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Comparative e.m.f. study of CaF_2 and β-alumina cells with Ni/NiF_2 and Fe/FeF_2 or Cr/CrF_2 electrodes

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The reliability of employing beta-alumina as electrolyte for fluorine potential measurement is examined by measuring the e.m.f.s of the galvanic cells with metal/metal fluoride electrodes and comparing with those obtained by using CaF_2 as electrolyte under identical conditions. The results from both types of galvanic cell can be superimposed to give the following standard Gibbs energy of formation, ΔG_f^0, of FeF_2 and CrF_2 over extended ranges of temperature:

$$\Delta G_f^0(FeF_2) = -702.0 + 0.125\,20T\,(K)\,(\pm 0.70)\,kJ\,mol^{-1}\,(506\text{–}1063\,K)$$

$$\Delta G_f^0(CrF_2) = -732.8 + 0.087\,90T\,(K)\,(\pm 0.64)\,kJ\,mol^{-1}\,(497\text{–}1063\,K)$$

The absence of significant temperature-dependent errors in both these measurements are verified by a third law treatment of the data yielding values of -716.8 and $-777.4\,kJ\,mol^{-1}$ for $\Delta H_{f,298}^0$ of FeF_2 and CrF_2, respectively.

The feasibility of using beta-alumina electrolyte cells for e.m.f. measurements on other metal/metal fluoride systems is discussed in the light of the existence of a useful potential domain of beta-alumina. High sodium potential in the electrode system can lead to sodium depletion. Likewise, low sodium potential may result in oxidation of the metals in the electrodes. Both these limiting factors are also examined.

1. Introduction

Beta-alumina, which is a sodium ion conductor, has been employed as electrolyte for fluorine potential measurements in galvanic cells [1]. However, the reliability of such measurements has not been established by a parallel study using CaF_2 e.m.f. cells with the same set of metal/metal fluoride electrodes. Such experiments may establish sodium potential probes made of beta-alumina with sealed-in fluoride electrodes for reference for commercial applications. In addition, thermodynamic data for even simple binary metal fluorides are more scarce and less reliable than for the corresponding oxides [2, 3]. In the case of simple initial oxides, 'absolute' measurements of standard Gibbs energy of formation, ΔG_f^0, are possible using pure oxygen or air directly as reference electrode materials. Use of these gaseous reference electrodes is possible due to the availability of oxide electrolytes in the form of long gas-impervious tubes [4–8]. However, such measurements are difficult in the case of fluorides due to the reactivity of fluorine, even in dilute gaseous mixtures. Hence, only the difference in the fluorine potentials between two different metal/metal fluoride coexisting mixtures can be determined from the e.m.f.s of cells with CaF_2 as a solid electrolyte [2, 9–12]. Nevertheless, the accuracy of these measurements can be assessed if the differences in fluorine potentials are monitored by an independent e.m.f. method. Choudhury [1] has reported the feasibility of measuring fluorine potentials as sodium potentials with the help of beta-alumina, which is reversible to sodium ions.

The present investigation demonstrates the generation of identical e.m.f. data from concentration cells reversible either to fluorine or to sodium. Such dual measurements are shown to

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facilitate extension of the temperature range of expressions for ΔG_f^0, besides upholding their accuracy.

2. Experimental details

For the preparation of electrodes, powdered iron and nickel (Alfa Ventron, USA) and chromium (Johnson Mathey, UK) of high purity (> 99.99%) and transition metal fluorides of reagent grade of purity > 99.8% (Koch-Light, USA) were used. The sodium fluoride, NaF, was of purity > 99.9% (Johnson Mathey, UK).

Cylindrical single crystal discs of CaF_2, 10 mm in diameter and 3 mm thick (Harshaw Chemical Company, USA), were employed as the solid electrolyte in fluoride concentration cells. Electrodes were prepared by compacting 3 : 1 weight ratio mixtures of metal and the required metal fluoride into pellets, 12 mm in diameter and 3–4 mm thick, under a pressure of 100 MPa. For sodium concentration cells an equal weight of NaF was added to the mixture before compacting under identical conditions. Superfine (Submicron) calcined beta-alumina ($Na_2O \cdot 11Al_2O_3$, Alcoa, Switzerland) was compacted into cylindrical discs, 12 mm in diameter and 2–3 mm thick, at a pressure of 1500 MPa. These discs were embedded in beta-alumina powder and were sintered at 1600° C for 15 h. The sintered discs were found to have a theoretical density of ~90% and were used in sodium concentration cells.

