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Electrochemical Determination of Thermodynamic Properties of MnF_2 and CoF_2

By Seth C. Schaefer



UNITED STATES DEPARTMENT OF THE INTERIOR



Report of Investigations 8973

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cal	calorie	min	minute
cal/mol	calorie per mol	mm	millimeter
cal/mV	calorie per millivolt	mol pct	mol percent
cm ³ /min	cubic centimeter per minute	MPa	megapascal
h	hour	mV	millivolt
J	joule	Pa	pascal
K	kelvin	wt pct	weight percent

ELECTROCHEMICAL DETERMINATION OF THERMODYNAMIC PROPERTIES OF MnF_2 AND CoF_2

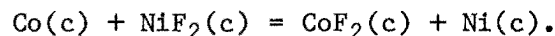
By Seth C. Schaefer¹

ABSTRACT

The Bureau of Mines investigated the standard Gibbs energies of formation, ΔG_f° , for MnF_2 (manganese difluoride) and CoF_2 (cobalt difluoride). High-temperature galvanic cells employing CaF_2 (calcium difluoride) as the solid electrolyte were used to measure the open-circuit potentials for the cell reactions



and



Combination of the standard Gibbs energy changes for these reactions with the standard Gibbs energy of formation of NiF_2 yielded the following:

$$\Delta G_f^\circ(MnF_2) = (-203,008 + 30.96T) \pm 560 \text{ (745.7-1,078.3 K)}$$

and
$$\Delta G_f^\circ(CoF_2) = (-159,090 + 32.13T) \pm 420 \text{ (769.5-1,026.8 K)},$$

where ΔG_f° is expressed in calories per mol (1 cal = 4.184 J) and T is expressed in kelvins. The standard enthalpies of formation ΔH_f° , derived by the third-law method, are

$$\Delta H_f^\circ_{298}(MnF_2) = -204,633 \pm 560 \text{ cal/mol}$$

and

$$\Delta H_f^\circ_{298}(CoF_2) = -161,166 \pm 420 \text{ cal/mol}.$$

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INTRODUCTION

Thermodynamic properties of MnF_2 and CoF_2 were investigated by the Bureau of Mines as a part of its program to expand the base of scientific information needed to devise innovative technologies. Many chemical and metallurgical processes involve halogen gases and metal halide compounds (1).² MnF_2 is used in electronics, optics, and as a catalyst in hydrocarbon isomerization. CoF_2 is used as a catalyst in isomerization and polymerization reactions. A review of existing data reported in compilations (2-5) shows considerable disagreement in the Gibbs energies of formation for these compounds and suggests a need for careful investigation to resolve some of these discrepancies.

Galvanic cells with solid CaF_2 electrolyte have been used successfully to obtain Gibbs energy data for fluorides, borides, and phosphides (5-6). Extensive investigation of the electrolytic behavior of CaF_2 and CaF_2 doped with YF_3 showed that conduction is ionic and that the transport number is essentially unity (7-9), even under strongly reducing conditions. The method is based on the measurement of the difference in chemical

potential of fluorine between a reference electrode of known fluorine potential and an electrode of unknown fluorine potential consisting of a metal and its coexisting fluoride or two coexisting fluorides. The relationship between the open-circuit potential of electromotive force (emf) cells and the Gibbs energy change for the actual cell reaction is

$$\Delta G(\text{reaction}) = -nFE, \quad (1)$$

where ΔG is the change in Gibbs energy for the cell reaction, n is the number of electrochemical equivalents in the reaction, F is the Faraday constant (23.061 cal/mV equivalent), and E is the emf in millivolts. The standard states for the solids involved in the reaction are the saturated coexisting phases. Intersolubility of the two-phase electrode mixtures was determined to be negligible by X-ray diffraction analyses. Consequently, no appreciable error was introduced in the Gibbs energies for the cell reactions by assuming unit activity for the reactants and products involved in the cell reactions.

EXPERIMENTAL WORK

MATERIALS

High-purity reagents were obtained from commercial sources and used without further purification. Analyses of these reagents were confirmed and are presented in table 1. Argon of 99.999-mol-pct purity was used to provide a protective atmosphere for the cell. Single crystals of CaF_2 , doped with approximately 1 mol pct YF_3 were used as the solid electrolyte.

