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Measurement of Gibbs energies of formation of CoF_2 and MnF_2 using a new composite dispersed solid electrolyte

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Abstract. Gibbs energies of formation of CoF_2 and MnF_2 have been measured in the temperature range from 700 to 1100 K using Al_2O_3-dispersed CaF_2 solid electrolyte and $Ni + NiF_2$ as the reference electrode. The dispersed solid electrolyte has higher conductivity than pure CaF_2 thus permitting accurate measurements at lower temperatures. However, to prevent reaction between Al_2O_3 in the solid electrolyte and NiF_2 (or CoF_2) at the electrode, the dispersed solid electrolyte was coated with pure CaF_2, thus creating a composite structure. The free energies of formation of CoF_2 and MnF_2 are (± 1700) J mol^{-1};

$$\Delta G_f^\circ(CoF_2, s) = -664{,}010 + 134{\cdot}38T \; (700\text{–}980 \text{ K})$$
$$\Delta G_f^\circ(MnF_2, s) = -848{,}270 + 129{\cdot}59T \; (700\text{–}980 \text{ K})$$
$$= -850{,}200 + 131{\cdot}56T \; (980\text{–}1100 \text{ K})$$

The third law analysis gives the enthalpy of formation of solid CoF_2 as $\Delta H^\circ(298{\cdot}15 \text{ K}) = -672{\cdot}69(\pm 0{\cdot}1)$ kJ mol^{-1}, which compares with a value of $-671{\cdot}5(\pm 4)$ kJ mol^{-1} given in Janaf tables. For solid MnF_2, $\Delta H^\circ(298{\cdot}15 \text{ K}) = -854{\cdot}97(\pm 0{\cdot}13)$ kJ mol^{-1}, which is significantly different from a value of $-803{\cdot}3$ kJ mol^{-1} given in the compilation by Barin *et al.*

Keywords. Chemical potential of fluorine; thermodynamic properties; electromotive force; enthalpy; entropy; free energy of formation.

1. Introduction

Solid state galvanic cells are extensively used for determining thermodynamic mixing properties of alloy systems (Jacob 1985). In most of the studies oxide electrodes and solid electrolytes are employed. In a few studies CaF_2 has been used as a solid electrolyte in conjunction with fluoride electrodes (Venkatraman and Hajra 1983; Egan 1985). One of the reasons for the less frequent use of fluoride solid state cells for the study of alloy thermodynamics is the lack of accurate thermochemical data on metal fluorides. Calorimetric measurements of the enthalpy of formation of CoF_2 and MnF_2 have not been reported in the literature. The free energy measurements for MnF_2 reported by Skelton and Patterson (1973) and by Rezukhina *et al* (1974) do not agree. Heat capacities and entropies of CoF_2 were measured by Catalano and Stout (1955) and Binford *et al* (1967), and those of MnF_2 by Stout and Adams (1942), and Ehlert and Hsia (1972/73). The standard heat of formation at 298·15 K can therefore be derived from accurate free energy measurements.

Recently it has been shown that a fine dispersion of inert insulating phases such as Al_2O_3 and CeO_2 in CaF_2 can increase its conductivity by two to three orders of magnitude at temperatures near 700 K. The conductivity of Al_2O_3-dispersed CaF_2 has been shown to be entirely ionic by Vaidehi *et al* (1986). One of the aims of the present study is to explore the use of Al_2O_3-dispersed CaF_2 electrolyte for thermodynamic studies, especially at lower temperatures where the response of conventional cells based on pure CaF_2 electrolyte is sluggish.

Fluorides of manganese and cobalt are used as catalysts in hydrocarbon isomerisation and polymerisation reactions. Manganese fluoride also finds application in optics and electronic industries. The knowledge of the stabilities of these fluorides would be useful in optimising the procedures for their synthesis and applications at elevated temperatures.

