JOURNAL OF APPLIED ELECTROCHEMISTRY 19 (1989) 475–484

REVIEWS OF APPLIED ELECTROCHEMISTRY 19

Factors affecting the functioning of solid state fluoride galvanic cells

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Received 11 October 1988; revised 24 November 1988

Fluoride galvanic cells employing CaF_2 as electrolyte have not been as extensively employed for thermodynamic characterization of alloys and compounds as the oxide electrolyte cells based on stabilized zirconia. However, CaF_2 galvanic cells have many advantages over oxide electrolyte cells. These advantages, as well as the factors affecting the proper functioning of the CaF_2 cells, are discussed, highlighting the experimental aspects, such as the interference by the gas phase, choice of the reference electrode, and the volatility and compatibility of the materials.

1. Introduction

The determination of the chemical potentials of components relative to their respective standard states directly in the condensed phase, with a precision of $\pm 0.5\,\mathrm{kJ\,mol^{-1}}$, is quite often accomplished by isothermal solid electrolyte galvanic cell techniques. Since the pioneering work of Kiukkola and Wagner [1] in 1957, electrochemical cells employing solid oxide electrolytes have proved to be applicable to many thermodynamic and kinetic investigations of binary and ternary oxide systems; a host of alloy systems have also been characterized at elevated temperatures [2–10]. The contemporary work by Ure [11], on transport numbers and diffusion coefficients of Ca in pure CaF_2 as well as in NaF-doped and YF_3-doped CaF_2 has shown the conductivity in CaF_2 to be exclusively by fluoride ion transport at high temperatures. This led to the use of CaF_2 as a purely fluoride ion-conducting solid electrolyte in galvanic cells designed for high-temperature thermodynamic investigations on metallic fluorides, carbides, borides, phosphides, sulphides, alloys and intermetallics as well as binary and ternary oxides [12–75]. Other aspects of stability, namely high melting point, absence of phase transitions, low vapour pressure, a very wide range of fluorine partial pressures over a sufficiently large temperature range, are also favourable to the use of CaF_2 in such measurements.

2. Merits and limitations of fluoride galvanic cells

A distinct advantage of fluoride galvanic cells in alloy studies is the fact that the transition metal fluorides exhibit much smaller non-stoichiometry compared with the corresponding oxides, as most of them are line compounds [2]. This brings out at least two advantageous features of measurements using fluoride electrolytes. Firstly, unlike the case of oxide electrolyte galvanic cells the serious interference by the omnipresence of oxygen in the blanket gas can be reduced to a minimum, if not completely eliminated. This aspect is very important in the case of alloy characterization. Secondly, the solubility of fluorine in metals and alloys is not known to be so significant as to call for inevitable corrections in the recorded voltages and therefore in the thermodynamic quantities thus computed. This again is in marked contrast to their oxide counterparts where the stoichiometry and composition of the equilibrium oxide phase can change with alloy composition and temperature of measurement. Sometimes ternary compounds might be the equilibrium phases at certain compositions so that a precise knowledge of the ternary system of the type A–B–O becomes essential. Situations similar to this, while working with fluoride galvanic cells, have not so far been cited in the literature. Although from a theoretical consideration, fluoride electrolyte cells offer certain advantages in alloy investigations, there are a few limitations in realizing these advantages. Firstly, the thermodynamic data for the transition metal fluorides have been rather limited and less reliable than those for the corresponding oxides. In the case of simple metal oxides, absolute measurements of standard Gibbs energy of formation are possible using pure oxygen or more conveniently air as the reference electrode material, by virtue of the availability of oxide electrolytes in the form of long impervious tubes [76–81]. However such an absolute measurement is difficult in the case of fluorides due to the reactivity of fluorine, even in dilute gaseous mixtures. Secondly, most of the fluorides of interest have considerable volatility and, consequently, no suitable non-volatile fluorides are available for the second- and third-period transition metals and also for metals of the fourth and the fifth group. The enhanced volatility of some fluorides may warrant recourse to an elaborate two-gas cell design [12, 75, 82–85]. This difficulty may be circumvented by maintaining a near-static atmosphere of the cover gas by an appropriate cell design, even in a single compartment cell (oxides, on the other hand, are generally less volatile and hence do not cause concern in this respect). The thermodynamic stability of CaF_2 with respect to its reactivity towards the gaseous environment and electrode materials is extremely important. The high chemical activity of CaF_2, which increases strongly with temperature, limits its use as a solid electrolyte compared with oxide electrolytes. One of the most significant limitations on the use of CaF_2 at elevated temperatures is its interaction with the electrodes under study [24, 59, 86–88]. The electrolyte–electrode interaction narrows the temperature range in which these cells may be used. These aspects will be discussed in subsequent sections.

3. Inert atmosphere in the galvanic cell assembly

An essentially 'inert' gaseous environment around each electrode is a necessity and is achieved by continuously flushing the electrode–electrolyte–electrode chamber with a purified inert gas such as argon or helium. A flowing inert gas has an advantage over vacuum in that the electrode–electrolyte contact can be checked by ascertaining the flow rate dependence of the cell EMF. A flow rate dependence would indicate that impurities are establishing a mixed potential at the electrode–electrolyte interface. The gas phase interaction, more pronounced when the assembly is in an open-cell stacked-pellet configuration (as is the case with most of the measurements based on the fluoride galvanic cell), should be eliminated completely in all measurements. Though the cost of helium is prohibitive, it is the simplest to purify. Practically all impurities in He (except hydrogen) can be retained in a thoroughly out-gassed molecular sieve trap, refrigerated with liquid nitrogen – a technique known as 'cryosorption'.