APPARATUS AND PROCEDURE

Internal arrangement of the cell components is illustrated in figure 1. A

detailed description of the cell and experimental procedure was previously published (10). Similar cell designs have been reported in the literature (5-6, 11-12).

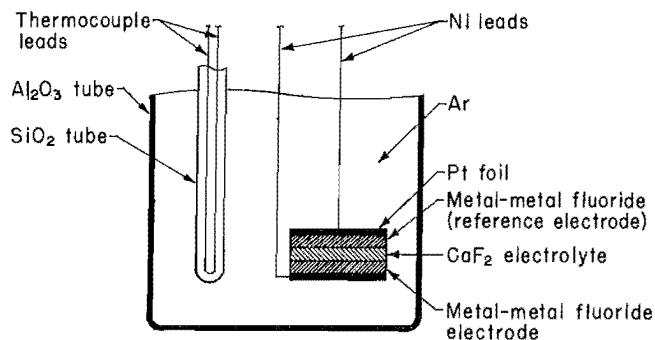


FIGURE 1. - High-temperature galvanic cell.

²Underlined numbers in parentheses refer to items in the list of references at end of this report.

TABLE 1. - Impurities¹ detected in reagents

Reagent and impurity elements	wt pct	Reagent and impurity elements	wt pct	Reagent and impurity elements	wt pct
Mn:		Ni:		CoF ₂ :	
Al.....	0.07	Co.....	0.045	Al.....	0.02
Ca.....	.02	NiF ₂ :		Ca.....	.27
Mg.....	<.03	Co.....	.032	Mg.....	.02
Ni.....	.03	Cu.....	.021	Mn.....	.07
Si.....	.17	Co:		Ni.....	.21
MnF ₂ :		Ni.....	.09	Si.....	.07
Ca.....	.1				

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

Electrodes were prepared by blending and compacting 1:1 molar mixtures of nickel, manganese, or cobalt with their respective coexisting fluorides NiF₂, MnF₂, or CoF₂. Pellets, 9 mm in OD by 3 mm thick, were formed in a steel die under a pressure of 210 MPa. Compacts of the metals and their coexisting fluorides were sintered in ultra-high-purity argon at 1,000 K for approximately 30 h. The surfaces of the sintered compacts were polished and fitted against a single crystal of CaF₂, 10 mm in OD and 3 mm thick. Assembled cells were purged with 20 cm³/min of argon and operated under a positive pressure of approximately 30 Pa. Cells were heated to 900 K and permitted to stabilize for 16 h. Emf measurements were made with a Keithley³ model 642 high-input-impedance digital electrometer. Measurements were completed during the first day following a preliminary 16-h stabilization period. Cell response to

temperature change was rapid, and potentials stabilized within 0.5 h after a steady-state temperature was obtained. Reversibility of the cell reactions was checked by approaching equilibrium from temperatures above and below a specified temperature. Reproducibility was checked by obtaining measurements from several cells for each determination. The cell was shielded from electric field effects in the high-impedance circuit by placing a grounded nickel shield around the cell. The cell was dismantled after completion of the experimental measurements, and the electrodes were removed for phase identification and lattice parameter measurements. There was no visible corrosion of the platinum contacts with the electrodes. X-ray analyses confirmed the products and reactants for the cell reactions and showed that intersolubility of the two-phase electrode mixtures was negligible.

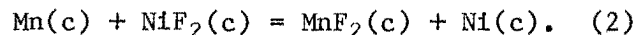
RESULTS AND DISCUSSION

MnF₂

The standard Gibbs energy formation, ΔG_f° , of MnF₂ was determined by measuring the open-circuit potentials for the reversible cell

Ni, Pt, Mn, MnF₂//CaF₂//NiF₂, Ni, Pt, Ni

with the overall cell reaction



Results of these measurements are reported in table 2. Representative emf-versus-temperature data are illustrated in figure 2. A standard Gibbs energy formation of MnF₂ was derived from the relationship

$$\Delta G^\circ(\text{reaction } 2) = -nFE = \Delta G_f^\circ(\text{MnF}_2) - \Delta G_f^\circ(\text{NiF}_2). \quad (3)$$

³Reference to specific trade names does not imply endorsement by the Bureau of Mines.