2. Experimental techniques

2.1 *Materials*

Ultrapure anhydrous CaF_2 (99·999%) powder was supplied by Alpha Ventron Division, USA. The alumina powder of 99·8% purity was prepared by precipitation from solution and subsequent calcination at 1400 K in air. The average particle size of Al_2O_3 was 0·02 μm. The Al_2O_3-dispersed CaF_2 electrolyte was prepared by mixing $CaF_2 + Al_2O_3$ powder in an agate mortar. The CaF_2 pellets containing 2 mol% Al_2O_3 in dispersed form were made from the intimate mixture by double end compression. The composite solid electrolytes were made by sprinkling a small amount of pure CaF_2 over the lower steel plunger, then the required amount of CaF_2 containing 2 mol% Al_2O_3 mixture was added, followed again by sprinkling pure CaF_2 powder in the steel die. The upper steel plunger was then inserted and compressed to 200 MPa. The result was a composite pellet of Al_2O_3-dispersed CaF_2 with a coating of pure CaF_2, approximately 100 μm in thickness, on the two flat surfaces as shown in figure 1. The pellets were sintered under prepurified argon gas at 1400 K for up to 180 ks. The argon gas, 99·99% pure, was dried by passing through magnesium perchlorate and then through soda asbestos for removal of CO_2. The gas was subsequently deoxidised using copper at 750 and titanium at 1150 K.

Powders of Mn, Co, Ni, MnF_2, CoF_2 and NiF_2 of puratronic grade were supplied by Johnson and Matthey Chemicals Ltd. Pellets containing equimolar mixture of $Ni + NiF_2$, $Co + CoF_2$ and $Mn + MnF_2$ were prepared by compression in a steel die. Single crystals of CaF_2 were supplied by Harshaw Chemical Company.

2.2 *Apparatus and procedure*

A schematic diagram of the apparatus is shown in figure 2. The electrode pellets are spring-loaded on either side of the solid electrolyte by a system made up of alumina

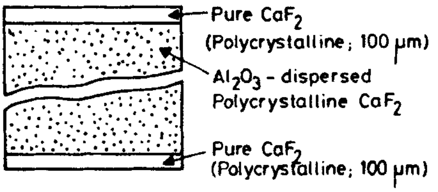

Figure 1. Structure of the composite solid electrolyte containing regions of pure CaF_2 and Al_2O_3-dispersed CaF_2.

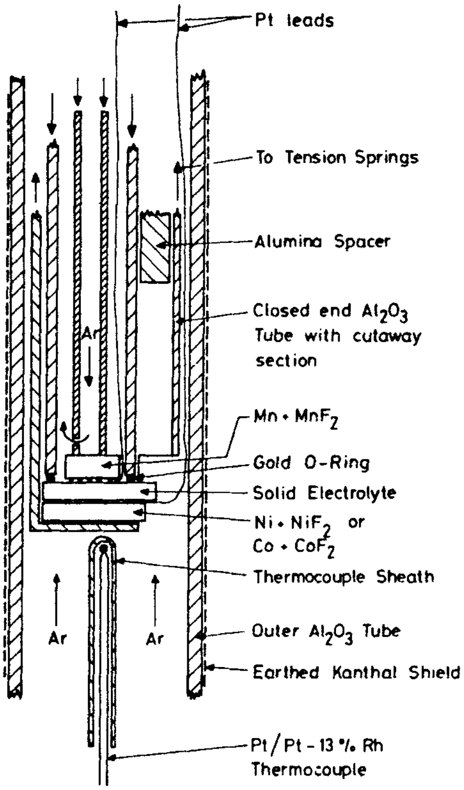

Figure 2. A schematic diagram of the apparatus used in this study.

slabs and tubes as shown in the figure. The gas phase around each electrode was separated by an alumina tube which was pressed against the CaF_2 pellet with a gold O-ring in between. The separation of the gas over each electrode was found to be essential to prevent vapour phase transport of species from one electrode to the other. The partial pressures of NiF_2, CoF_2 and MnF_2 are 0·6, 0·4 and 0·15 Pa at 1100 K. Separate streams of purified argon gas were flown past each electrode. Initially, flow rates were in the range of 4 ml s^{-1} but were reduced to 0·2 ml s^{-1} after the apparatus was completely purged. Electrical contacts to electrode pellets were made by platinum. The cell was enclosed in an outer alumina tube which was suspended in a vertical resistance furnace wound with Kanthal. The cell was electrically shielded by a Kanthal tape wound round the outer alumina tube and earthed. The temperature of the furnace was controlled to ± 1 K. The temperature was measured by a calibrated Pt/Pt–13% Rh thermocouple.

