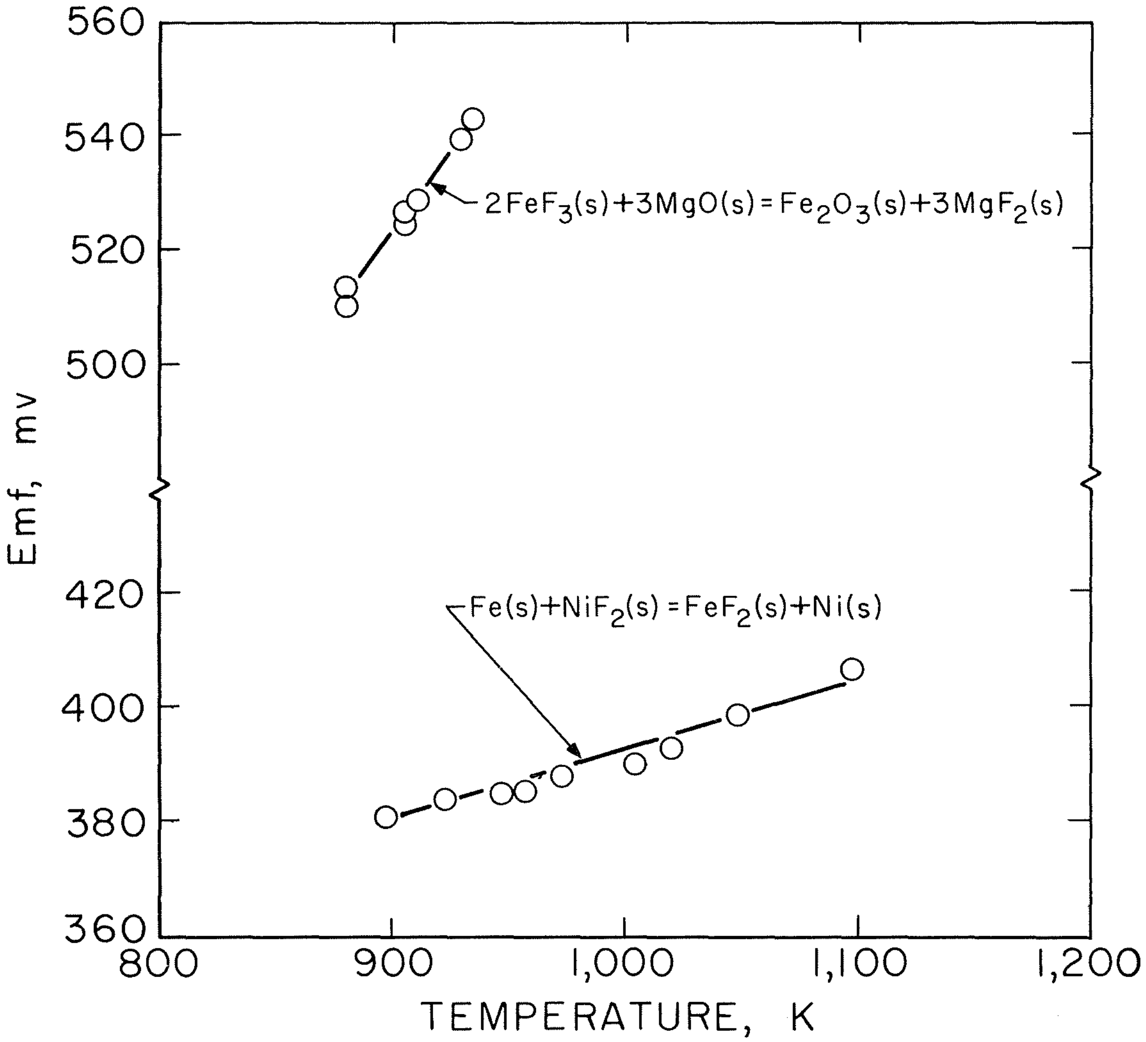

FIGURE 2. - Emf versus temperature for cell reactions.