TABLE 2. - Emf (E) of cell and thermodynamic properties of MnF_2

Experiment	Temperature, K	Emf (E), mV ¹	$-\Delta G_f^\circ(\text{MnF}_2)$, cal/mol	$-\Delta H_f^\circ_{298}(\text{MnF}_2)$, cal/mol
1.....	745.7	1,093.15	179,688	204,330
2.....	768.4	1,095.85	178,994	204,349
3.....	769.4	1,095.45	178,939	204,326
4.....	790.8	1,099.55	178,351	204,408
5.....	792.0	1,100.25	178,345	204,439
6.....	813.6	1,102.85	177,685	204,458
7.....	814.1	1,103.05	177,676	204,464
8.....	834.3	1,105.85	177,076	204,501
9.....	835.8	1,105.95	177,027	204,500
10.....	856.4	1,108.55	176,403	204,523
11.....	856.7	1,108.15	176,373	204,502
12.....	906.4	1,115.65	174,925	204,609
13.....	909.8	1,119.15	174,963	204,753
14.....	932.6	1,122.25	174,284	204,784
15.....	934.0	1,121.95	174,220	204,764
16.....	934.9	1,122.75	174,223	204,795
17.....	956.8	1,125.45	173,073	204,327
18.....	958.2	1,125.65	173,516	204,812
19.....	959.9	1,125.45	173,446	204,795
20.....	981.0	1,128.95	172,845	204,848
21.....	982.8	1,128.55	172,762	204,821
22.....	1,004.7	1,132.45	172,151	204,888
23.....	1,006.6	1,130.15	171,977	204,773
24.....	1,028.6	1,133.35	171,330	204,807
25.....	1,031.1	1,133.25	171,249	204,772
26.....	1,052.7	1,136.55	170,608	204,830
27.....	1,078.3	1,141.05	169,891	204,902
Average.....	Nap	Nap	Nap	² 204,633±196

Nap Not applicable.

¹Average of 2 measurements (± 0.05 mV) taken at 20-min intervals.

²Error from these measurements corresponds to a standard deviation; precision uncertainty is ± 392 cal/mol; overall accuracy is ± 560 cal/mol.

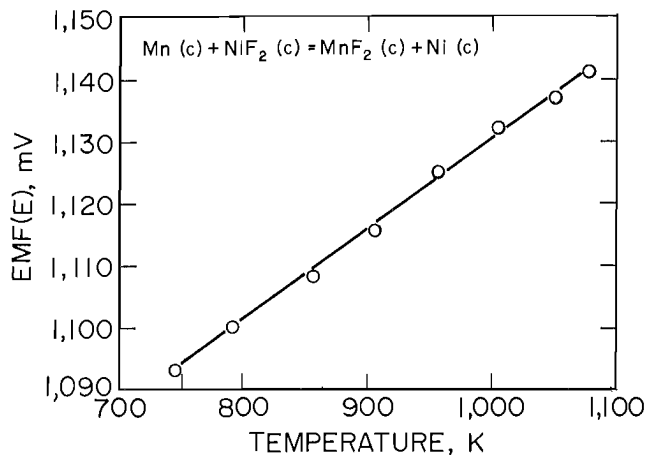


FIGURE 2. - Emf (E) versus temperature for MnF_2 cell.

The values of $\Delta G_f^\circ(\text{NiF}_2)$, obtained by interpolation of data reported in a compilation (13) and the values of E listed in table 2, were substituted in equation 3 to derive $\Delta G_f^\circ(\text{MnF}_2)$ for each temperature. The results are listed in column 4 of table 2.

