Letter to the Editors

Redox condition in molten fluoride salts Definition and control

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Abstract

The loosely-used term 'redox condition' as applied to molten fluoride salts such as flibe is defined quantitatively as the fluorine potential. Several methods of controlling the property of the melt are discussed. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

In the molten reactor experiment (MSRE) of the fifties and sixties and in the current interest in molten fluorides for fusion reactors, the term 'redox state' has been loosely applied as a measure of the propensity for corrosion of the container metals. The purpose of this note is to quantify this ill-defined term by replacing it with a quantity directly related to the chemical potential of the species that controls the reactivity of the salt.

'Redox' is a generalized term that is made specific according to the anion X that is exchanged between two valence states of a cation M. The 'redox condition' is related to the chemical potential of the anion species. Since the anion species is usually an elemental gas in its normal state, the chemical potential is defined in terms of its partial pressure. The chemical potential fixes the ratio of the high and low valence states of a cation that is simultaneously present in the gas, or vice versa, the relative amounts of the oxidized and reduced forms of M in the molten salt determine the chemical potential of the gaseous anionic species.

The 'X-potential' is defined in terms of the partial molar Gibbs free energy of the diatomic gas X_2, where $X = O, S, F, Cl, \ldots$:

$$\Delta \overline{G}_{X_2} \equiv RT \ln p_{X_2}. \tag{1}$$

This particular definition follows from the equilibrium expression of the generalized oxidation reaction:

$$MX_n + \tfrac{1}{2}X_2(g) = MX_{n+1} \quad \text{where } 0 \leqslant n \leqslant 4. \tag{2}$$
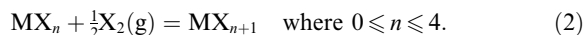
The most common redox potential is the oxygen potential, where $X = O$. This potential is an important thermodynamic property of oxide systems containing multivalent cations, such as U and Pu in nuclear fuels. The multivalent cation can be contained in a gas (e.g., $M = H_2$ or CO, $n = 0$), a metal (e.g., $M = Ca$, $n = 0$), or an oxide (e.g., $M = Ti$, $n = 1$). It is not necessary that O_2 be physically present in the system; a metal and its oxide can be enclosed in a gas-free container yet still exhibit an oxygen pressure.

In the now-defunct MSRE program at ORNL, and in current fusion energy designs, molten fluoride salts are integral components. For molten fluoride salts such as $2LiF + BeF_2$ (flibe), it is clear that $X = F$; the redox condition is properly termed the *fluorine potential*:

$$\Delta \overline{G}_{F_2} \equiv RT \ln p_{F_2}. \tag{3}$$

There are (at least) three ways of controlling the fluorine potential of flibe: by the gas mixture H_2/HF; by one of the major metals of flibe (Be or Li); or by a minor salt such as CeF_3/CeF_4. The thermodynamics of each of these methods are described below.

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2. Gas-phase control

In a mixture of H_2 and HF, the gas-phase equilibrium reaction establishing the F_2 partial pressure is

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}F_2 = HF(g) \tag{4}$$

for which the law of mass action is

$$\frac{p_{HF}}{\sqrt{p_{H_2}}\sqrt{p_{F_2}}} = \exp\left(-\frac{\Delta G_{HF}^0}{RT}\right). \tag{5}$$

Or, the fluorine potential is

$$\Delta \overline{G}_{F_2} \equiv RT \ln p_{F_2} = 2RT \ln\left(p_{HF}/\sqrt{p_{H_2}}\right) + 2\Delta G_{HF}^0, \tag{6}$$

where ΔG_{HF}^0 is the standard free energy of formation of HF(g). At 900 K, $\Delta G_{HF}^0 = -66.1$ kcal/mol [1]. For a gas with a 10:1 H_2/HF mol ratio at 1 atm total pressure, Eq. (6) gives $\Delta \overline{G}_{F_2} = -141$ kcal/mol. The flibe acquires this fluorine potential by virtue of sufficient exposure to the equilibrium gas mixture of Eq. (4). This is analogous to fixing the oxygen potential of urania by contact with a gas phase with a specified ratio of H_2O to H_2.