The emf of the cells was measured by a Keithley digital electrometer (model 617) with an impedance exceeding 10^{12} ohms. The reversibility of the cells was checked by passing a small current (~ 5 μA) in either direction through the cell and ensuring that the emfs returned to the constant initial values before titration. The emfs were reproducible on temperature cycling. The emfs were also independent of the flow rate of the inert gas at temperatures below 900 K. At higher temperatures emfs were found to be slightly dependent on the flow rate of the argon gas, presumably because of the removal of volatile fluorides. Below a flow rate of 0·4 ml s^{-1}, the emfs were not affected. The emfs of the following cells were measured as a function of temperature:

I Pt, $Mn+MnF_2 \parallel CaF_2+2\,mol\%\,Al_2O_3 \parallel Ni+NiF_2$, Pt
II Pt, $Mn+MnF_2 \parallel CaF_2 \parallel Ni+NiF_2$, Pt
III Pt, $Mn+MnF_2 \parallel CaF_2+2\,mol\%\,Al_2O_3 \parallel Co+CoF_2$, Pt
IV Pt, $Mn+MnF_2 \parallel CaF_2 \parallel Co+CoF_2$, Pt

The cells are written such that the right hand electrodes are positive. Single crystals of CaF_2 were used in cells II and IV.

Preliminary experiments with cells I and III were conducted with Al_2O_3-dispersed CaF_2 without a thin layer of pure CaF_2 on the flat surfaces of the electrolyte. It was found that the cell emf began to drop gradually after approximately 85 ks at temperatures above 1000 K. After 250 ks the emf dropped by 8 mV. Careful examination of the electrolyte/electrode interface after the experiment by electron microscope (diffraction) indicated small islands of AlF_3. This phase was found at the interface between CaF_2-2 mol% Al_2O_3 electrolyte and $Ni+NiF_2$ (or $Co+CoF_2$) electrode. Thermodynamic data suggest that the formation of AlF_3 occurs by the following reactions:

$$Al_2O_3(s)+3\,NiF_2(s)\rightarrow 2\,AlF_3(s)+3\,NiO(s);\ \Delta G_R^\circ=-92{\cdot}8\ \mathrm{kJ\,mol^{-1}}, \quad (1)$$

$$Al_2O_3(s)+3\,CoF_2(s)\rightarrow 2\,AlF_3(s)+3\,CoO(s);\ \Delta G_R^\circ=-53{\cdot}0\ \mathrm{kJ\,mol^{-1}}. \quad (2)$$

The contact between Al_2O_3 in the electrolyte and NiF_2 (or CoF_2) at the electrode was avoided in the subsequent experiments by using composite dispersed solid electrolytes, which had a thin coating of pure CaF_2 on the electrolyte surface. With composite solid electrolytes the emfs were stable up to 500 ks at 1100 K. All data reported in this paper were obtained using the composite dispersed solid electrolyte. Measurements with cells I and III incorporating Al_2O_3-dispersed CaF_2 composite electrolyte were conducted in the temperature range from 700 to 1100 K. Experiments using pure CaF_2 electrolyte (cells II and IV) were confined to temperatures above 950 K where the response was rapid. The electrodes in cells I and II are identical. Similarly the only difference between the cells III and IV is the composition of the electrolyte.

3. Results

The reversible emfs of cells I to IV are summarized in tables 1 and 2. The variation of emf of the cells I and II with temperature is shown in figure 3.