The values for $\Delta H_f^\circ_{298}(\text{MnF}_2)$, listed in the fifth column of table 2, were obtained by the third-law method as described in the literature (14), using the Gibbs energy function, $G_f \equiv \{G^\circ(T) - H^\circ(298)\}/T$, listed in the literature (15-17) and substituting $\Delta G_f^\circ(\text{MnF}_2)$ for each temperature into the following identity corresponding to $\text{Mn}(c) + \text{F}_2(g) = \text{MnF}_2(c)$:

$$\Delta G_{\text{ef}} \equiv \Delta \{G^\circ(T) - H^\circ(298)\}/T$$

$$\equiv \{\Delta G_{\text{f}}^\circ(T) - \Delta H_{\text{f}}^\circ(298)\}/T. \quad (4)$$

The values of G_{ef} and ΔG_{ef} for the formation reaction $\text{Mn}(c) + \text{F}_2(g) = \text{MnF}_2(c)$ are listed in table 3. The value of ΔG_{ef} for each temperature in table 2 was calculated by interpolation or short extrapolation of the values in table 3. $\Delta H_{\text{f}}^\circ_{298}$ of MnF_2 for each temperature was derived by rearranging equation 4 and substituting the values of $\Delta G_{\text{f}}^\circ(\text{MnF}_2)$ that are listed in column 4 of table 2 and the interpolated values of ΔG_{ef} from table 3. The average of all values for $\Delta H_{\text{f}}^\circ(\text{MnF}_2)$ is $-204,633 \pm 196$ cal/mol. The standard deviation of ± 196 cal/mol refers to the present measurements in table 2. Additional errors and uncertainties are those associated with the thermal quantities involved in the calculations. For example, the uncertainty in $\Delta G_{\text{f}}^\circ(\text{NiF}_2)$ is ± 400 cal/mol (13). The overall uncertainty of $\Delta H_{\text{f}}^\circ_{298}$ was derived by obtaining the square root of the sum of the squares of the uncertainty from these measurements (± 392 cal/mol) and the uncertainty in $\Delta G_{\text{f}}^\circ(\text{NiF}_2)$ of ± 400 cal/mol to yield

$$\Delta H_{\text{f}}^\circ_{298}(\text{MnF}_2) = -204,633 \pm 560 \text{ cal/mol.} \quad (5)$$

A least squares treatment of the data for E fitted to an equation linear in T and extrapolation to 298.15 K by a second-law method yields $\Delta H_{\text{f}}^\circ_{298}(\text{MnF}_2) = -204,626 \pm 560$ cal/mol. Agreement with equation 5 is good; however, the recommended value is that based on the third-law method.

Combination of equation 5 from the present investigation with the tabulated data from the literature (15-17) yields, from the results of the third-law method (14),

$$\Delta G_{\text{f}}^\circ(\text{MnF}_2)$$

$$= (-203,008 + 30.96T) \pm 560 \text{ cal/mol}$$

$$(745.7-1,078.3 \text{ K}) \quad (6)$$

for the reaction $\text{Mn}(c) + \text{F}_2(g) = \text{MnF}_2(c)$. The constants in equation 6 are $\Delta H^\circ = -203,008$ and $\Delta S^\circ = -30.96$. Both constants refer to 912 K, the midpoint in the temperature range 745.7 to 1,078.3 K of this investigation; however, both terms remain fairly constant, and within experimental errors, equation 6 may be used to express $\Delta G_{\text{f}}^\circ(\text{MnF}_2)$ for the entire range of these measurements. A similar study (5) for reaction 2 reported

$$\Delta G_{\text{f}}^\circ(\text{MnF}_2) = -197,000 + 22.28T \text{ cal/mol}$$

$$(732-1,071 \text{ K}). \quad (7)$$

Results of another electrochemical investigation (18) for the cell reaction $3\text{MnF}_2(c) + 2\text{Al}(c) = 2\text{AlF}_3 + 3\text{Mn}(c)$ were expressed as

$$\Delta G_{\text{f}}^\circ(\text{MnF}_2) = -204,120 + 32.77T \text{ cal/mol}$$

$$(740-820 \text{ K}), \quad (8)$$

and a third-law value for the enthalpy of formation was reported as

$$\Delta H_{\text{f}}^\circ_{298}(\text{MnF}_2)$$

$$= -205,400 \pm 1,000 \text{ cal/mol.} \quad (9)$$

Comparison of equations 7 and 6 shows considerable difference in the constants ΔH° and $-\Delta S^\circ$. Agreement between equations 8 and 6 is better; however, equation 8 is valid for the narrow temperature range of 740 to 820 K, whereas the present investigation was conducted over a wider temperature range of 745.7 to 1,078.3 K.