3. Major-metal control

Addition of the metals Be or Li to the molten flibe can be used to control the fluorine potential because their fluoride salts in the melt provide the other half of the redox couple. For beryllium, the reaction is

$$Be(s) + F_2 = BeF_2(soln). \tag{7}$$

The law of mass action for this reaction is

$$\frac{a_2}{p_{F_2}} = \exp\left(-\frac{\Delta G_{BeF_2}^0}{RT}\right). \tag{8}$$

and the fluorine potential is:

$$\Delta \overline{G}_{F_2} \equiv RT \ln p_{F_2} = RT \ln a_2 + \Delta G_{BeF_2}^0, \tag{9}$$

where $\Delta G_{BeF_2}^0$ is the standard free energy of formation of pure BeF_2 liquid at 900 K and a_2 is the activity of BeF_2 in flibe. At 900 K, $\Delta G_{BeF_2}^0 = -209.2$ kcal/mol [1]. For a BeF_2 mol fraction of 0.33, the activity coefficient of this component is 0.08 [2]. The activity is the product of these two factors, or $a_2 = 0.026$. Substituting these values into Eq. (9) gives $\Delta \overline{G}_{F_2} = -215.7$ kcal/mol.

For lithium metal in contact with the salt, the reaction controlling the fluorine potential is

$$Li(L) + \tfrac{1}{2}F_2 = LiF(soln). \tag{10}$$

The equilibrium expression is

$$\frac{a_1}{\sqrt{p_{F_2}}} = \exp\left(-\frac{\Delta G_{LiF}^0}{RT}\right), \tag{11}$$

where ΔG_{LiF}^0 is the standard free energy of formation of LiF (s) (-125.6 kcal/mol at 900 K [1]) and a_1 is the activity of LiF in flibe. The mol fraction of LiF in flibe is 0.67 and the activity coefficient is 0.7 [2]. With these values, the fluorine potential is

$$\Delta \overline{G}_{F_2} \equiv RT \ln p_{F_2} = 2RT \ln a_1 + 2\Delta G_{LiF}^0 = -253.4 \text{ kcal/mol}. \tag{12}$$

The fluorine potential established by adding metallic lithium to the melt is about 40 kcal/mol more negative than that achieved with metallic beryllium addition. However, Li(L) cannot be used for controlling the fluorine potential because it would reduce BeF_2 to Be(m).

4. Dissolved-salt control

Fluoride salts that are soluble in flibe and have two valence states close in energy can be used to control the fluorine potential. The MSRE utilized UF_3/UF_4 for this purpose. For the flibe in fusion reactor applications, the CeF_3/CeF_4 couple has been considered. The reaction that controls the fluorine potential in this case is

$$CeF_3(soln) + \tfrac{1}{2}F_2 = CeF_4(soln). \tag{13}$$
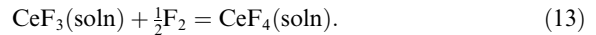
The equilibrium of this reaction satisfies

$$\frac{a_4}{a_3 \sqrt{p_{F_2}}} = \exp\left(-\frac{\Delta G_{34}^0}{RT}\right) \tag{14}$$

or

$$\Delta \overline{G}_{F_2} \equiv RT \ln p_{F_2} = 2RT \ln(a_4/a_3) + 2\Delta G_{34}^0. \tag{15}$$

ΔG_{34}^0 is the standard free energy change of reaction (13). At 900 K, it is estimated to be -5 kcal/mol [1,3]. a_3 and a_4 are the activities of CeF_3 and CeF_4 respectively in flibe. These depend on the activity coefficients (unknown for CeF_4) and the mol ratio. Assuming the activity ratio to be 0.1, the fluorine potential established by the cerium couple is -18 kcal/mol.