The major impurities in the gas phase used as a blanket around the cell, as far as the fluorides are concerned, are oxygen, hydrogen and water. Hydrogen, which is present to the extent of 40–100 ppm in cylinder He, can be removed by passing the gas through a bed containing Cu–Cu_2O turnings heated to 775–825 K whereupon hydrogen is oxidized to water vapour and then through the refrigerated molecular sieve trap.

The problem of impurity interference can, in principle, be avoided by working in a static vacuum, provided adequate precautions are taken; otherwise residual oil vapours and the products of their cracking and oxidation in the vacuum system would reduce the electrode. Also, if the alloy components or the fluorides have significant vapour pressures at operating temperature, there will be a continuous loss of material under the conditions of dynamic vacuum, leading to non-equilibrium fluorine potentials. Thus a dynamic inert atmosphere around the galvanic cell has an obvious advantage over a vacuum. However, an optimum flow rate has to be maintained to strike a balance between volatilization of material and the sweeping away of impurities.

The influence of impurities in the gas phase and other factors which affect the functioning of fluoride galvanic cells are discussed in subsequent sections.

4. Thermodynamic stability of fluorides with respect to impurities in the gaseous environment

For a gaseous environment to be really inert, it should not interfere in any way with the composition and properties of a condensed phase. Obviously the term 'inert' is a misleading one and thermodynamically ill defined. Practically, a gaseous environment may be called inert if the impurities present in it can be reduced to a level below the limits of chemical detection. In order to appreciate the effects of impurities it is necessary to calculate the driving force (ΔG_R^0) for the possible side reactions between the fluorides and gaseous impurities by unequivocally establishing the appropriate chemical equilibria between the buffer mixtures. The effect of various major impurities present in the inert gas stream on fluorides is discussed in this section.

4.1. *Pyrohydrolytic reactions*

The presence of moisture in the surrounding atmosphere changes the electrolytic properties of CaF_2 for the worse. Water reacts with fluorides at high temperatures to produce hydrogen fluoride, according to the following equation [12, 56, 89]:

$$CaF_2(s) + H_2O(g) \longrightarrow CaO(s) + 2HF(g) \quad (1a)$$

$$MF_n(s) + n/2H_2O(g) \longrightarrow MO_{n/2}(s) + nHF(g) \quad (1b)$$

where MF_n is the metal fluoride present in the electrode. The hydrogen fluoride so produced attacks the cell container material and may also become a source of fluorine transfer from one electrode to the other. The rate of Reaction 1a is appreciable even at 373 K [90] and Messier [91], who studied the kinetics of hydrolysis of single crystal CaF_2 from 1273 to 1393 K by thermogravimetry at water vapour partial pressures ranging between 1 to 20 mm (131.6 to 2632 Pa), had assigned a paralinear rate behaviour to it. Reactions of the electrolyte and/or electrode material with moisture may cause the growth of an insulating oxide layer which may subsequently affect the electrolyte–electrode contact or may modify the electrochemical reactions at the electrolyte–electrode interface, giving rise to mixed potentials.

Applying the law of mass action to the general pyrohydrolytic Reaction 1b, one gets:

$$\begin{aligned}\Delta G_R^0 &= (\Delta G_f^0 MO_{n/2} + n\Delta G_f^0 HF) \\ &\quad - (\Delta G_f^0 MF_n + n/2\Delta G_f^0 H_2O) \quad (2) \\ &= -RT \ln (p_{HF}^n / p_{H_2O}^{n/2}) \quad (3)\end{aligned}$$

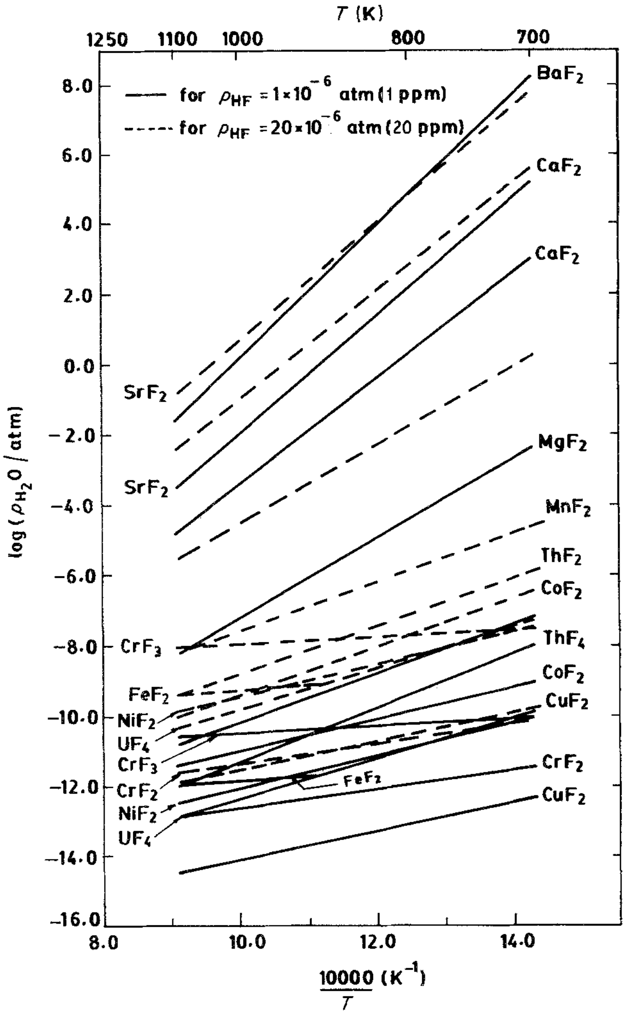

Fig. 1. Effect of water vapour on binary fluorides for two typical levels of HF formed as a result of pyrohydrolytic reaction.

assuming solid MF_n and $MO_{n/2}$ to be in the standard state of unit activity.