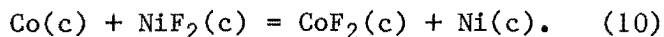
TABLE 3. - Auxiliary thermodynamic data for MnF_2 reaction

Temperature, K	-Gef, cal/mol			ΔG_{ef} , cal/mol
	Mn(c) (15)	$\text{F}_2(g)$ (15)	$\text{MnF}_2(c)$ (16-17)	
700.....	9.547	50.648	27.0529	33.1421
800.....	10.130	51.303	28.5025	32.9305
900.....	10.700	51.936	29.8756	32.7604
1,000...	11.264	52.537	31.2100	32.5910
1,100...	11.854	53.111	32.5300	32.4350

CoF₂

The standard Gibbs energy of formation of CoF₂ was determined by measuring the open-circuit potential for the cell

Ni, Pt, Co, CoF₂//CaF₂//NiF₂, Ni, Pt, Ni
with the overall cell reaction



Potential measurements for reaction 10 are listed in table 4. Representative emf-versus-temperature data are illustrated in figure 3. A standard Gibbs energy of formation of CoF₂ can be derived from the relationship

$$\begin{aligned} \Delta G^\circ(\text{reaction 10}) &= -nFE = \Delta G_f^\circ(\text{CoF}_2) \\ &\quad - \Delta G_f^\circ(\text{NiF}_2). \quad (11) \end{aligned}$$

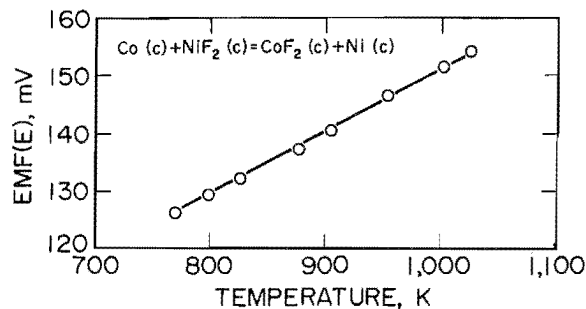


FIGURE 3. - Emf (E) versus temperature for CoF₂ cell.

Values of $\Delta G_f^\circ(\text{NiF}_2)$, obtained by interpolation from a compilation (13) and values of E in table 4, were substituted in equation 11 to derive $\Delta G_f^\circ(\text{CoF}_2)$ at each temperature, as listed in the fourth column of table 4.

The third-law values of $\Delta H_f^\circ(\text{CoF}_2)$ were derived in a similar manner to that described for MnF₂ and are listed in the fifth column of table 4. Values of G_f at several temperatures intervals for Co

TABLE 4. - Emf (E) of cell and thermodynamic properties of CoF₂

Experiment	Temperature, K	Emf (E), mV ¹	$-\Delta G_f^\circ(\text{CoF}_2)$, cal/mol	$-\Delta H_f^\circ(\text{CoF}_2)$, cal/mol
1.....	769.5	126.65	134,252	161,021
2.....	798.1	129.55	133,354	161,053
3.....	826.0	132.35	132,475	161,082
4.....	852.4	132.85	131,545	161,007
5.....	878.5	138.45	130,862	161,164
6.....	879.3	138.95	130,856	161,184
7.....	904.1	140.85	130,048	161,172
8.....	904.5	139.95	129,989	161,129
9.....	905.0	140.55	130,002	161,155
10.....	905.3	141.95	130,056	161,218
11.....	929.7	143.15	129,230	161,174
12.....	930.0	144.55	129,265	161,219
13.....	930.3	143.45	129,222	161,187
14.....	930.7	143.05	129,190	161,166
15.....	954.7	146.75	128,493	161,234
16.....	955.0	145.85	128,442	161,193
17.....	955.1	145.05	128,401	161,155
18.....	955.1	145.15	128,406	161,160
19.....	978.5	149.35	127,754	161,252
20.....	979.0	148.15	127,681	161,195
21.....	979.3	147.35	127,633	161,156
22.....	1,002.7	151.75	126,991	161,256
23.....	1,026.8	154.35	126,242	161,276
Average.....	Nap	Nap	Nap	² 161,166±69

Nap Not applicable.

¹Average of 2 measurements (± 0.05 mV) taken at 20-min intervals.

