

Thermodynamics of Charge-unsymmetrical Anion Mixtures. III. The Liquid System PbO–PbF₂

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The enthalpies of mixing of the liquid mixtures of PbO+PbF₂ have been measured by liquid-liquid calorimetry at 1170 K. The values are negative and show a well-defined minimum of about -320 J mol^{-1} near $N_{\text{PbO}}=0.7$. The partial enthalpies of PbO and PbF₂ are combined with corresponding Gibbs energies from several emf investigations to yield partial entropies of mixing. These entropies agree well with values predicted from the Temkin model.

On the basis of high temperature heat of mixing calorimetry combined with phase diagram analysis we have in two recent communications discussed the thermodynamic properties of the mixed anion-common cation liquid mixtures of AF (A=Li,Na,K) with A₂SO₄¹ and with A₂MoO₄ and A₂WO₄.² In these systems we found that the entropies of mixing show significant positive deviations from the ideal Temkin molten salt model.³ A Flory-type model⁴ in which the divalent ion is treated as if it were a dimer yielded entropies in better agreement with the experiment. However, it was not clear from these studies whether the observed positive entropy deviations were due to the difference in charge or to the difference in size between the small F⁻ and the larger SO₄²⁻, MoO₄²⁻ and WO₄²⁻ anions. In an effort to resolve this question we consider in the present study the liquid system PbO–PbF₂. The ionic radii of O²⁻ and F⁻ are 1.40Å and 1.36Å, respectively.⁵ Since this difference in size is trivial, possible deviations from the ideal Temkin entropy would have to be attributed to the difference in charge.

There have been a number of emf studies of the system PbO–PbF₂, in which the partial Gibbs energies (chemical potentials) of PbO⁶⁻⁹ or of PbF₂¹⁰ are reported as functions of composition and temperature. The results reported by Frohberg *et al.*,⁷ by Grau *et al.*,⁸ and by Caley and Masson¹⁰ are in reasonably good agreement with each other. However, the data of Iwase *et al.*⁹ differs somewhat, and that of Jeffes and Sridhar⁶ considerably, from the other studies.

Some of these authors have attempted to derive partial enthalpies from the temperature dependence of their emfs, or by assuming an ideal Temkin entropy of mixing. It is not surprising that these enthalpies vary a great deal from one study to the next.

In the present paper we report enthalpies of mixing at 1170 K determined by high temperature calorimetry for the liquid system PbO–PbF₂. From our observed integral

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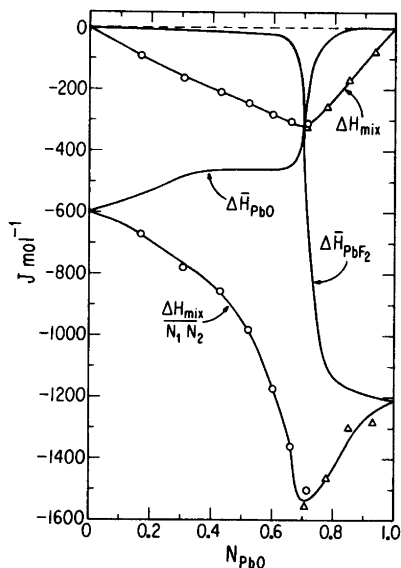


Fig. 1. Molar enthalpies of mixing in the liquid system PbO-PbF₂ at $T=1170$ K: O Series I; Δ Series II.

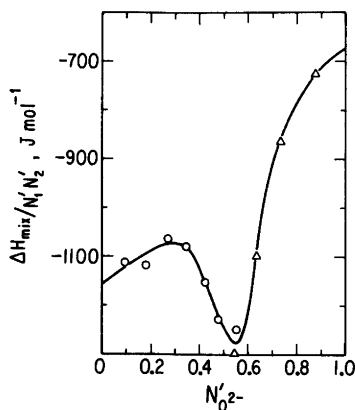


Fig. 2. Plot of enthalpy interaction parameter, $\Delta H_{\text{mix}}/N_1^1 N_2^1$ against the equivalent fraction of O^{2-} , $N'_{\text{O}^{2-}}$.

enthalpies we have derived the partial enthalpies for both components. These values are compared with the corresponding Gibbs energies of Froberg *et al.*,⁷ of Grau *et al.*,⁸ and of Caley and Masson¹⁰ to yield partial entropies of mixing.

EXPERIMENTAL

As in our earlier work the calorimetric measurements were carried out in a Calvet-type twin microcalorimeter designed for continuous operation up to about 1400 K. In the present study the calorimeter was maintained at 1170 ± 2 K. All experiments were of the liquid-liquid type, with both components maintained at calorimeter temperature. In the initial experiments we measured the enthalpies of mixing for melts with mole fractions of PbO of 0.166 (Series I) and 0.934 (Series II), respectively. To these mixtures we added, in several consecutive calorimetric experiments, pure PbO or PbF₂, until we reached the compositions $N_{\text{PbO}}=0.711$ (I) and $N_{\text{PbO}}=0.707$ (II). The molar integral enthalpies of mixing were calculated by summing the observed heat effects, correcting for the changes in the total amount of mixture. The actually observed enthalpies ranged from about -2.5 to -6.5 J. Note that the experimental errors in each series of measurements are cumulative. Hence it is gratifying to find that the experimental values of ΔH_{mix} for the two final mixtures of nearly identical compositions ($N_{\text{PbO}}=0.711$ and 0.707) differed by less than 4%.