On simplification Equation 3 may be rewritten as

$$\log p_{H_2O} = 2 \log p_{HF} + \frac{2\Delta G_R^0}{2.303nRT} \qquad (4)$$

A plot of log p_{H_2O} against reciprocal temperature for a number of solid binary fluorides for two typical levels, namely 1 and 20 ppm of HF formed is shown in Fig. 1 over the range 700–1100 K. It can be seen from this figure that, among the various fluorides, those of alkaline earth metals appear to be less prone to the pyrohydrolytic reactions at low temperatures. Otherwise the severity of the effect of moisture on all the fluorides used as electrode materials can be appreciated from the magnitude of p_{H_2O} required to make Reaction 1 proceed in the forward direction. The fluorides of Ba and Sr appear to be more stable than CaF_2 with respect to pyrohydrolysis over a wider temperature range. Nevertheless, even in these cases the effect of moisture cannot be completely ignored. Figure 1 also brings out the fact that, while studying systems of ferrous metals and also those of U and Th, the utmost care must be exercised to reduce the moisture level in the main gas stream to sub-ppm levels, besides checking the concentration of other gaseous impurities which may lead to the *in situ* formation of water vapour during the cell operation. Pyrohydrolysis of fluorides below those of ferrous metals cannot be prevented as is evident from Fig. 1, but can be minimized using near-static conditions and by restricting the period of operation of galvanic cells and by the use of *in situ* oxygen scavengers (see Section 4.3).

4.2. *Effect of oxygen*

The thermodynamic stability of CaF_2 and other commonly used fluorides (as electrode materials) towards oxygen is greater than towards moisture. This is evident from the magnitudes of the Gibbs energy of Reactions 1 and 5:

$$CaF_2(s) + 1/2O_2(g) \longrightarrow CaO(s) + F_2(g) \qquad (5a)$$

$$MF_n(s) + n/4O_2(g) \longrightarrow MO_{n/2}(s) + n/2F_2(g) \qquad (5b)$$

The free energy changes for Reactions 1 and 5 at two typical temperatures, namely 700 and 1100 K are given in Tables 1 and 2, respectively, for a number of fluorides for a ready comparison of the magnitude of the driving force for each of these reactions.

Applying considerations similar to those for the pyrohydrolytic reactions in Section 4.1, one can write for the general reactions of the type 5b:

$$\log p_{F_2} = 1/2 \log p_{O_2} - \frac{2\Delta G_R^0}{2.303nRT} \qquad (6)$$

A plot of log p_{F_2} versus reciprocal temperature for a typical impurity level of 100 ppm (10^{-4} atm) of oxygen over the temperature range 700–1100 K is shown in Fig. 2 for a number of binary fluorides.

The fluorine partial pressure developed as a result of Reaction 5 is well within the electrolytic domain of

Table 1. Standard Gibbs energy change for the pyrohydrolytic reaction [a] *of binary fluorides*

Metal fluoride	$\Delta G^0_{R(1)}$ *(kJ) at:*	
	700 K	*1100 K*
CaF_2^c	200.4	151.8
BaF_2^c	270.0	218.7
SrF_2^c	229.8	179.4
UF_4^c	57.4	−38.2
ThF_4^c	94.1	−0.8
MgF_2^d	128.6	79.2
MnF_2^e	64.7	26.0
CrF_2^c	7.0	−19.1
FeF_2^c	5.7^b	−0.2
CoF_2^f	38.5	−12.4
MiF_2^f	25.6	−10.6
CuF_2^c	−5.4	−52.6

[a] Oxide free energy data from [113].
[b] At 900 K, as 'FeO' is unstable below 833 K [33].
[c] Free energy of formation [33].
[d] Free energy of formation from [97].
[e] Free energy of formation from [34, 35].
[f] Free energy of formation from [92].

Table 2. Standard Gibbs energy change for the pyroxidative reaction of binary fluorides

Metal fluoride	$G_{R(S)}$ *(kJ) at:*	
	700 K	*1100 K*
CaF_2	547.3	523.9
BaF_2	616.9	590.8
SrF_2	576.7	551.5
UF_4	751.2	706.0
ThF_4	787.9	743.3
MgF_2	475.5	451.3
MnF_2	411.6	398.1
CrF_2	270.4	289.5
FeF_2	383.5[a]	371.3
CoF_2	385.4	359.6
NiF_2	372.5	346.3
CuF_2	341.5	319.4

[a] At 900 K, as 'FeO' is unstable below 833 K [33].