In the temperature range 800 to 1,100 K the standard free energy of formation of NiF_2 (10) may be expressed as follows:

$$\Delta Gf°(NiF_2) = -156.19 + 36.16 \times 10^{-3}T \pm 0.40 \text{ kcal/mole } (800 - 1,100 \text{ K}) \quad (10)$$

Combination of the foregoing relationships yields a standard free energy of formation (ΔGf°) of ferrous fluoride which may be expressed as follows:

$$\Delta Gf°(FeF_2) = -168.74 + 30.63 \times 10^{-3}T \pm 0.41 \text{ kcal/mole } (897 - 1,098 \text{ K}).$$

The standard free energy of formation (ΔGf°) of ferric fluoride (FeF_3) was determined by measuring the open-circuit potential for the cell

$$MgO, MgF_2 // CaF_2 // FeF_3, Fe_2O_3 \quad (III)$$

with the overall cell reaction

$$3MgO(s) + 2FeF_3(s) = 3MgF_2(s) + Fe_2O_3(s).$$

A composite of 11 potential measurements representing two separate cells can be described by the least-squares equation and a standard estimate of error as follows:

$$E = 14.9111 + 0.56456T \pm 0.892, \qquad (11)$$

where E is expressed in millivolts. Potential measurements and their corresponding smooth emf values, derived from the foregoing equation are presented in columns 3 and 4 of table 3. Representative emf versus temperature data are plotted in figure 2.

TABLE 3. - Electromotive force of cell Ni, Pt, $MgO + MgF_2$ // CaF_2 // $FeF_3 + Fe_2O_3$, Pt, Ni

Experiment number[1]	Temp, K	E, mv	
		Measured[2]	Calculated[3]
4	880.9	510.60±0.10	512.23
7	881.2	512.53± .065	512.40
5	881.4	514.35± .05	512.51
9	905.6	526.72± .075	526.17
3	906.1	525.55± .05	526.47
11	910.3	528.45± .125	528.78
8	929.7	540.34± .08	539.78
6	931.8	540.15± .05	540.97
1	932.1	541.81± .07	541.13
2	932.8	541.45± .05	541.53
10	934.6	542.61± .05	542.55

[1] Chronological order of measurements.
[2] Average of two measurements taken at approximately 30-minute intervals.
[3] Calculated from linear equation $E = 14.9111 + 0.56456T \pm 0.892$.

The standard free energy for the foregoing cell reaction is obtained from the following relationship:

$$\Delta G^\circ(\text{cell reaction}) = -nFE = 3\Delta Gf^\circ(MgF_2) + \Delta Gf^\circ(Fe_2O_3) - 3\Delta Gf^\circ(MgO) - 2\Delta Gf^\circ(FeF_3) \qquad (12)$$

and may be expressed by the linear equation as:

$$\Delta G^\circ_T(\text{cell reaction}) = -2.0632 - 78.12 \times 10^{-3}T \pm 0.123 \text{ kcal} \quad (880 - 935 \text{ K}). \qquad (13)$$

Free energy data from the literature (3) for MgF_2, Fe_2O_3, and MgO are combined with the free energy of reaction data obtained from the present investigation to yield a least-squares equation and a standard error of estimate for the free energy of formation of FeF_3 as follows:

$$\Delta Gf°(FeF_3) = -281.45 + 90.46 \times 10^{-3}T \pm 0.67 \text{ kcal/mole } (880 - 935 \text{ K}).$$

X-ray diffraction analyses and parametric measurements of the electrode samples obtained from these experiments identified only the desired two phases and indicated very limited intersolubility as shown in table 4. The lattice parameter of a solid solution generally changes with composition up to the saturation limit and then remains constant beyond that point. X-ray diffraction data, presented in table 4, show no major changes in lattice parameters or shift in the lines of X-ray patterns for the various components. Consequently, the intersolubility of the components is limited and the assumption of unit activity for the reactants and products involved in the cell reactions would introduce no appreciable error in the free energies of formation of ferrous and ferric fluoride. Comparison of the lattice parameters for reagents with data reported in the literature (5, 8, 14-15) is indicative of the relative purity of the reagents used in the present investigation.

TABLE 4. - X-ray diffraction analyses of reagents and electrode mixtures

Sample designation	Phases identified	Crystal structure	Lattice parameters, A			
			Measured		Literature	
			a_0	c_0	a_0	c_0
FeF_3	FeF_3	Hexagonal	5.201	13.360	5.198 (5)	13.331 (5)
MgF_2	MgF_2	Tetragonal	4.6214	3.0511	4.623 (14)	3.052 (14)
MgO	MgO	Cubic	4.2132	-	4.213 (15)	-
Fe_2O_3	Fe_2O_3	Hexagonal	5.0337	13.5721	5.0340 (8)	13.572 (8)
Fe_2O_3 + FeF_3	Fe_2O_3 +	Hexagonal	5.036	13.710	-	-
	FeF_3	Hexagonal	5.199	13.371	-	-
MgO + MgF_2	MgO +	Cubic	4.2128	-	-	-
	MgF_2	Tetragonal	4.6218	3.0502	-	-
Fe + FeF_2 (initial)	Alpha Fe + FeF_2	No detectable shift in lines from initial to final sample. All patterns not of sufficient quality for precise lattice parameter measurements.				
Fe + FeF_2 (final)	Alpha Fe + FeF_2					
Ni + NiF_2 (initial)	Ni + NiF_2					
Ni + NiF_2 (final)	Ni + NiF_2					