The experimental set-up was very similar to that used in our earlier work, with crucible, dippers and plungers made from a 90% gold-10% palladium alloy. However, the experiments now were carried out in an oxygen atmosphere, and the 20 mm diameter nickel protection tube was replaced by a similar tube made from 90% platinum-10% rhodium.

The calorimeter was calibrated by dropping pieces of 2 mm platinum wire from room temperature into the calorimeter crucible at 1170 K. The resulting heat effects were calculated using enthalpy data for platinum recommended by Kelley.¹¹ The reproducibility of the calibration experiments was about $\pm 1\%$.

The chemicals were PbO (Litharge), Baker Analyzed Reagent (99.6 % PbO), and PbF₂, Materials Research Corporation (99.9 % PbF₂). Prior to use both chemicals were dried under vacuum at 160 °C for 24 h.

RESULTS AND DISCUSSION

The enthalpy of mixing. The experimental results are given in Table 1 and are shown graphically in Fig. 1. The partial enthalpies of PbO and PbF₂ given in Fig. 1 were obtained by the method of intercepts, i.e. by drawing tangents to a large scale graph of the integral enthalpies of mixing.

From Fig. 1 it is seen that the enthalpy of mixing shows a fairly well-defined minimum near $N_{\text{PbO}}=0.7$. This corresponds roughly to the composition where there are equal numbers of F⁻ and O²⁻ ions in the mixture ($N_{\text{PbO}}=0.67$). Note also that the limiting value of the partial enthalpy of solution of PbF₂ in PbO is very nearly twice as large as for PbO in PbF₂.

These observations suggest that the enthalpies of mixing in large measure are caused by a 1:1 interaction between O²⁻ and F⁻ ions. This is consistent with simplified models of molten salt mixtures proposed by Förland,¹² Lumsden,¹³ and others. From these models it is expected that there will be two principal exothermic contributions of electrostatic origin to the enthalpy of mixing. These are, on the one hand, the reduction in Coulomb repulsion between second nearest neighbors (for charge-unsymmetrical systems, see, e.g., Braunstein *et al.*,¹⁴) and, on the other, the polarization of the common ion, in this case Pb²⁺. Both of these effects will be maximized at compositions with the highest probability of the O²⁻Pb²⁺F⁻ configurations, i.e., for an equal number of O²⁻ and F⁻ anions.

The well-defined minima near $N_{\text{PbO}}=0.7$, both in the mixing enthalpy and in the interaction parameter [$\Delta H_{\text{mix}}/N(1-N)$], are considerably sharper than one would expect for a system with a very small enthalpy of mixing. If the total heat effect arises from second nearest neighbor interactions (i.e., F⁻Pb²⁺O²⁻), and if one has a statistical distribution of F⁻ and O²⁻ ions, a plot of the interaction parameter based on the equivalent fractions of the anions, $\Delta H_{\text{mix}}/N_1^1 N_2^1$, against the equivalent fraction of O²⁻, $N_{\text{O}^{2-}}$, should yield a straight line. Such a plot is given in Fig. 2, which shows a sharp minimum near $N_{\text{O}^{2-}} \approx 0.55$. Since the magnitude of the heat effect is too small to cause significant deviations from a random distribution of the anions (this is also supported by the entropy data given in the next section), this curve cannot be explained purely in terms of second nearest neighbor interactions. Thus it seems likely that the mixing process also gives rise to a change in *nearest neighbor interactions*, i.e., in the covalent interaction between oxygen and lead and presumably to a lesser extent fluorine and lead, across the binary system. It is possible, for example, that as the amount of PbF₂ is increased, there may be also an increase in the coordination of oxygen by lead in the mixture. This point could perhaps be followed up if the melts were studied by structure-sensitive techniques.

In the introduction we mentioned that several authors have attempted to derive heat of mixing information from their electrochemical studies. Thus, by assuming a regular solution model Froberg *et al.*⁷ calculated such data; from their Fig. 6 we derive an enthalpy interaction parameter of about -1300 J mol^{-1} , i.e., roughly of the same order as the calorimetric values. However, the enthalpies of Jeffes and Sridhar⁶ and of Iwase *et al.*⁹ differ very considerably from our experimental results.