An open-cell, stacked-pellet assembly was used throughout this investigation, the details of which have been described elsewhere [13]. The only modification in this galvanic cell assembly was the replacement of the outer jacket, made of fused silica, by a recrystallized alumina tube, with one end closed in order to minimize permeability of oxygen through the outer jacket. A Pt–10% Rh/Pt thermocouple calibrated at the freezing points of tin, bismuth, zinc, antimony and silver was used to measure the temperature of the cell. The head of the galvanic cell assembly was located in the isothermal zone of a non-inductively wound furnace, whose temperature was regulated with a PID temperature controller to be within ±0.5 K. The cell readings were usually taken only after initially heating the cell to the highest temperature of the range covered in a given e.m.f. run and after maintaining it at that temperature till the drift in the e.m.f. was less than $\pm 1.0\,\mathrm{mV\,h^{-1}}$. The reproducibility of the e.m.f. values was checked both by thermal cycling and by measurements on different electrode pellets. The e.m.f. readings were taken with the help of a $5\frac{1}{2}$ digit digital voltmeter with an input impedence of $10^9\,\Omega$. The absence of asymetric potentials and other thermoelectric contributions was confirmed by the nearly null e.m.f. of cells with indentical electrodes, as well as by internal consistency checks amongst galvanic cells formed by combining any two of the three reference electrodes, namely Ni/NiF_2, Fe/FeF_2 and Cr/CrF_2 [14].

3. Results

The e.m.f. results of the cells

$$\mathrm{Pt, Fe, FeF_2/CaF_2/NiF_2, Ni, Pt} \qquad \mathrm{I}$$

and

$$\mathrm{Pt, Fe, FeF_2, NaF/\beta\text{-}alumina/NaF, NiF_2, Ni, Pt} \qquad \mathrm{II}$$

are shown in Fig. 1, with different symbols for the two types. Similarly, the temperature dependence of the e.m.f. values for the following cells are shown in Fig. 2.

$$\mathrm{Pt, Cr, CrF_2/CaF_2/NiF_2, Ni, Pt} \qquad \mathrm{III}$$

$$\mathrm{Pt, Cr, CrF_2, NaF/\beta\text{-}alumina/NaF, NiF_2, Ni, Pt} \qquad \mathrm{IV}$$

The temperature dependence of e.m.f.s from Figs 1 and 2, namely E and E', can be summarized by the least-square expressions given below:

$$E = 244.6 + 0.1378T(\mathrm{K})\ (\pm 3.5)\,\mathrm{mV} \qquad (1)$$

$$E' = 409.8 + 0.3281T(\mathrm{K})\ (\pm 2.5)\,\mathrm{mV} \qquad (2)$$

Equations 1 and 2 are valid over the ranges 506 to 1063 K and 497 to 1063 K, respectively.

4. Discussion

4.1. *Equivalence of CaF_2 and beta-alumina cells*

Galvanic cells based on CaF_2 as electrolyte are

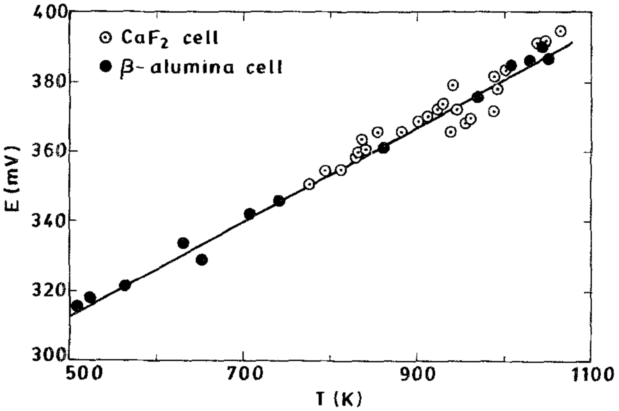

Fig. 1. Temperature dependence of the e.m.f. values of cells I and II.