calcium fluoride [56, 92]. Hence there is no onset of an electronic conductivity having a theoretical dependence on the oxygen partial pressure. On the other hand, it has been shown in the literature than annealing of CaF_2 in air at 1273 K leads to an improved conductivity and that it preserves its anionic conductivity in pure oxygen below 1273 K [93]. CaF_2 dissolves about 0.2 mol % of oxygen at temperatures above 1073 K. According to Levitskii *et al.* [94] the total electrical conductivity of single crystal CaF_2 increases with increasing oxygen partial pressure. This increase in conductivity was, however, shown [95] to be irreversible as it remained constant with decrease in oxygen partial pressure. By virtue of the very close ionic radii of the oxygen ion and the fluoride ion ($\sigma_{O^{2-}} = 1.36$ Å; $\sigma_{F^-} = 1.33$ Å), the observed increase in the conductivity might be related to the formation of substitutional and other defects. The oxygen substitution appears to be on anion lattice sites (O'_F) and not on interstitial sites (O''_i) [96]. In addition, the doping of the electrolyte with CaO (0.2 w/o) does not influence t_{F^-} [12]. Nevertheless, oxygen present in trace amounts in the inert atmosphere sometimes forms an oxide film on the surface of metal present in the electrode. This results in a decrease in the chemical potential of the metal in the electrode and a corresponding increase in the fluorine potential leading to EMF values different from those corresponding to the equilibrium of $M(a_M = 1)/MF_n$.

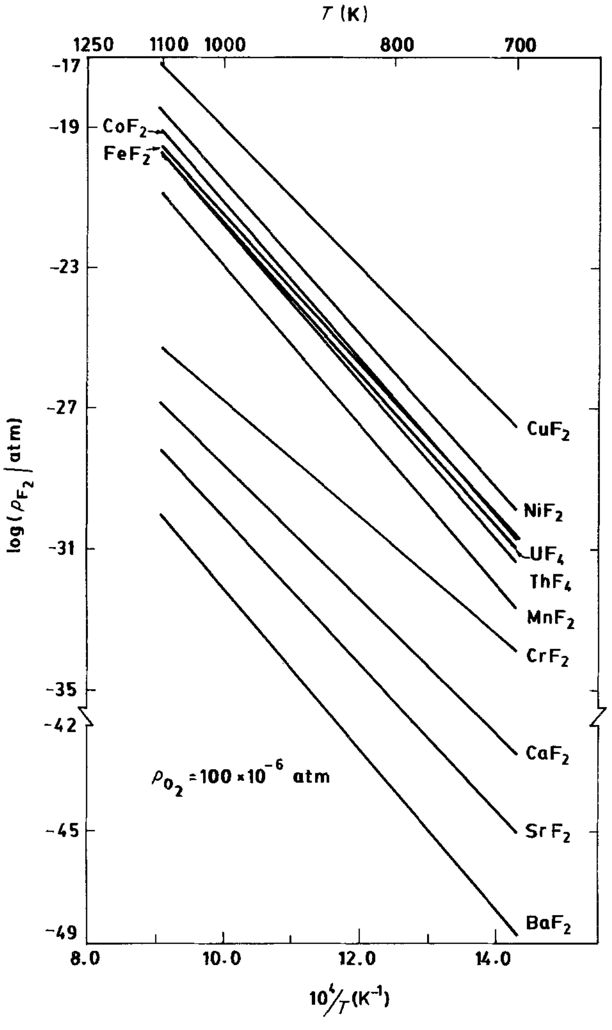

Fig. 2. Effect of oxygen on binary fluorides as a result of pyrooxidative reaction.

4.3. *Effect of hydrogen*

The interaction of hydrogen impurities in the blanket gas, with the electrolyte and/or electrodes, can be represented as:

$$CaF_2(s) + H_2(g) \longrightarrow Ca(s) + 2HF(g) \quad (8a)$$

$$MF_n(s) + n/2H_2(g) \longrightarrow M(s) + nHF(g) \quad (8b)$$

As pointed out in Section 4.1, the HF so formed may interfere with the functioning of the galvanic cells by promoting the transfer of fluorine from one electrode to the other and by attacking the container material. This necessitates the reduction of the hydrogen content in the flowing gas to below a tolerable threshold.

Applying the law of mass action to Reaction 8, one may write:

$$\log p_{HF} = 1/2 \log p_{H_2} - \frac{\Delta G_R^0}{2.303nRT} \quad (9)$$

The level of hydrogen in cylinder helium gas is of the order of 10–100 ppm (1×10^{-6} to 1×10^{-4} atm). Thus the partial pressures of HF, for two levels of hydrogen, namely 1 ppm and 100 ppm, were computed using the standard free energies of formation of various fluorides and are plotted in Fig. 3 as a function of reciprocal temperature over the range 700–1100 K.

It can be seen from Fig. 3 that the effect of hydrogen on the fluorides of U, Th and alkaline earth metals is not as deleterious as it is on those of 3d-transition metals. Since the fluorides of the latter category are the ones used most frequently in reference as well as in test electrodes in alloy characterization, sufficient care should be taken to remove the inherent hydrogen impurities from the inert gas. The presence of hydrogen also assumes importance in terms of water vapour formation by interacting with oxygen impurities present in the main gas stream. This makes the opera-