The emfs of the two cells are identical within experimental error, confirming that electric conduction in the biphasic dispersed solid electrolyte is entirely ionic. The reproducibility of emf at a fixed temperature is ±0·3 mV. There appears to be a change in slope of the curve at 980 K which corresponds to transformation of Mn from α to β form. The least mean squares regression analysis gives the following expression for combined emf of cells I and II:

$$E=1{,}008{\cdot}4+0{\cdot}1133T\,(\pm 0{\cdot}3)\ \mathrm{mV}, \quad (3)$$

for the temperature range 700 to 980 K. For high temperatures (980 to 1100 K), emfs are given by

$$E=1{,}018{\cdot}4+0{\cdot}1031T\,(\pm 0{\cdot}36)\ \mathrm{mV}. \quad (4)$$

Table 1. Emf of the cells I and II and $\Delta G_f^\circ(T)$ and $\Delta H^\circ_{298\cdot15}$ (third-law) of MnF_2.

T(K)	Emf (mV)	$-\Delta G_f^\circ(MnF_2,s)$ (kJ mol^{-1})	$-\Delta H^\circ_{298\cdot15}(MnF_2,s)$ (kJ mol^{-1})
Pt, Mn + MnF_2 ‖ CaF_2 + 2 mol%Al_2O_3 ‖ Ni + NiF_2, Pt			
703	1088·0	757·16	854·66
757	1094·5	750·24	854·89
809	1099·6	743·34	854·82
851	1104·5	737·93	854·95
867	1107·0	735·98	855·11
900	1110·6	731·68	855·11
947	1115·5	725·51	855·04
984	1120·0	720·78	855·13
1015	1122·8	716·62	855·02
1037	1125·1	713·73	854·98
1070	1129·0	709·49	854·98
1096	1131·0	705·94	854·77
Pt, Mn + MnF_2 ‖ CaF_2 ‖ Ni + NiF_2, Pt			
970	1118·4	722·34	855·11
1079	1130·1	708·34	854·99
1050	1127·0	712·13	855·06

Table 2. Emf of the cells III and IV and $\Delta G^\circ(T)$ and $\Delta H^\circ_{298\cdot15}$ (third-law) of CoF_2.

T(K)	Emf (mV)	$-\Delta G_f^\circ(CoF_2,s)$ (kJ mol^{-1})	$-\Delta H^\circ_{298\cdot15}(CoF_2,s)$ (kJ mol^{-1})
Pt, Mn + MnF_2 ‖ CaF_2 + 2 mol%Al_2O_3 ‖ Co + CoF_2, Pt			
699	972·1	570·1	672·45
730	972·7	565·96	672·59
758	973·7	562·14	672·61
800	974·6	556·53	672·71
840	975·8	551·11	672·75
844	975·4	550·67	672·85
860	976·3	548·42	672·76
879	976·8	545·86	672·76
901	977·3	542·92	672·77
930	977·7	539·08	672·84
950	978·6	536·32	672·75
990	979·2	530·99	672·76
1010	979·5	528·30	672·74
1060	980·3	521·57	672·67
1080	980·4	518·92	672·67
1101	980·7	516·10	672·63
Pt, Mn + MnF_2 ‖ CaF_2 ‖ Co + CoF_2, Pt			
966	978·9	534·96	673·54
1040	979·9	524·28	672·72
1060	980·1	521·61	672·70
1092	980·8	517·27	672·60