essentially fluorine concentration cells in which the e.m.f., E, of cell I or III is related to the fluorine potential, μ'_{F_2} (in Ni/NiF_2) and μ''_{F_2} (in M/MF_2, where M is iron or chromium), through the following equation:

$$E = -\frac{1}{2F}\int_{\mu'_{F_2}}^{\mu''_{F_2}} t_{F^-}\, d\mu_{F_2} \qquad (3)$$

If the chemical potentials μ'_{F_2} and μ''_{F_2}, corresponding to the partial pressures P'_{F_2} and P''_{F_2}, are well within the electrolytic domain of CaF_2, then the transference number of the fluoride ion, t_{F^-}, in the electrolyte can be assumed to be unity. This enables the integration of Equation 3 to yield

$$E = -\frac{1}{2F}\Delta\mu_{F_2}$$

where

$$\begin{aligned}\Delta\mu_{F_2} &= \mu''_{F_2} - \mu'_{F_2} \\ &= \Delta G^0_f(MF_2) - \Delta G^0_f(NiF_2) \qquad (4)\end{aligned}$$

For the cells II and IV the e.m.f. is related to μ'_{Na} (in $NiF_2/Ni/NaF$) and μ''_{Na} (in $MF_2/M/NaF$) as follows:

$$E = -\frac{1}{F}\int_{\mu'_{Na}}^{\mu''_{Na}} t_{Na^+}\, d\mu_{Na} \qquad (5)$$

For the beta-alumina electrolyte, if the sodium potentials encountered are within its electrolytic domain, then the sodium ion transference number, t_{Na^+}, may be assumed to be unity. This leads to

$$E = -\frac{1}{F}\Delta\mu_{Na} \qquad (6)$$

where

$$\Delta\mu_{Na} = \mu''_{Na} - \mu'_{Na}$$

However, the half-cell reactions for cells II and IV are different from those of cells I and III. For instance, the half-cell reaction in the three-phase mixture, $NiF_2/Ni/NaF$, is

$$2NaF + Ni \longrightarrow NiF_2 + 2Na \qquad (7)$$

for which

$$\Delta G^0_{(7)} = \Delta G^0_f(NiF_2) - 2\Delta G^0_f(NaF) \qquad (8)$$

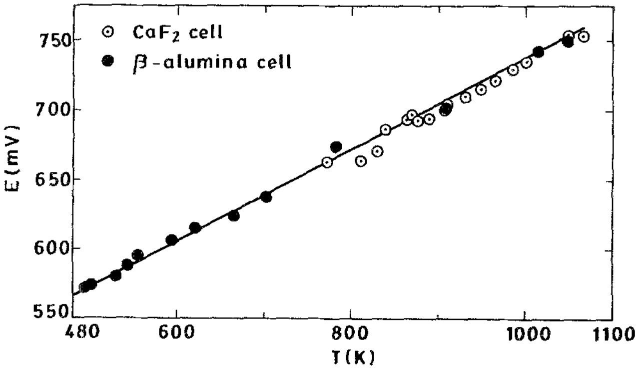

Fig. 2. Temperature dependence of the e.m.f. values of cells III and IV.

Similarly, for the MF/M/NaF electrode, the half-cell reaction is

$$2NaF + M \longrightarrow MF_2 + 2Na \qquad (9)$$

for which

$$\Delta G^0_{(9)} = \Delta G^0_f(MF_2) - 2\Delta G^0_f(NaF) \qquad (10)$$

If the two half-cell reactions 7 and 9 are combined, this gives rise to the same net reaction as in cells I and III for the passage of two faradays of electricity, namely

$$NiF_2 + M \longrightarrow MF_2 + Ni \qquad (11)$$

Thus

$$E = \frac{RT}{2F}\ln(P'_{F_2}/P''_{F_2}) = \frac{RT}{F}\ln(P'_{Na}/P''_{Na})$$
$$= \frac{1}{2F}[\Delta G^0_f(MF_2) - \Delta G^0_f(NiF_2)] \qquad (12)$$