²Error from these measurements corresponds to a standard deviation; precision uncertainty is ± 138 cal/mol; overall accuracy is ± 420 cal/mol.

(15), F_2 (15), and CoF_2 (19), and ΔG_{ef} for the reaction $Co(c) + F_2(g) = CoF_2(c)$ are given in table 5. $\Delta H_{f,298}^\circ(CoF_2)$ for each temperature was derived by rearranging equation 4 and substituting the interpolated values of ΔG_{ef} from table 5 and the values of $\Delta G_{ef}(CoF_2)$ that are listed in table 4. The average value of $\Delta H_{f,298}^\circ(CoF_2)$ is $-161,166 \pm 69$ cal/mol. The standard deviation of ± 69 cal/mol refers to the present measurements listed in table 4. Additional errors and uncertainties are associated with the various thermal quantities involved in the calculation. For example, the uncertainty for $\Delta G_{ef}(NiF_2)$ is ± 400 cal/mol. Combination of these errors with the uncertainty of ± 138 cal/mol (2×69) from the present measurements yields

$$\Delta H_{f,298}^\circ(CoF_2) = -161,166 \pm 420 \text{ cal/mol. (12)}$$

A least squares treatment of the data for E fitted to an equation linear in T and extrapolation to 298.15 by a second-law method yields $\Delta H_{f,298}^\circ(CoF_2) = -161,148 \pm 420$ cal/mol. Agreement with equation 12 is good; however, the recommended value is from equation 12, based on the third-law method.

TABLE 5. - Auxiliary thermodynamic data for CoF_2 reaction

Temperature, K	-G _{ef} , cal/mol			ΔG_{ef} , cal/mol
	Co(c) (15)	$F_2(g)$ (15)	$CoF_2(c)$ (19)	
700.....	8.961	50.648	24.627	34.982
800.....	9.530	51.303	26.131	34.702
900.....	10.076	51.936	27.576	34.436
1,000...	10.596	52.537	28.954	34.179
1,100...	11.116	53.111	30.265	33.962

SUMMARY AND CONCLUSIONS

Standard Gibbs energies of formation of MnF_2 and CoF_2 were determined by emf measurements from reversible high-temperature galvanic cells using CaF_2 as the electrolyte. Third-law analyses of

Combination of equation 12 with the tabulated data (16, 19) using the results for the third-law method yields

$$\begin{aligned} \Delta G_{f,298}^\circ(CoF_2) \\ = (-159,090 + 32.13T) \pm 420 \text{ cal/mol} \\ (769.5-1,026.8 \text{ K}) \end{aligned} \quad (13)$$

for the reaction $Co(c) + F_2(g) = CoF_2(c)$. The constants in equation 13 are $\Delta H^\circ = -159,090$ and $\Delta S^\circ = -32.13$. Both constants refer to 898 K; however, they vary only slightly with temperature. Within experimental errors, equation 13 may be used to express ΔG° for the indicated range of temperature.

A compilation (19) based on gas-phase equilibration studies reported $\Delta H_{f,298}^\circ = -160,200 \pm 1,000$ cal/mol, which compares favorably with $-161,166 \pm 420$ cal/mol from this investigation. Similar emf studies (5, 20) for reaction 10 reported the following results:

$$\begin{aligned} \Delta G_{f,298}^\circ(CoF_2) = -163,000 + 34.17T \text{ cal/mol} \\ (581-1,066 \text{ K}) \end{aligned} \quad (14)$$

and $\Delta G_{f,298}^\circ(CoF_2)$

$$\begin{aligned} = (-158,542 + 32.37T) \pm 600 \text{ cal/mol} \\ (850-1,050). \end{aligned} \quad (15)$$

Comparison of equation 14 with the present results expressed by equation 13 shows considerable difference in both constants (ΔH° and $-\Delta S^\circ$). Equation 15 agrees favorably with the results from this investigation as expressed by equation 13.

the present data yield standard enthalpies of formation

$$\begin{aligned} \Delta H_{f,298}^\circ(MnF_2) = -204,633 \pm 560 \text{ cal/mol} \\ \text{and } \Delta H_{f,298}^\circ(CoF_2) = -161,166 \pm 420 \text{ cal/mol.} \end{aligned}$$