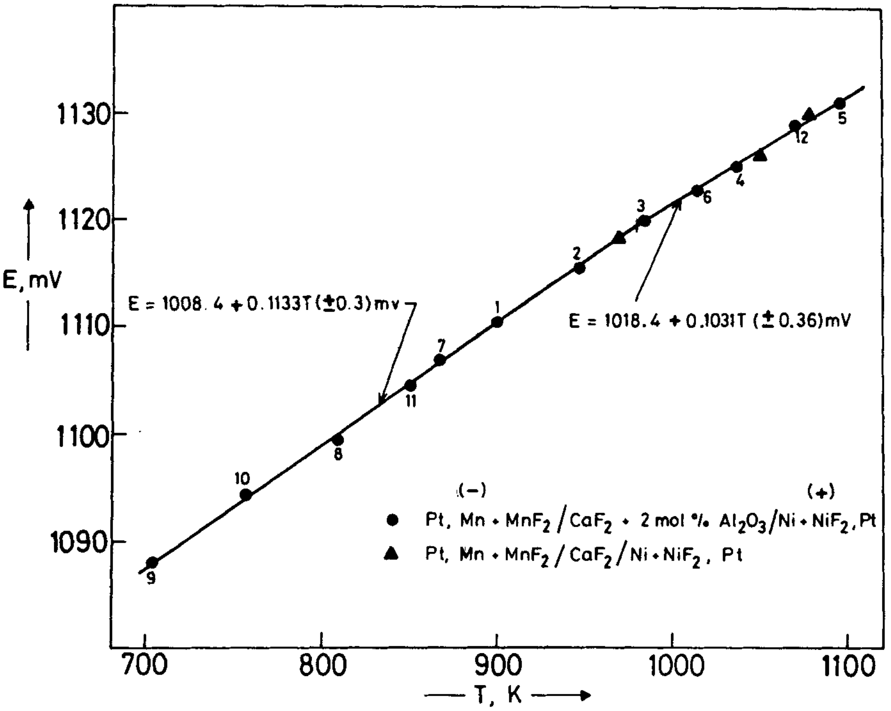

Figure 3. Variation of the emf of cells I and II with temperature.

The net reaction for cells I and II is

$$NiF_2\,(s) + Mn\,(s) = MnF_2\,(s) + Ni\,(s). \qquad (5)$$

Gibbs energy change for this reaction is given by

$$\Delta G^\circ_R = \Delta G^\circ_{MnF_2} - \Delta G^\circ_{NiF_2} = -2FE, \qquad (6)$$

where E is the emf in volts and F is the Faraday constant. The Gibbs energy of formation of NiF_2 is well established in the literature (Mah and Pankratz 1976). In the temperature range 700 to 1100 K, the standard Gibbs energy of formation of NiF_2 can be expressed by:

$$\Delta G^\circ_f(NiF_2,s) = -653{,}680 + 151{\cdot}46T (\pm 1650)\ \mathrm{J\,mol^{-1}}. \qquad (7)$$

Combining this with (4) the standard free energy of formation of MnF_2 is obtained. For the temperature range 700 to 980 K

$$\Delta G^\circ_f(MnF_2,s) = -848{,}270 + 129{\cdot}59T (\pm 1700)\ \mathrm{J\,mol^{-1}}. \qquad (8)$$

For the higher temperature range from 980 to 1100 K, ΔG°_f of MnF_2 is given by

$$\Delta G^\circ_f(MnF_2,s) = -850{,}200 + 131{\cdot}56T (\pm 1700)\ \mathrm{J\,mol^{-1}}. \qquad (9)$$

The uncertainty limits are evaluated considering the errors in temperature and emf measurements as well as uncertainty in free energy of formation of NiF_2.

The temperature dependence of emfs of the cells III and IV is displayed in figure 4. Within experimental error, the emfs of both the cells are identical. Again there