The equivalence of the e.m.f. of the fluorine as well as the sodium concentration cells dictated by Equation 12 is proved by the experimental e.m.f. results shown in Figs 1 and 2. The upper limit of the temperature range of the galvanic cells with transition metal fluorides is dictated by their high volatility. However, the lower limit of the range is possibly restricted by the high resistance of the single crystal, CaF_2, and by the absence of an electrochemical catalyst like NaF. The use of beta-alumina in place of CaF_2 has considerably extended the lower limit, probably by overcoming these restrictions, at least in part. Hence, it was meaningful to derive a single best-fit, least-square expression for each of the plots in Figs 1 and 2, covering the entire temperature range, instead of distinguishing the source of data to be from CaF_2 or beta-alumina cells.

4.2. *Standard Gibbs' energy of formation of iron(II) fluoride*

To compute the ΔG^0_f of FeF_2 from Equations 1 and 12, precise values of the ΔG^0_f of NiF_2(s) are required. Since NiF_2(s) is known to be a line compound and also appears to be better characterized [15–18], it is chosen as the reference material. The ΔG^0_f of NiF_2(s) from calorimetry [19–21] is given by

$$\Delta G^0_f(NiF_2) = -654.2 + 0.1512T(K)\,\mathrm{kJ\,mol^{-1}} \qquad (13)$$

Combining Equations 12 and 13 with the e.m.f. data in Fig. 1, the ΔG^0_f of FeF_2 was calculated at every temperature of measurement. All the data points so computed could not be used for deriving a least-square expression without the evaluation of temperature-dependent errors. Such an assessment can be performed by resorting to a third law evaluation [6, 22] of the standard enthalpy of formation of FeF_2 at 298.15 K, $\Delta H^0_{f,298}$. This treatment also verifies the consistency of the directly measured Gibbs' energy results with the calorimetric data. For this purpose, use must be made of the free energy function, ϕ, defined by Pitzer and Brewer [22] as

$$\phi = (G^0_T - H^0_{298})/T \qquad (14)$$

Pitzer and Brewer [22] have found ϕ to be a slower varying function of temperature than the change in standard Gibbs' energy. Further, the change, $\Delta\phi$, in this function for a given reaction is even slower varying with temperature so as to minimize the error of interpolation. Thus for a formation reaction,

$$\Delta\phi = (\Delta G^0_{f,T} - \Delta H^0_{f,298})/T \qquad (15)$$

and the standard enthalpy change for the reaction, $\Delta H^0_{f,298}$, is given by

$$\Delta H^0_{f,298} = \Delta G^0_{f,T} + T\Delta\phi \qquad (16)$$

The interpolated values of the free energy function employed for this purpose are listed in Table 1. The values of $\Delta H^0_{f,298}$ were also computed from the original e.m.f. data on cell I, reported by Chattopadhyay [23] and Schaefer and Gokcen [15]. Based on the values of $\Delta H^0_{f,298}$ screened by this method, the following expression is derived for $\Delta G^0_f(FeF_2)$ for the acceptable values of e.m.f. (97 points out of a total of 101 points):

$$G^0_f = -702.0 + 0.1252T(K)(\pm 0.7)\,\mathrm{kJ\,mol^{-1}} \qquad (17)$$

An average value of -716.8 (± 4.0) kJ mol^{-1} was also derived for $\Delta H^0_{f,298}$ of FeF_2.

4.3. *Standard Gibbs' energy of formation of chromium(II) fluoride*

A similar third law treatment was carried out on the e.m.f. points in Fig. 2 as well as on the

Table 1. Comparison of $\Delta H^0_{f,298}(CrF_2)$ *from cells III and IV with values computed from the literature*

Temperature range (K)	ΔG^0_f *(CrF₂)*[a]		$\Delta H^0_{f,298}$ *(CrF₂)*[b] using $\Delta G^0_{f,T}$		*Reference*
	850 K	*1050 K*	*850 K*	*1050 K*	
731–1068	−658.8	−641.4	−794.4	−775.3	[8]
858–965	−664.5	−644.1	−800.1	−778.0[c]	[16]
497–1063	−658.1	−640.5	−793.7	−774.4	This work

[a] Computed using $\Delta G^0_f(NiF_2)$ from Equation 13.