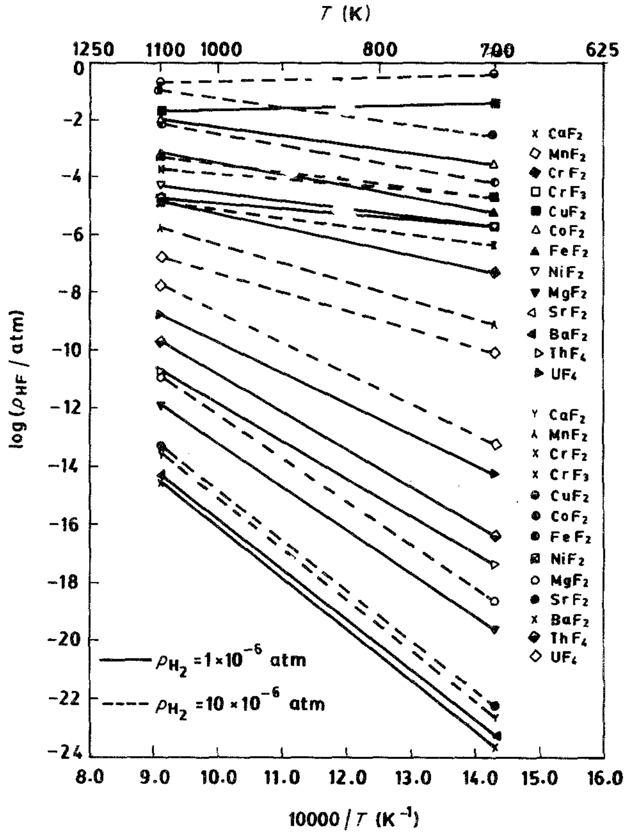

Fig. 3. Effect of hydrogen on binary fluorides as a function of temperature.

tion of fluoride cells almost impossible. The effect of hydrogen can be made less pronounced by using *in situ* oxygen scavengers such as titanium sponge, uranium or zirconium chips, tantalum foils, etc.

5. Volatility of fluorides

Most of the fluorides have appreciable vapour pressure and no solid fluorides of Si, Ge, Sn, As and Sb are known even at room temperature. Vapour pressures of some of the binary fluorides from the data available in the literature [97] are plotted in Fig. 4 in the range 700–1100 K. Such a high volatility of fluorides interferes with the working of fluoride galvanic cells specially at high temperature and, in fact, this parameter fixes the upper temperature limit of operation of fluoride galvanic cells. The disadvantage becomes more pronounced in the case of a stacked-pellet assembly and is probably one of the reasons for non-attainment of true equilibrium in the case of fluoride galvanic cells where EMFs with large scatter are observed.

6. Effect of aliovalent doping

Addition of impurities, for instance doping by YF_3, results in an increase of conductivity owing to the increase in the concentration of interstitial F^- ions

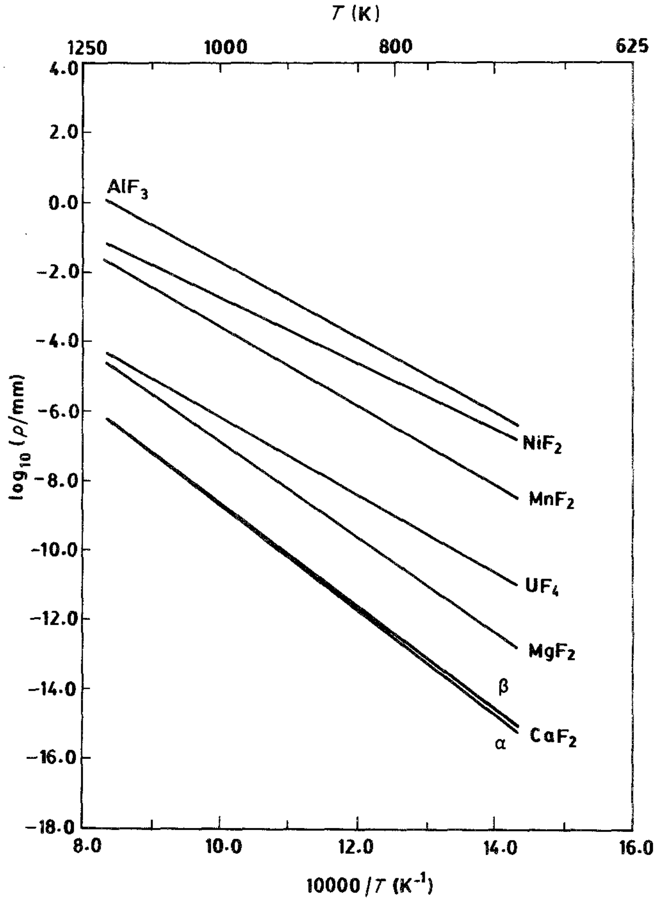

Fig. 4. Vapour pressure of some binary fluorides as a function of temperature [97].

according to the reaction:

$$YF_3 \text{ (in } CaF_2) = Y^{\bullet}_{Ca} + F'_i \qquad (10)$$

Extensive doping studies with YF_3 doping of CaF_2 [98] have revealed that the conductivity of CaF_2 increases with dopant concentration up to 35 mol %. However this also increases the cation mobility and, hence, the use of YF_3-doped CaF_2 is restricted due to a narrowing of the range of pure anionic conductivity. Diffusion data of Short and Roy [99] for calcium in YF_3-doped CaF_2 at 1373 K, suggest a Schottky-type disorder in the cationic sublattice:

$$O \longrightarrow V''_{Ca} + 2V^{\bullet}_F \qquad (11)$$

for which

$$K = [V''_{Ca}][V^{\bullet}_F]^2 \qquad (12)$$

They measured the calcium diffusion coefficients in 'pure', in 20% YF_3-doped and in 40% YF_3-doped CaF_2 to be 8.6×10^{-15}, 1.9×10^{-14} and $1.6 \times 10^{-13}\ m^2\ s^{-1}$, respectively. On the other hand, results on doping of CaF_2 with NaF are inconsistent. While Ure [11] observed that CaF_2 doping with NaF increased its conductivity as well as $t_{Ca^{2+}}$, Short and Roy [99] observed a decrease in the magnitude of the self-diffusion coefficient of Ca. For instance, in 3 mol % NaF-doped CaF_2 the diffusion coefficient was found to be 0.7 times that in pure CaF_2 at 1033 K. The following defect model:

$$NaF(\text{in } CaF_2) = Na'_{Ca} + V^{\bullet}_F \qquad (13)$$

which leads to

$$t_{Ca^{2+}} \propto 1/[V^{\bullet}_F]$$

is consistent with the observations of Short and Roy [99]. The conductivity increases with concentration of NaF up to 0.5 mol %. In either case, however, doping of CaF_2 with NaF does not significantly improve the electrolytic properties of CaF_2. Recently, Vaidehi *et al.* [100] and Akila and Jacob [101] have shown that the dispersion of Al_2O_3 as well as CeO_2 in CaF_2 enhanced the conductivity of CaF_2. At 650 K the ionic conductivity of the dispersed solid electrolyte system was found to be higher by about two orders of magnitude in the case of alumina dispersion, while it was by about three orders of magnitude with ceria dispersion in relation to the conductivity of the host electrolyte. This increase in ionic conductivity of CaF_2 at low temperatures was attributed to the substantial enhancement in the vacancy concentration, brought about by the attraction of F^- ions to the surface of the dispersed phase.

7. Electrolytic domain of the electrolyte

The electrolytic domain of a solid electrolyte is the region in three-dimensional conductivity–temperature–p_{X_2} space in which the ionic conductivity of the X ion is at least 100 times larger than the electronic or hole conductivities. In very high and very low p_{X_2} regions, hole and electron conduction begin to contribute. The higher the electron or hole conductivity, the greater will be the electrochemical permeability of the anion through the electrolyte, resulting in polarization of the electrode. Minimum permeability is achieved in the middle of the electrolytic domain where electron and hole conductivites are equal.

Calcium fluoride is characterized by a very wide p_{F_2} and T range where $t_{F^-} \geqslant 0.99$. Hinze and Patterson [102] experimentally determined the electrolytic domain by measuring the total conductivity of a single crystal CaF_2 as a function of temperature and fluorine partial pressures. The fluorine chemical potentials were varied by using M/MF_2 type coexistence electrodes. Their measurement at only one fixed frequency was improved by Ono *et al.* [89] based on cell impedance measurements over a wide range of frequency, thereby separating pure ohmic resistance of the sample from the total cell impedance. These results, shown in Fig. 5, suggest that the isothermal conductivity of CaF_2 remains constant down to the fluorine partial pressure of Mg/MgF_2 coexistence and that the gentle rise occurs only at Ca/CaF_2 coexistence which is the stability limit of CaF_2 given by the equation:

$$\log (p_{F_2}/\text{atm}) = 9.0 - 63400/T \qquad (14)$$

The difficulties associated with the conductivity and/or EMF measurements with CaF_2 at high fluorine pressures and elevated temperatures have not permitted the determination of the upper electrolytic boundary of CaF_2. Nevertheless, in the light of the very large electronegativity difference between Ca^{2+} and F^- ions (1.0 and 4.0 eV, respectively) and a sufficiently large band gap (12.2. eV), Patterson [103] envisaged the upper boundary to lie even above one atmosphere of fluorine.

Apart from the extensively used CaF_2, other fluorides such as MgF_2, SrF_2, BaF_2 and PbF_2, which are also exclusively fluoride ion conductors ($t_{F^-} = 1$), have been employed as solid electrolytes [12, 61, 104–106]. Although there is no doubt about the pure ionic conductivity and nature of the mobile species in them, the application of these compounds in galvanic cells as solid electrolytes has been very limited; this could be due to their narrow temperature range of use and high chemical reactivity. Moreover, their electrolytic domains are not well established.

8. Temperature range of operation

Fluoride galvanic cells in general suffer from a rather low temperature range of operation in comparison to that of oxide or β-alumina galvanic cells. This temperature range is, in fact, a strong function of the inertness of the CaF_2 electrolyte and the chemical reactivity of various fluorides used as electrode materials. From a practical point of view, the inertness range of the electrolyte dictates the lower limit of temperature, where it may have high electrical impedance, while the extent of chemical reactivity,