The entropy of mixing. In Fig. 3 we show the partial excess entropies, $\Delta \bar{S}_{\text{PbO}}^{\text{ex}}$ and $\Delta \bar{S}_{\text{PbF}_2}^{\text{ex}}$, obtained from our calorimetric partial enthalpies combined with the corresponding Gibbs

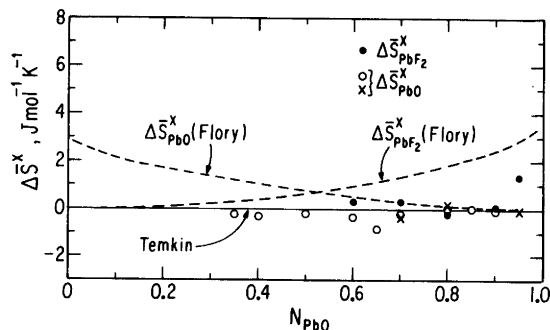


Fig. 3. Excess partial entropies of PbO and PbF₂ at 1170 K. Points calculated from previously published partial Gibbs energy data, and present calorimetric results: ○ Caley and Masson;¹⁰ ● Frohberg *et al.*;⁷ × Grau *et al.*⁸

energies of Frohberg *et al.* (PbO),⁷ of Grau *et al.* (PbO),⁸ and of Caley and Masson (PbF₂).¹⁰ The model for the ideal entropy of mixing (*i.e.*, $\Delta\bar{S}_{\text{PbO}}^{\text{x}} = \Delta\bar{S}_{\text{PbF}_2}^{\text{x}} = 0$) was the Temkin model (see below). The reported partial Gibbs energies were all in analytical form given as functions of T ; the plotted values of the partial entropies apply at the temperature of the calorimetric measurements, 1170 K.

The data of Jeffes and Sridhar⁶ were not included in this comparison since they differ considerably from the results of the three other studies. The probable reasons for this were discussed by Frohberg *et al.*⁷ Iwase *et al.*⁹ did not present their results in analytical form. Their values also differ somewhat from those of the other investigations.

The Temkin model would, in this case, predict the entropies to be:

$$\Delta S_{\text{mix}} = -R \left[n_{\text{PbO}} \ln \left(\frac{n_{\text{PbO}}}{n_{\text{PbO}} + 2n_{\text{PbF}_2}} \right) + 2n_{\text{PbF}_2} \ln \left(\frac{2n_{\text{PbF}_2}}{n_{\text{PbO}} + 2n_{\text{PbF}_2}} \right) \right] \quad (1)$$

$$\Delta\bar{S}_{\text{PbF}_2} = -2R \ln \left[\frac{2n_{\text{PbF}_2}}{n_{\text{PbO}} + 2n_{\text{PbF}_2}} \right] \quad (1a)$$

$$\Delta\bar{S}_{\text{PbO}} = -R \ln \left[\frac{n_{\text{PbO}}}{n_{\text{PbO}} + 2n_{\text{PbF}_2}} \right] \quad (1b)$$

In Fig. 3 the solid line at $\Delta S^{\text{x}} = 0$ represents the prediction of this model. Also shown in this figure as broken lines are the partial excess entropies, relative to the Temkin model, predicted by a Flory-type model, in which the O²⁻ ion is treated as if it were a dimer. The relevant expressions are:

$$\Delta S_{\text{mix}} = -R(2n_{\text{PbF}_2} \ln N_{\text{PbF}_2} + n_{\text{PbO}} \ln N_{\text{PbO}}) \quad (2)$$

$$\Delta\bar{S}_{\text{PbF}_2} = -R \ln N_{\text{PbF}_2} - RN_{\text{PbO}} \quad (2a)$$

$$\Delta\bar{S}_{\text{PbO}} = -R \ln N_{\text{PbO}} + RN_{\text{PbF}_2} \quad (2b)$$

From Fig. 3 we see that the experimental partial entropies both for PbO and for PbF₂, generally agree well with the Temkin model. Clearly there is no agreement with the Flory model, as was found for the systems considered in our earlier work. This strongly suggests that the positive deviations from the Temkin model found in AF-A₂SO₄, AF-A₂MoO₄, and AF-A₂WO₄ must be attributed to the large difference in size between the small F⁻ and the large SO₄²⁻, MoO₄²⁻, and WO₄²⁻ ions rather than to the difference in charge.

In this context it is of interest to review briefly also the thermodynamic behavior of charge-unsymmetrical mixed cation-common anion systems with small enthalpies of mixing. From the extensive investigations of Østvoid¹⁵ we know that in charge-unsymmetrical systems in which the difference in the size of the two cations is small the enthalpy interaction parameter is also quite small (e.g., LiCl-MgCl₂; NaCl-SrCl₂; KCl-BaCl₂). For such systems the entropies of mixing agree well with the Temkin model. For NaCl-BaCl₂, where the difference in size of the two cations is larger (Na⁺: 0.95 Å; Ba²⁺: 1.35 Å) the entropies of mixing seem to show small positive deviations from the Temkin model. On the other hand, when the enthalpy interaction parameter has large negative values, one has in all cases negative entropy deviations, presumably caused by short range order and vibrational effects.

As size effects clearly are of importance in determining the magnitude of the entropy, it would be desirable to have a method based on ionic volumes to calculate the entropy of mixing. In this respect the usual pseudo-lattice models are not very useful. However, Hildebrand¹⁶ suggested an approach to the configurational entropy of mixing of macromolecules based on this idea. A similar approach recently was applied by Julsrud¹⁷ to molten salt mixtures. This treatment requires information on the density of liquid PbO and PbF₂. Since we have found no such information on PbF₂ in the published literature, we are not able to pursue this matter for the considered system at the present time.

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