[b] Computed using Equation 15 along with the least-square expressions for ΔG^0_f derived from e.m.f. results of [8, 16] on cell II.

[c] Extrapolated value.

values of e.m.f. for cell III, reported by Schaefer [16]. This yielded an average value of -777.4 $(\pm 4.0)\,\mathrm{kJ\,mol^{-1}}$ for $\Delta H^0_{f,298}(CrF_2)$, and the following expression for $\Delta G^0_f(CrF_2)$:

$$\Delta G^0_f = -732.8 + 0.08795T(\mathrm{K}) \times (\pm 0.64)\,\mathrm{kJ\,mol^{-1}} \qquad (18)$$

4.4. *Sodium potential domain of beta-alumina as an electrolyte for fluoride cells*

The use of beta-alumina for the fluoride cells described above immediately leads to the question of the sodium potential range over which this electrolyte could be employed in such applications. It is well known that even pure liquid sodium can be used with beta-alumina in sodium concentration cells in inert atmospheres [24–31]. Likewise, it is also used in Na_2O concentration cells with Na_2O as the reference even at the ambient P_{O_2} of 0.21 atm. However, as the sodium potential decreases, there is a possibility of a beta-alumina entering into a two-phase field depending on the oxygen potential prevailing in the environment. In the pseudobinary system Na_2O–Al_2O_3, there are three two-phase fields, namely $NaAlO_2/\beta''$-alumina, β''/β-alumina and β/α-alumina. In each of these biphase regions, $\Delta\bar{G}_{Na_2O}$ is a constant at a given temperature. In order to fix $\Delta\bar{G}_{Na}$ in these regions, $\Delta\bar{G}_{O_2}$ should be fixed.

For the above fluoride cells, a purified helium gas was used to provide an inert atmosphere. However, in such purified gases the oxygen potential is not a well-defined quantity. It is assumed that the oxygen potential is sufficiently low as not to cause oxidation of M′ in a M′F$_n$/M′/NaF mixture. Thus, the log P_{O_2} value of the M′/M′O$_m$ phase boundary should give the limiting value of the oxygen potential to avoid oxidation of M′. For each of the three biphase regions, namely $\alpha + \beta$-alumina, $\beta + \beta''$-alumina and $\beta'' + NaAlO_2$, the dependence of log a_{Na} on log P_{O_2} at 1000 K is shown in Fig. 3. For constructing this isotherm, values of $\Delta\bar{G}_{Na_2O}$ in the $\alpha + \beta$- and $\beta + \beta''$-phase fields were taken from Itoh *et al.* [32], while those in the $\beta'' + NaAlO_2$ phase interpolated from the data reported by Choudhury [33] and Jacob [34] at 600 and 1173 K, respectively. As to which biphase field of the electrolyte is relevant depends on the sodium potential in the electrode. The values of sodium potential computed for different M′F$_n$/M′/NaF mixtures from the literature [20, 21], including those of chromium and iron from this work, are shown in Fig. 4. These values of sodium potential should be superimposed on Fig. 3 in order to obtain the sodium potential domain of the respective biphase field for such measurements on the M′F$_n$/M′/NaF system. Besides revealing the limits for oxidation, this domain picture can also be used to avoid the biphase region of $\alpha + \beta$-alumina which is likely to have a higher electrical impedence. This in turn limits the lower temperature capability of a beta-alumina-based electrolyte. The area bounded by the M′/M′/NaF and M′/M′O$_m$ planes is the region amenable to metal activity measurements by beta-alumina in an alloy of M with more noble elements. It should be noted that the buffering of $\Delta\bar{G}_{Na_2O}$ in the two-phase regions did not seem to affect the functioning of cells II and IV, the sodium potential of whose electrodes lie in these regions.