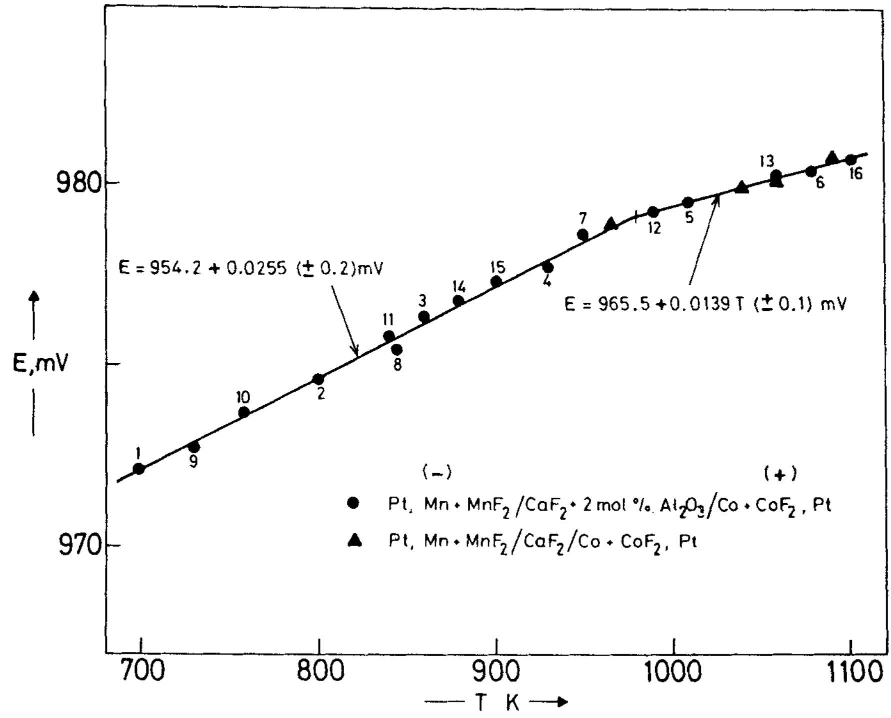

Figure 4. Temperature dependence of the emf of cells III and IV.

appears to be a change of slope at 980 K. The mean squares regression analysis gives the following expressions for the emf:

$$E = 954{\cdot}2 + 0{\cdot}0255T\,(\pm 0{\cdot}2)\ \text{mV}\ (700\text{–}980\ \text{K}), \qquad (10)$$

$$E = 965{\cdot}5 + 0{\cdot}0139T\,(\pm 0{\cdot}1)\ \text{mV}\ (980\text{–}1100\ \text{K}). \qquad (11)$$

The emf corresponds to the cell reaction

$$\mathrm{CoF_2\,(s) + Mn\,(s) = MnF_2\,(s) + Co\,(s)}, \qquad (12)$$

$$\Delta G^\circ_R = \Delta G^\circ_f(\mathrm{MnF_2}) - \Delta G^\circ_f(\mathrm{CoF_2}) = -2FE. \qquad (13)$$

Using values for the standard Gibbs energy of formation of MnF_2 given by (8) and (9) Gibbs energy of formation of CoF_2 can be computed from the emf of cells III and IV

$$\Delta G^\circ_f(\mathrm{CoF_2,s}) = -664{,}140 + 134{\cdot}51\,T(\pm 1700)\ \text{J mol}^{-1}\ (700\text{–}980\ \text{K}), \qquad (14)$$

$$\Delta G^\circ_f(\mathrm{CoF_2,s}) = -663{,}880 + 134{\cdot}24\,T(\pm 1700)\ \text{J mol}^{-1}\ (980\text{–}1100\ \text{K}). \qquad (15)$$

The coefficients of (14) and (15) are almost identical within experimental error. Since there are no transformations of either metallic cobalt or cobalt fluoride in temperature range of 700 to 1100 K, there is little theoretical justification for separate equations in this range. Therefore Gibbs energy of formation of CoF_2 is expressed as

$$\Delta G^\circ_f(\mathrm{CoF_2,s}) = -664{,}010 + 134{\cdot}38\,T(\pm 1700)\ \text{J mol}^{-1}. \qquad (16)$$

4. Discussion

The Gibbs energy of formation of MnF_2 obtained in this study is compared with the data reported by Rezukhina *et al* (1974) and Skelton and Patterson (1973) in figure 5. The results of this study are in excellent agreement with the data of Rezukhina *et al* (1974) obtained by using a CaF_2 cell with $Al + AlF_3$ as the reference electrode. However, the data of Skelton and Patterson (1973) obtained by using $Ni + NiF_2$ as reference electrode are more negative than the present data by approximately 4 kJ mol^{-1} at 1070 K. The smaller emfs obtained by Skelton and Patterson (1973) may be attributed to the transport of materials between electrodes via the vapour phase in their open stacked pellet assembly.