Free energies and fluorine pressures for the univariant dissociation reactions,

$$FeF_2(s) = Fe(s) + F_2(g) \tag{14}$$

and

$$2FeF_3(s) = 2FeF_2(s) + F_2(g), \tag{15}$$

as obtained by the present investigation are reported in tables 5 and 6, respectively. Figure 3 illustrates the thermodynamic stability of the Fe-F system for the 900 K isotherm. At 900 K, FeF_2 is stable at fluorine pressures ranging from 5.63 X 10^{-35} to 2.55 X 10^{-29} atm as noted by the vertical line shown in figure 3. Two horizontal lines shown in figure 3 represent the fluorine pressures in equilibrium with the condensed phases of the two univariant equilibria. If the temperature is fixed, all other intensive properties for each phase of the univariant equilibrium become determinate.

TABLE 5. - Free energy and equilibrium fluorine pressure for reaction, $FeF_2(s) = Fe(s) + F_2(g)$

Temp, K	ΔG°, kcal[1]	P_{F_2}, atm
890	141.481	1.81 X 10^{-35}
900	141.175	5.63 X 10^{-35}
920	140.562	4.06 X 10^{-34}
940	139.950	2.89 X 10^{-33}
960	139.337	1.90 X 10^{-32}
980	138.725	1.16 X 10^{-31}
1,000	138.112	6.54 X 10^{-31}
1,020	137.499	3.46 X 10^{-30}
1,040	136.887	1.71 X 10^{-29}
1,060	136.274	8.00 X 10^{-29}
1,080	135.662	3.53 X 10^{-28}
1,100	135.049	1.47 X 10^{-27}

[1] Standard error of estimate is ±0.41 kcal.

TABLE 6. - Free energy and equilibrium fluorine pressure for reaction, $2FeF_3(s) = 2FeF_2(s) + F_2(g)$

Temp, K	ΔG°, kcal[1]	P_{F_2}, atm
890	118.943	6.20 X 10^{-30}
900	117.746	2.55 X 10^{-29}
910	116.549	1.02 X 10^{-28}
920	115.353	3.96 X 10^{-28}
930	114.156	1.49 X 10^{-27}
940	112.960	5.45 X 10^{-27}
950	111.763	1.94 X 10^{-26}

[1] Standard error of estimate is ±1.57 kcal.

General agreement of the standard free energy of formation (ΔGf°) at 900 K for ferrous fluoride (FeF_2) with results of recent emf investigations (1, 9, 11-12) is noted in table 7. Results of one emf investigation (17) are lower and appear to be in error. The Gibbs free energies of formation of FeF_2, listed in table 7, were derived by combining ΔGf° of NiF_2 (10) with the free energies of the cell reaction which were measured by the various investigators. The convention of expressing high-temperature emf data,

