Are Defect Structure Models Applicable to Molten Salts?

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Fig. 1. lg a_{MgO} as a function of $10^4/T$. (lg = $\log_{10}$).

In a previous communication, it was shown that red-ox equilibria in molten $FeO-Fe_2O_3$ mixtures can be calculated from a simple model based on a spinel structure. In this model, the Fe(II) and Fe(III) ions are statistically distributed in the cation positions, and oxygen ions and vacancies in the anion positions [1].

One could then ask whether this model can also be applied to other systems where the radius ratio and charge ratio of the cation to anion are similar, for example when FeO is replaced by MgO (or LiF) and Fe_2O_3 by Al_2O_3 etc.

In the following some arguments will be presented which favour the opinion that the anion vacancy model might be better for describing the thermodynamic properties of systems of this type than for example the Temkin model.

(1) It is *well* established that on quenching molten Al_2O_3, the spinel modification γ-Al_2O_3 readily results. This would indicate that molten Al_2O_3 has a structure more similar to the spinel than to the corundum lattice.

The available data of the heat of fusion of a-Al_2O_3 compared with the $\gamma \rightarrow a$ heat of transition together with the densities reported for a, γ and liquid Al_2O_3 also indicate strongly that γ-Al_2O_3 is more related to the liquid than to the corundum structure.

Another observation may also support this. It is known (compare the $MgO-Al_2O_3$ phase diagram [2]) that the spinel $MgO \cdot Al_2O_3$ at higher temperature forms solid solutions with Al_2O_3. This region of solubility increases rapidly with increasing temperature. The solid solution curve expresses the equilibrium:

$$a\text{-}Al_2O_3 = \gamma\text{-}Al_2O_3 \text{ (MgO} \cdot Al_2O_3\text{) s.s.}$$
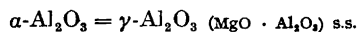
Extrapolation of the solid solution curve to $N_{Al_2O_3} = 1$, should give the transition

temperature for $a \rightleftharpoons \gamma$. It is evident that this temperature must be very close to the melting point of a-Al_2O_3 ($\approx 2\,050°C$).

(2) The liquidus line of MgO in the system $MgO-Al_2O_3$ has not been accurately determined because of the extremely high temperature involved. Still an estimated position of the line is shown in the phase diagram, compare Muan and Osborn [3]. In Fig. 1 the activity of MgO is shown as a function of temperature, calculated from the following three models:

(a) Statistically distributed Mg^{2+} and Al^{3+} ions:

$$a_{MgO} = N_{Mg^{2+}} \cdot N_{O^{2-}}$$

where N = ionic fraction; $N_{O^{2-}} = 1$ (Temkin model)

(b) Spinel model with statistically distributed Mg^{2+} and Al^{3+} in the cation positions, and O^{2-} and $\boxminus$ in the anion positions:

$$a_{MgO} = c \cdot N_{Mg^{2+}} \cdot N_{O^{2-}} \cdot N^{\frac{1}{3}}_{\boxminus}$$

where $c = 3^{\frac{3}{4}} \cdot 4^{\frac{4}{3}}$ (from entropy of pure MgO of the chosen structure) N = ionic position fraction (Spinel model, disorder).

(c) Spinel model where the Al^{3+} occupy only the octahedral positions (normal spinel).

$$a_{MgO} = c' \cdot N_{Mg(IV)} \cdot N^{\frac{2}{3}}_{Mg(VI)} \cdot N_{O^{2-}} \cdot N^{\frac{1}{3}}_{\boxminus}$$

where c' = constant; $N_{Mg(IV)} = 1$ (Spinel model, order).

(According to the latest information [4], the heat of formation of $MgO \cdot Al_2O_3$ from MgO and Al_2O_3 is < 5 kcal and hence lower than RT in the actual temperature range. An $Al^{3+} - Mg^{2+}$ disorder according to (b) should therefore be expected).

The three straight lines drawn in Fig. 1 are calculated from

$$\ln a_{\text{MgO}} = \frac{\varDelta S_f}{R}\left(1 - \frac{T_f}{T}\right)$$

where the value of $\varDelta S_f$, the entropy of fusion, is chosen to be 5, 6.2 and 7 e.u. respectively. The MgO activity calculated with the normal value for alkali-halides, $\varDelta S_f = 6.2$ e.u., are in a remarkably good agreement with the disorder model (b).

(3) The change in volume on melting of LiF is $\varDelta V/V_f = 29.4$ % [5]. If contribution of the Li ions is neglected, the volume change according to the transition

$$\text{LiF}_{(\text{NaCl})} \rightarrow \text{LiF}\boxminus\tfrac{1}{3}\text{(Spinel)}$$
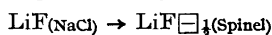
should be $\varDelta V/V_f = 33$ %, which is in astonishingly good agreement with the expansion on melting.

Of course this does not mean that the spinel model, as suggested above, is identical to the real structure of the liquid phase. However, it seems that an improvement in the evelution of the thermodynamic properties is possible if in addition to a Temkin statistical ion distribution one takes into account statistically distributed vacancy positions.

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Reversible Transformation of the Acceptor Specificity of Yeast D-Lactic Cytochrome c Reductase

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D-Lactic cytochrome c reductase (D-LcR), which is highly specific for cytochrome c as acceptor [1,2], is inhibited cytochrome c-competitively by the polyvalent cation protamine [3]. With increasing concentrations of protamine added to the assay medium, however, D-LcR acquires the ability to reduce ferricyanide. The decrease of the cytochrome c reduction and the increase of the ferricyanide reduction is shown in Fig. 1. The maximum rate obtained with ferricyanide as acceptor approximates that obtained with cytochrome c as acceptor; 2,6-dichlorophenol indophenol is not reduced.

The positively charged proteins lysozyme and ribonuclease, which likewise inhibit D-LcR in a cytochrome c-competitive man-
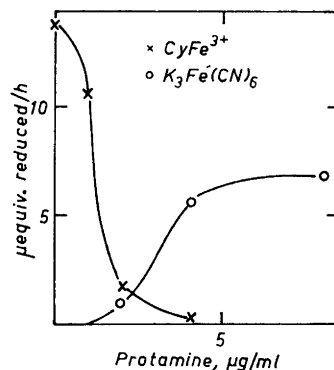

Fig. 1. Change of the acceptor specificity of D-LcR by the addition of protamine sulfate to the assay solution; the rate is expressed as μ-equiv. of acceptor reduced per hour, both when cytochrome c and when ferricyanide is used as acceptor. Buffer, sodium phosphate, $\varGamma/20.01$, + 0.001 M Versene; pH 6.8; D-lactate, 5×10^{-3} M; 23°; ×———×, cytochrome c, 4×10^{-6} M; o———o, ferricyanide, 1.4×10^{-4} M.