REFERENCES

1. Reddy, S. N. S., and R. A. Rapp. The Solubility and Diffusivity of Fluorine in Solid Copper From Electrochemical Measurements. *Metall. Trans. B*, v. 9B, 1978, pp. 559-565.
2. Wicks, C. E., and F. E. Block. Thermodynamic Properties of 65 Elements--Their Oxides, Halides, Carbides, and Nitrides. *BuMines B* 605, 1963, 146 pp.
3. 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, 1965, pp. 750-755.
4. Pankratz, L. B. Thermodynamic Properties of Halides. *BuMines B* 674, 1984, 826 pp.
5. Skelton, W. H., and J. W. Patterson. Free Energy Determinations by Solid Galvanic Cell Measurements for Selected Metal, Metal-Fluoride Reactions. *J. Less-Common Met.*, v. 31, 1973, pp. 47-60.
6. Markin, T. L. Galvanic Cells Reversible to Fluoride Ions. Ch. in *Electromotive Force Measurements in High-Temperature Systems*, ed. by C. B. Alcock. Grosvenor Press, Portsmouth, England, 1968, pp. 91-97.
7. Hinze, J. W., and J. W. Patterson. Electrolytic Behavior of CaF_2 Crystals Under Reducing Conditions. *J. Electrochem. Soc.*, v. 120, 1973, pp. 96-98.
8. Ure, R. W., Jr. Ionic Conductivity of Calcium Fluoride Crystals. *J. Chem. Phys.*, v. 115, 1957, pp. 1363-1373.
9. Wagner, C. J. Limitation of the Use of CaF_2 in Galvanic Cells for Thermodynamic Measurements Due to Onset of Electronic Conduction Under Reducing Conditions. *J. Electrochem. Soc.*, v. 115, 1968, pp. 933-935.
10. Schaefer, S. C. Free Energies of Formation of Ferrous and Ferric Fluoride by Electromotive Force Measurements. *BuMines RI* 8096, 1975, 14 pp.
11. Lofgren, N. L., and E. J. McIver. Thermodynamic Properties of Some Fluoride Systems. U.K. At. Energy Res. Establ. Rep. 5169, 1966, 14 pp.
12. Heus, R. J., and J. J. Egan. Free Energies of Formation of Some Inorganic Fluorides by Solid State Electromotive Force Measurements. *Z. Phys. Chem.*, v. 49, No. 102, 1966, pp. 38-43.
13. Mah, A. D., and L. B. Pankratz. Contributions to the Data on Theoretical Metallurgy. XVI. Thermodynamic Properties of Nickel and Its Inorganic Compounds. *BuMines B* 668, 1976, 125 pp.
14. Gokcen, N. A. Thermodynamics. Techscience Inc., Hawthorne, CA, 1975, 460 pp.
15. Pankratz, L. B. Thermodynamic Properties of Elements and Oxides. *BuMines B* 672, 1982, 509 pp.
16. Ehlert, T. C., and M. Hsia. Mass Spectrometric and Thermochemical Studies of the Manganese Fluorides. *J. Fluorine Chem.*, v. 2, No. 1, 1972/73, pp. 22-51.
17. Stout, J. W., and H. E. Adams. Magnetism and the Third Law of Thermodynamics. The Heat Capacity of Manganous Fluoride From 13 to 320° K. *J. Am. Chem. Soc.*, v. 64, 1942, pp. 1535-1538.
18. Rezhukhina, T. N., T. F. Sisoeva, L. I. Holokhonova, and E. G. Ippolitov. The Thermodynamic Properties of Some Metal Fluorides. Solid-Electrolyte Galvanic-Cell Studies. *J. Chem. Thermodyn.*, v. 6, 1974, pp. 883-893.
19. Dow Chemical Co., Thermal Research Laboratory. JANAF Thermochemical Tables. NSRDS-NBS 37, 2d ed., 1971, 1141 pp.
20. Chattopadhyay, G., M. D. Karkhanavala, and M. S. Chandrasekhariah. Standard Free Energies of Formation of Metal Fluorides by Solid Electrolytic Galvanic Cell Method. I. Metal Difluorides. *J. Electrochem. Soc.*, v. 122, 1975, pp. 325-327.