Figure 6 shows the comparison of Gibbs energy data obtained in this study for CoF_2 with values reported in the literature. The present data are in good agreement ($\pm 2{\cdot}5$ kJ mol^{-1}) with those of Chattopadhyay *et al* (1975) between 850 and 1050 K and Skelton and Patterson (1973) in the temperature range 580 to 1066 K. Both sets of data in the literature obtained using solid state cells almost identical to that employed in this study indicate a slightly more positive free energies of formation of CoF_2. Since fluorine potentials at both electrodes are similar, emfs of cells III and IV are smaller. Problems due to gas transport between electrodes are therefore, likely to be less significant.

The standard enthalpy of formation of MnF_2 at 298·15 K, calculated from the free energy of formation at different temperatures by the third law method using entropy and heat capacity functions from the literature is listed in table 1. The values of $\Delta S^\circ_{298{\cdot}15}$, $S^\circ_T - S^\circ_{298{\cdot}15}$ and $H^\circ_T - H^\circ_{298{\cdot}15}$ for MnF_2 are obtained from Stout and Adams (1942), Ehlert and Hsia (1972/73); the corresponding values for fluorine gas are from Stull and Prophet (1971) and those of solid Mn are from Barin *et al* (1977). The average value for $\Delta H^\circ_f(298{\cdot}15\ K)$ for (MnF_2,s) obtained from this study is $-854{\cdot}97$ ($\pm 0{\cdot}13$) kJ mol^{-1}. The values of $\Delta H^\circ_f(298{\cdot}15\ K)$ obtained in this study are plotted as a function of the temperature of the free energy measurement in figure 7. It

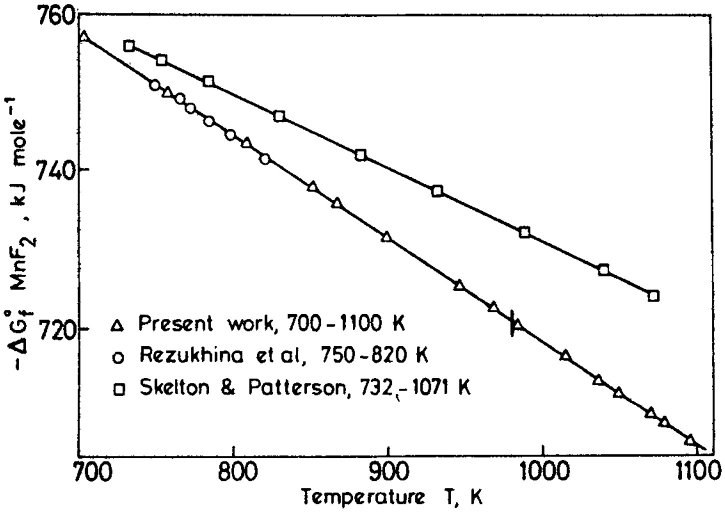

Figure 5. Gibbs energy of formation of MnF_2—Comparison with data in the literature.