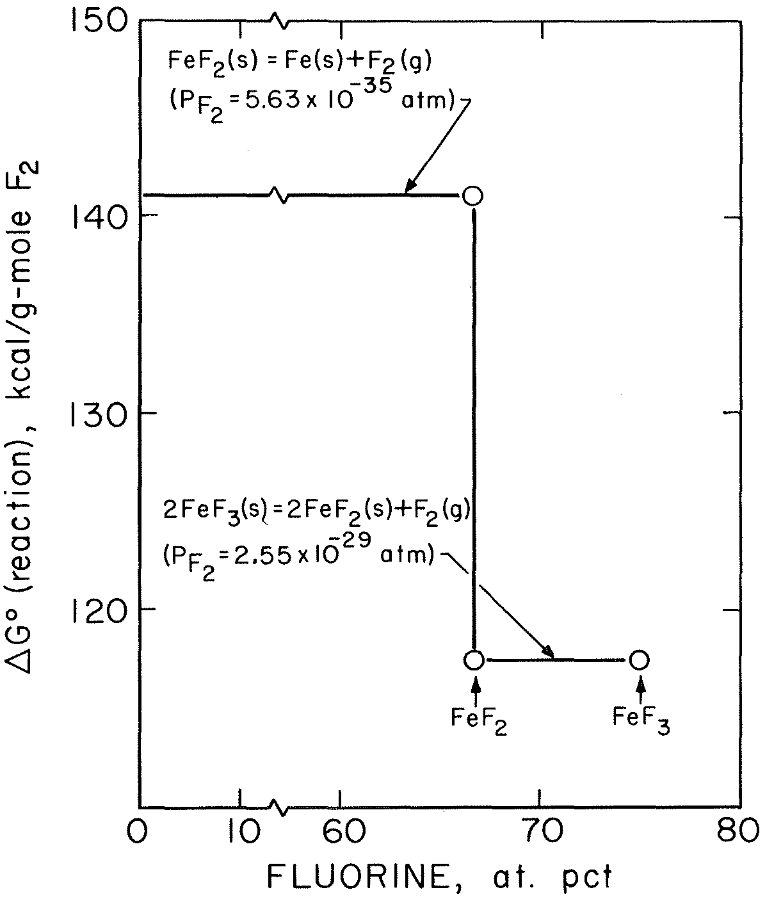

FIGURE 3. - Free energy and equilibrium fluorine pressure for the Fe-F system at 900 K.

obtained over short temperature ranges, by linear equations has been adopted by most emf investigators (1, 9, 11-12, 17). Slight deviations from linearity in emf versus temperature data for the two cell reactions, illustrated in figure 2, can be attributed to experimental limitations. Small specific heat effects, other than a phase change such as melting, would be difficult to detect with this technique, especially at lower temperatures where reactions become sluggish and cell resistance becomes extremely high. At high temperatures the rate of change of free energies of formation approaches a constant value. These linear equations are valid only over specified temperature ranges and are generally not suitable for extraction of values of heat and entropy of formation. Values of thermodynamic properties of FeF$_2$ which have been reported in compilations (3-4, 13, 19) are based on uncertain equilibrium measurements, low-temperature heat capacity data, and estimated high-temperature heat capacity data.

A third-law analysis, employing the present ΔG°(cell reaction) data, entropy and enthalpy data for Fe, F$_2$, and FeF$_2$ (3), yields a standard enthalpy of formation of FeF$_2$ as follows:

$$\Delta Hf^{\circ}_{298.15} = -170.9 \text{ kcal/mole.} \qquad (16)$$

This value is more negative than the reported value of -168.6±10 kcal/mole (3) but is within the large limit of uncertainty.

A similar third-law analysis, employing the entropy and enthalpy data for Fe, F$_2$, and FeF$_3$ (3), together with the present ΔG°(cell reaction) data, yields a standard enthalpy of formation of FeF$_3$ as follows:

$$\Delta Hf^{\circ}_{298.15} = -248.4 \text{ kcal/mole.} \qquad (17)$$

This value is in excellent agreement with the reported value of 249±3 kcal/mole (3).

TABLE 7. - Emf and free energy data for FeF_2(s) and FeF_3(s)

Reaction	E, mv	Temp, K	$\Delta G°$, kcal		References
			Reaction[1]	$\Delta Gf°$[2]	
$Fe(s) + NiF_2(s) = FeF_2(s) + Ni(s)$	376.86±1.65	873	-17.38	-142.00	This investigation, 10
	380.10±1.65	900	-17.53	-141.18	
	392.09±1.65	1,000	-18.08	-138.11	
	374.5 ±1.0	873	-17.27	-140.60	9-10
	374.0 ±3.0	873	-17.25	-140.08	10-11
	85.2 ±2.6	900	-3.93	-127.56	10, 17
	387.0 ±2.0	900	-17.85	-141.48	1, 10
	376.9 ±2.0	900	-17.38	-141.01	10, 12
	387.8 ±2.0	1,000	-17.89	-137.82	10, 12
		900		(-135.70)	19
		900		(-138.97)	4
		900		(-138.38)	13
		900		(-138.96)	3
$3MgO(s) + 2FeF_3(s) = 3MgF_2(s) + Fe_2O_3(s)$	523.01±0.89	900	-72.370	-200.04	This investigation
		900		(-187.90)	19
		900		(-188.04)	13
		900		(-190.24)	4
		900		(-200.61)	3

---

[1] ΔG for reaction = -nFE.

[2] Items 1 to 13 reported as kcal/g-mole FeF_2. Items 14 to 18 reported in kcal/g-mole FeF_3. Values in parentheses are based on estimates given in compilations.