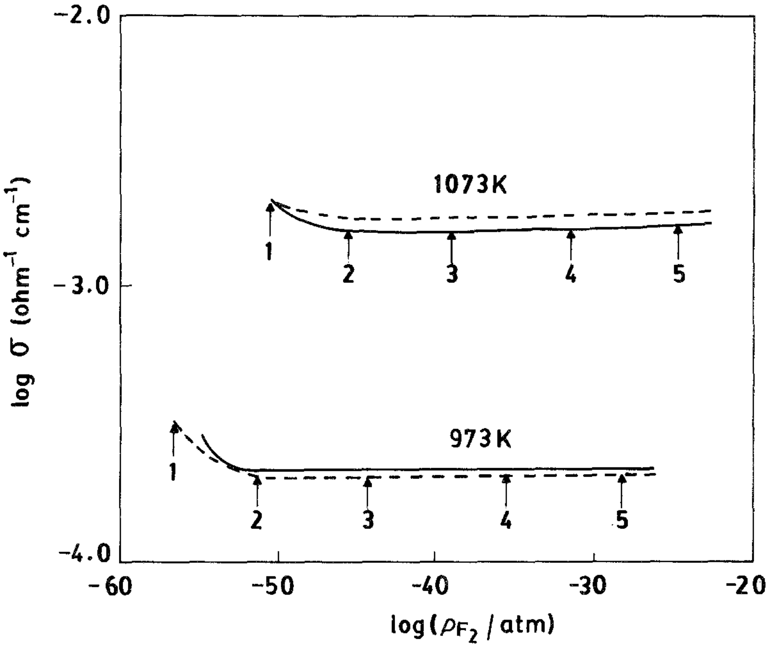

Fig. 5. Total conductivity of CaF_2 as a function of fluoride partial pressure: (1) Ca–CaF_2; (2)Mg–MgF_2; (3) Al–AlF_3; (4) Mn–MnF_2; (5) Co–CoF_2. —— Ono *et al.* [89]; - - - Hinze and Patterson [102].

such as pyrohydrolysis, volatility and interference by various impurities set the upper limit of operation. Most authors have used the fluoride galvanic cells for thermodynamic measurements over the range 773–1273 K. However, recently Egami *et al.* [75] have extended their measurements up to 1372 K. It is worth pointing out here that, from the reactivity point of view, single crystal CaF_2 is found to be more suitable as an electrolyte than polycrystalline ones, as the former are less prone to environmental effects owing to the absence of grain boundaries (which otherwise make the penetration of fluorides under study into the electrolyte possible and offer reaction sites for impurities).

9. Choice of reference electrode materials

Fluoride galvanic cells most frequently suffer from the lack of availability of precise thermodynamic data for the coexisting fluorides used in the reference as well as in the test electrodes, over the temperature range of interest. Chandrasekharaiah *et al.* [2] have enumerated in detail several conditions that should be satisfied by an electrode system for selection as a reference. Among these, the reversibility of all electrode processes with minimum polarization under the measuring conditions, absence of, or negligibly small, non-stoichiometry of the coexisting fluoride phase with temperature, equilibrium fluorine potential of the reference electrode within the electrolytic domain of the electrolyte, fluorine potential of the reference within a few orders of magnitude of that of the test electrode ($\ln p_{F_2}^{ref}/\ln p_{F_2}^{test} \simeq 2$–3) and the absence of electrode–electrolyte interaction at elevated temperatures are most important. According to Tretyakov and Kaul [56], the most significant limitation of fluoride galvanic cells using CaF_2 as the electrolyte is their interaction with the electrodes under study. Chattopadhyay [12] envisaged the following cases of such electrode–electrolyte interactions: (i) finite solubility of the electrode material in the electrolyte; (ii) compound formation between the electrolyte and the electrode material; (iii) eutectic formation between the electrolyte and the electrode material. In each case, however, the magnitude of error introduced by these interactions largely depends on the transport properties of the reaction products. Heus and Egan [107], who studied the cell:

$$\text{Th, ThF}_4|\text{CaF}_2|\text{NiF}_2\text{, Ni} \qquad (14)$$

where ThF_4 had considerable solubility in CaF_2, observed no significant change in the EMF by the dissolution process. Errors may become large and significant if the fluoride happens to be that of a transition metal, exhibiting variable valency where the electron transport number of the solid solution should be appreciable. Compound formation between the electrode and the electrolyte generally leads either to a drop in EMF to a very low value compared to the theoretical or gives rise to highly unstable values of EMF. Thus, in such cases it should be clearly established that the coexisting fluoride is present at unit activity which means the absence of solid solubility of the fluoride in CaF_2.

For the galvanic cell of the type

$$\text{M, MF}_2|\text{CaF}_2|\text{M–X, MF}_2 \qquad (15)$$

where M is the more electropositive component of the alloy, it is necessary that the fluoride MF_2 be more stable than the corresponding fluoride of the component X. In an analysis of the possible occurrence of a direct displacement reaction of the type:

$$\text{MF}_2 + \text{X} \longrightarrow \text{M} + \text{XF}_2 \qquad (16)$$

Wagner and Werner [108] envisaged that the standard Gibbs energy change for this reaction should be