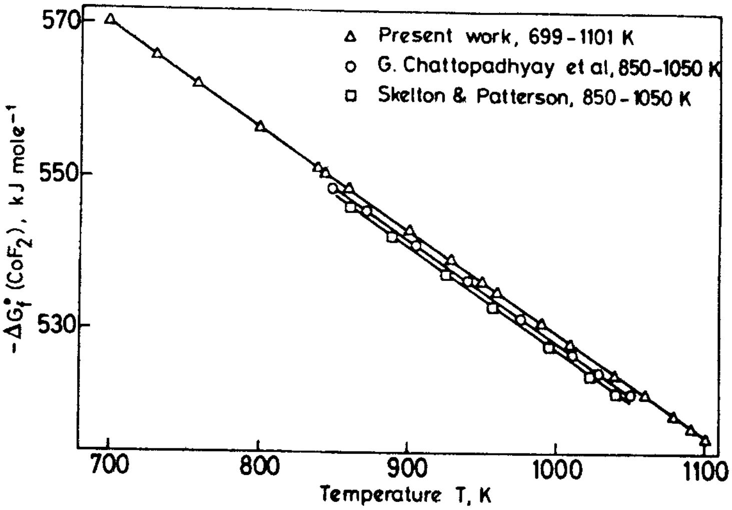

Figure 6. Comparison of free energy of formation of CoF_2 obtained in this study with previous work.

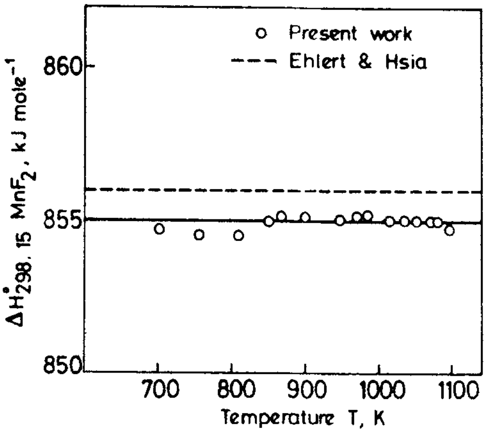

Figure 7. $\Delta H^\circ_{298.15}$ (third-law) for $Mn(s) + F_2(g) = MnF_2(s)$.

is seen that the values are virtually constant throughout the temperature range suggesting the absence of systematic temperature-dependent errors in the free energy measurement. The value of $\Delta H_f^\circ(298{\cdot}15\ K)$ obtained in this study is significantly more negative than the value of $-795\ (\pm 20)$ kJ mol^{-1} suggested by Brewer *et al* (1950), the value of -793 kJ mol^{-1} suggested by Mah (1960) or the value of -803 kJ mol^{-1} given in the compilation of Barin *et al*(1977). The results of this study are in reasonable agreement with the value of -849 ± 20 kJ mol^{-1} suggested by Ehlert and Hsia (1972/73).

The third law enthalpy of formation of CoF_2 at 298·15 K evaluated from each free energy value obtained in the study is plotted as a function of temperature in figure 8. The average value of $\Delta H^\circ_{298.15} = -672{\cdot}69\ (\pm 0{\cdot}1)$ kJ mol^{-1}, compares with a value of

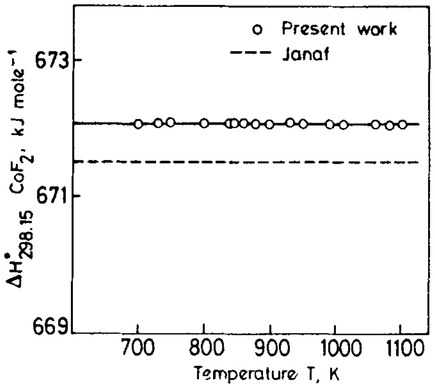

Figure 8. $\Delta H^\circ_{298 \cdot 15}$ (third-law) for $Co(s) + F_2(g) = CoF_2(s)$.

$-671 \cdot 5\,(\pm 4)\,kJ\,mol^{-1}$ given in Janaf tables (Stull and Prophet 1971) based on earlier free energy measurements using gas equilibration and emf techniques.

5. Conclusion

The use of dispersed solid electrolytes in galvanic cells permits accurate measurements at temperatures lower than those permitted by conventional electrolytes. Problems arising from the interaction of the electrode materials with the dispersoid can be overcome by having a thin layer ($\sim 100\,\mu m$) of pure electrolyte at the contact surfaces. Such engineered composite solid electrolytes are expected to enlarge the temperature range available for thermodynamic measurements with galvanic cells in the future.

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