REFERENCES

1. Bagshaw, A. N. Comments on the paper by R. A. Vecher and L. M. Rogach, "An Electromotive Force Study of the Thermodynamic Properties of Iron (II) Fluoride." J. Phys. Chem., U.S.S.R., v. 46, No. 6, 1972, pp. 939-940.

2. Brawer, G., and M. Eichner. Iron (II, III) Fluoride. Z. Anorg. Allgem. Chem., v. 296, 1958, pp. 13-19.

3. Dow Chemical Co., Thermal Research Laboratory. JANAF Thermochemical Tables, Second Edition. NSRDS-NBS 37, SN03030872, U.S. Government Printing Office, Washington, D.C., 1971, 1141 pp.

4. Hamer, W. J., M. S. Malmberg, and B. Rubin. Theoretical Electromotive Forces for Cells Containing a Single Solid or Molten Fluoride, Bromide, or Iodide. J. Electrochem. Soc., v. 112, No. 7, 1965, pp. 750-755.

5. Hepworth, M. A., K. H. Jack, R. D. Peacock, and G. J. Westland. The Crystal Structure of the Trifluorides of Iron, Cobalt, Ruthenium, Rhodium, Palladium, and Iridium. Acta Cryst., v. 10, 1957, pp. 63-69.

6. Hinze, J. W., and J. W. Patterson. Electrolytic Behavior of CaF_2 Crystals Under Reducing Conditions. J. Electrochem. Soc., v. 120, No. 1, 1973, pp. 96-98.

7. Jenkins, H. W., and G. Mamantov. E.M.F. Measurements on the Nickel-Nickel (II) Couple in Molten Fluorides. J. Electroanalytical Chem., v. 19, 1968, pp. 385-389.

8. Kastalsky, V., and M. F. Westcott. Accurate Unit Cell Dimensions of Hematite (α-Fe_2O_3). Australian J. Chem., v. 21, No. 4, 1968, pp. 1061-1062.

9. Lofgren, N. L., and E. J. McIver. Thermodynamic Properties of Some Fluoride Systems. Atomic Energy Res. Establishment Rept. 5169, 1966, 14 pp.

10. Mah, A. D., and L. B. Pankratz. Contributions to the Data on Theoretical Metallurgy. XVI. Thermodynamic Properties of Nickel and Its Inorganic Compounds. BuMines Bull. 668, in press.

11. Markin, T. L. Galvanic Cells Reversible to Fluoride Ions. Ch. in Electromotive Force Measurements in High-Temperature Systems. C. B. Alcock, ed., Proc. of a Symp. Held by the Nuffield Res. Group, Imperial College, London, Apr. 13 and 14, 1967. Eyre and Spottiswoode Limited, Grosvener Press, Portsmouth, England, 1968, pp. 91-97.

12. Skelton, W. H., and J. W. Patterson. Free Energy Determinations by Solid Galvanic Cell Measurements for Selected Metal, Metal-Fluoride Reactions. J. Less-Common Metals, v. 31, 1973, pp. 47-60.

13. Steinmetz, E., and H. Roth. The Free Energy of Formation of Chlorides and Fluorides. J. Less-Common Metals, v. 16, 1968, pp. 295-342.

14. Swanson, H. E., R. K. Fuijat, and G. M. Ugrinic. Standard X-ray Diffraction Patterns. NBS Circ. 539, v. 4, 1955, p. 23.

15. Swanson, H. E., and E. Tatge. Standard X-ray Diffraction Patterns. NBS Circ. 539, v. 1, 1953, pp. 37-39.

16. Ure, R. W., Jr. Ionic Conductivity of Calcium Fluoride Crystals. J. Chem. Phys., v. 26, No. 6, 1957, pp. 1363-1373.

17. Vecher, R. A., and L. M. Rogach. Thermodynamic Properties of Iron (II) Fluoride by Electromotive Force Method. J. Phys. Chem., U.S.S.R, v. 44, No. 6, 1970, pp. 863-864.

18. Wagner, C. Limitation of the Use of CaF_2 in Galvanic Cells for Thermodynamic Measurements Due to the Onset of Electronic Conduction Under Reducing Conditions. J. Electrochem. Soc., v. 115, No. 9, 1968, pp. 933-935.

19. Wicks, C. E., and F. E. Block. Thermodynamic Properties of 65 Elements--Their Oxides, Halides, Carbides, and Nitrides. BuMines Bull. 605, 1963, 146 pp.

INT.-BU.OF MINES,PGH.,PA. 20704