5. Structural metal corrosion

As an example of the use of the fluorine potential, the thermodynamics of the corrosion of iron by flibe is considered. Corrosion can be caused by any agent that controls the fluorine potential, but for simplicity, HF/H_2 will be used. The corrosion reaction is

$$Fe(s) + 2HF(g) = FeF_2(soln) + H_2(g). \tag{16}$$
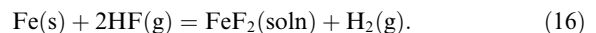
The question that can be answered by thermodynamics is the following: What is the mol fraction of FeF_2 in flibe that is in equilibrium with pure metallic iron

when the temperature and the fluorine potential of the system are specified?

The equilibrium expression for reaction (16) is

$$\frac{p_{H_2} a_{FeF_2}}{p_{HF}^2} = \exp\left(-\frac{\Delta G^0_{FeF_2} - 2\Delta G^0_{HF}}{RT}\right), \quad (17)$$

where $\Delta G^0_{FeF_2}$ is the standard free energy of formation of FeF_2 (L). At 900 K, $\Delta G^0_{FeF_2} = -139$ kcal/mol [1]. Using Eq. (6) to eliminate the partial pressures of H_2 and HF yields

$$RT \ln a_{FeF_2} = \Delta \overline{G}_{F_2} - \Delta G^0_{FeF_2}. \quad (18)$$

The activity (concentration) of iron in the salt is governed by the fluorine potential of the system, whether it is controlled by a gas phase fluorine couple, by a major-metal addition, or by a multivalent dissolved salt. The activity of iron in solution is the product of its cation fraction and activity coefficient (unknown).

Table 1 shows the results of calculation of the iron cation fraction in flibe when the Fe/FeF_2 couple is controlled by the fluorine potentials described above.

An effective thermodynamic redox control in the flibe coolant loop of a fusion reactor is afforded by addition of the major metal (Be). The disadvantage of this method is the probable very low solubility of Be in flibe. If the solubility of Be in flibe is low, the redox conditions may be adequate at the location of the metal addition, but the effect might not last over the entire loop.

The use of the cerium couple appears to be marginal because very low concentrations of Ce(IV) are required in order to establish the necessary low fluorine potential. Even slight oxidation of Ce(III) to Ce(IV) would destroy the corrosion protection of this couple.

To ensure that reducing conditions prevail over an entire coolant loop, beryllium metal addition *plus* CeF_3 dissolved in the melt might prove to be an effective redox control technique. [1] With CeF_3 in addition to Be, the latter would fix the valence of the Ce at III at the location of the added beryllium metal. This reducing agent

would be carried throughout the loop to provide the requisite low fluorine potential.

6. Conclusions

The redox condition of molten fluoride salts is quantitatively described by the fluorine potential.

At least four fluorine couples are available to control the fluorine potential of flibe. At 900 K, the values of $\Delta \overline{G}_{F_2}$ range from -253 kcal/mol to -18 kcal/mol.

The fluorine potential, however applied, controls the equilibrium concentrations of structural metals dissolved in flibe.

Table 1
Thermodynamically limited cation fractions of iron in flibe at 900 K

Redox couple	Fluorine potential (kcal/mol)	Cation fraction iron[a]
H_2/HF[b]	−141	0.33
Be/BeF_2	−216	2×10^{-19}
Li/LiF	−253	2×10^{-28}
CeF_3/CeF_4[c]	−18	>1

[a] Assumes $\gamma_{FeF_2} = 1$.
[b] Assumes 10:1 mol ratio, 1 atm total pressure.
[c] Assumes $a_4/a_3 = 0.1$.

References

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[1] Beryllium metal cannot reduce CeF_3 to metallic cerium [1]. Lithium metal, on the other hand, appears to be capable of producing cerium metal if the CeF_3 mol fraction is greater than $\sim 2.5 \times 10^{-5}$ [1]. This result depends on the CeF_3 activity coefficient inferred from the solubility of this salt in flibe [4].