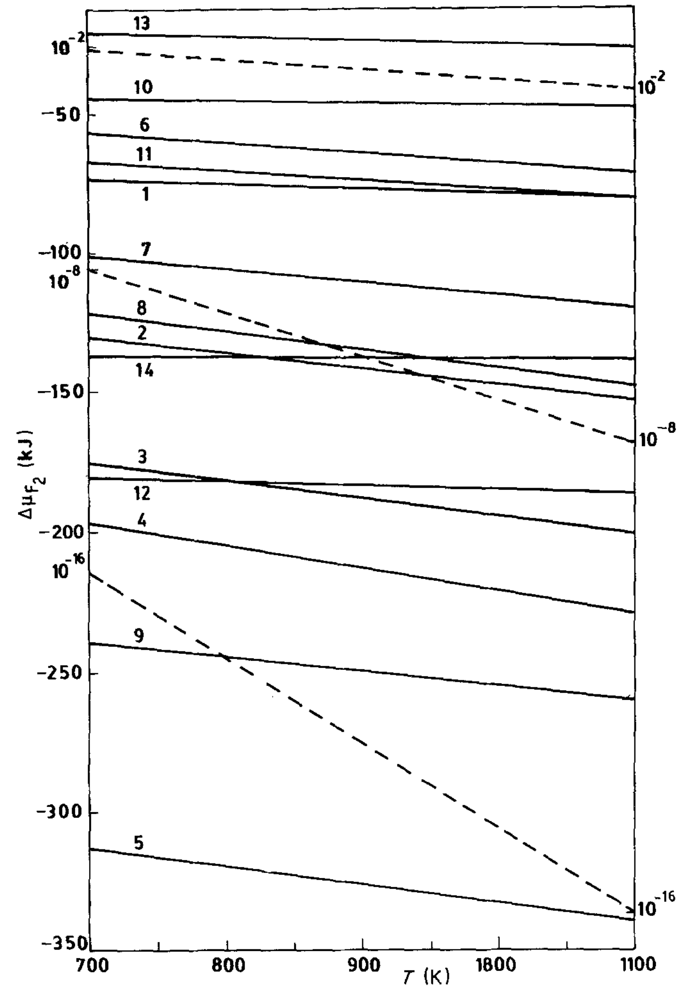

Fig. 6. Change in fluorine potential for various couples of binary fluorides: (1–5) MnF_2 vs CrF_2, FeF_2, CoF_2, NiF_2 and CuF_2, respectively; (6–9) CrF_2 vs FeF_2, CoF_2, NiF_2 and CuF_2, respectively; (10–12) FeF_2 vs CoF_2, NiF_2 and CuF_2, respectively; (13, 14) CoF_2 vs NiF_2 and CuF_2, respectively.

positive and greater than about 85 TJ when T is expressed in K. Jacob [109] has set the tentative limit of free energy change for the direct displacement reaction of the kind shown above to be about 170 TJ, which however is not an absolute criterion. In the case of strong attractive interaction in the binary system, this quantity will be correspondingly larger. Moreover, while M should be more reactive than X, it should not be reactive enough to cause the reaction

$$M + CaF_2 \longrightarrow MF_2 + Ca \qquad (17)$$

to proceed in the forward direction. In other words, the Gibbs energy change for the above reaction should be a sufficiently large positive quantity [110].

10. Sensitivity

In a case where the alloy studies are feasible with both the oxide as well as fluoride galvanic cell techniques, the ultimate choice depends upon the temperature range of interest. Oxide electrolyte galvanic cells are generally known to function well at relatively higher temperatures. For example, in the case of a chromium-bearing alloy, the Cr/Cr_2O_3 electrode shows reversibility at sufficiently high temperatures, as evident from the work of Pugliese and Fitterer [111] and Mazandarany and Pehlke [112] on Ni–Cr alloys where the minimum temperatures were 1073 and 1273 K, respectively. Therefore, low-temperature measurements are generally not possible with oxide cells, whereas the fluoride technique works efficiently down to 750 K. If the direct current (d.c.) signal of EMF were the only criterion, then for the same difference in the order of magnitude of non-metal chemical potential, the EMF of the fluoride cell would be higher than that of the corresponding oxide cell. A higher EMF means higher resolution and, hence, higher sensitivity.

11. Proximity criterion of the electrode system

It was pointed out in Section 9 that the fluorine partial pressure of the reference electrode must be close to that of the test electrode, so that the driving force for fluorine diffusion through the electrolyte is at a minimum, thereby retarding the kinetics of diffusion. In order to make the best choice among the various reference electrodes for a given test electrode, a 'proximity criterion' has to be evolved. This can be done by computing the difference in the fluorine chemical potentials of the two ($\Delta\mu_{F_2} = \mu_{F_2}^{test} - \mu_{F_2}^{ref}$) or by simply computing $\Delta \log p_{F_2}$ of the two electrode systems. The results of such a computation are plotted in Fig. 6 against temperature over the range

700–1100 K for various combinations of electrode materials.

Unlike the oxide galvanic cells, where the dissociation pressure of the electrode material is quite high, the corresponding fluorides have sufficiently low fluorine dissociation pressures at any given temperature. In this respect fluoride cells have an advantage over their oxide counterparts in that the interference in the electrode processes through the gas phase (with respect to surface concentration depletion, thin oxide layer formation, etc.) are minimal. Moreover, electronic conduction, conduction through planar defects, shorting by impurities in the gas phase (such as HF) and other surface effects will not be insignificant if $\Delta \log p_{F_2}$ is more than about 10 orders of magnitude. In general, if $\log p_{F_2}$ of the electrodes differ by more than 10 orders, the EMF values show larger scatter in the data reported. Figure 6 is useful in effecting a choice of reference electrode in the case of ferrous metal alloy studies. Tentatively the fluorides having $\Delta\mu_{F_2}$ values $\approx 100\,\mathrm{kJ\,mol^{-1}}$ in the temperature range of interest would form a suitable couple.

If there is a serious limitation with respect to one of the factors discussed above, it could seriously impede the functioning of a fluoride galvanic cell, especially for the measurements of thermodynamic parameters of materials. It is hoped that the criteria listed here will assist in the formulation of fluoride galvanic cells as complementary to oxide cells for precise thermodynamic characterization.

Acknowledgements

The authors are greatly indebted to Dr P. Rodriguez, Head, Metallurgy and Materials Programme and to Shri J. B. Gnanamoorthy, Head, Metallurgy Division for their interest and encouragement during the course of this work.

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