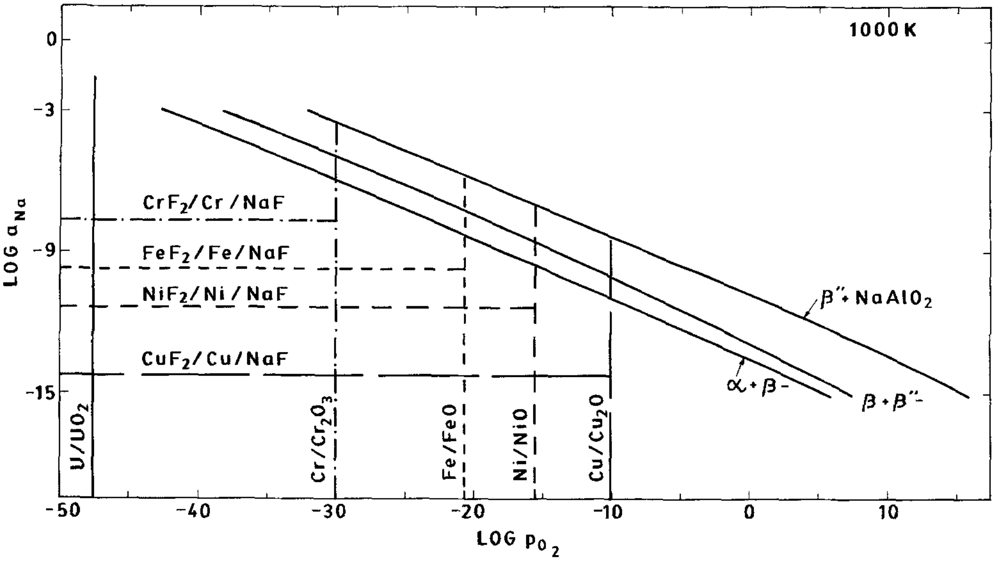

Fig. 3. Sodium potential domain at 1000 K for the phase boundaries in Na_2O–Al_2O_3 system. Also given are the cut-off values of log p_{O_2} for the formation of oxide phase in M′/M′F_n/NaF electrodes.

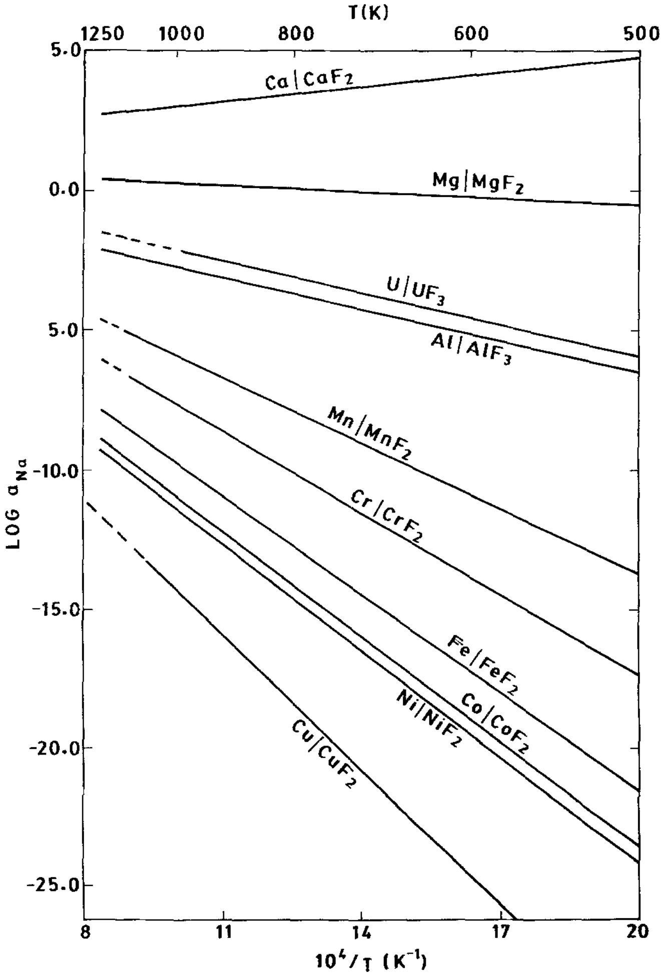

Fig. 4. Values of sodium potential calculated for different M′F_n/M′/NaF mixtures.

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