

## CALORIMETRIC INVESTIGATION OF THE RbF–Rb<sub>2</sub>SO<sub>4</sub> LIQUID SYSTEM AND COMPARISON OF THE EXCESS THERMODYNAMIC FUNCTIONS IN THE AF–A<sub>2</sub>SO<sub>4</sub> (A = Li, Na, K, Rb) MOLTEN SALT MIXTURES

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(Received 10 March 1982)

### ABSTRACT

The experimental values of the excess enthalpy, obtained by direct calorimetry, are reported in this work for the RbF–Rb<sub>2</sub>SO<sub>4</sub> liquid system. The entropy of mixing of this system was calculated from the equilibrium phase diagram.

Many expressions have been presented in the literature for the ideal entropy of mixing of AB<sub>2</sub>–A'B asymmetrical systems and we have pointed out, here, a criterion allowing the selection of one of them for a further evaluation of the excess entropy.

A comparative study of the thermodynamic excess functions ( $\Delta H$ ,  $\Delta S^E$ ) was carried out on the series of AF–A<sub>2</sub>SO<sub>4</sub> mixtures (A = Li, Na, K, Rb).

### INTRODUCTION

Calorimetric investigations of common binary cation molten salt mixtures showed that the excess enthalpy is generally small and positive over the whole concentration range for systems including ions with the same valency [1,2]. In these mixtures, the main energetic contributions to the excess enthalpy,  $\Delta H$ , are of two kinds [3].

(a) The first one, positive, arises from the variation during mixing of London–van der Waals interactions between second–nearest-neighbour anions [4,5].

(b) The second, negative, due to the reduction in the Coulomb repulsive energy between the same ions [6]. The former term has the greater absolute value for mixtures such as A(Cl, I) [2], A(Br, I) [2], A(Br, Cl) [2], A(NO<sub>3</sub>, Cl) [1] with A = Li, Na, K, Rb.

Few experimental data are available for common cation systems containing ions with different valency.

In the course of a general thermodynamic investigation of A, B//F, SO<sub>4</sub> ternary reciprocal mixtures (A or B = Li, Na, K, Rb), we measured the excess enthalpy of some limiting systems AF-A<sub>2</sub>SO<sub>4</sub> (A = Li [8], Na [7], K [7]): this excess enthalpy was found positive for systems with lithium or sodium and negative for the KF-K<sub>2</sub>SO<sub>4</sub> mixture. In order to verify whether the thermodynamic behaviour of the latter system is abnormal with respect to the others or the reduction in the Coulomb repulsive energy prevails, we have initiated the study of the RbF-Rb<sub>2</sub>SO<sub>4</sub> mixture.

In this paper we measured by high temperature calorimetry the excess enthalpy of the RbF-Rb<sub>2</sub>SO<sub>4</sub> system and we performed a complete computer-assisted analysis of the thermodynamic properties and phase equilibria in this binary system. Furthermore a comparative study of both these excess functions was carried out on the complete series of AF-A<sub>2</sub>SO<sub>4</sub> systems (A = Li, Na, K, Rb), and the choice of the ideal reference state was discussed.

#### ENTHALPY OF MIXING OF THE RbF-Rb<sub>2</sub>SO<sub>4</sub> SYSTEM

##### *Experimental*

The calorimetric experiments reported in the present work were carried out with a high temperature calorimeter suitable for work up to 1800 K. A detailed description of this apparatus has already been given [9,10]; only the main features of the furnace and of the calorimetric detector will be briefly recalled here together with the method used in performing liquid mixtures.

The furnace assembly which surrounds the calorimeter consists of a graphite resistor; the geometry of this heater is such as to provide a constant temperature zone in its central part.

The calorimetric detector (thermopile), located in this zone, consists of 132 Pt-6% Rh/Pt-30% Rh junctions alternatively in contact with the laboratory crucible and with the reference crucible.

Mixing was obtained by the "indirect drop" method. One component A, liquid, is placed in the laboratory crucible at the experimental temperature  $T_E$ ; the mixture is obtained by dropping the solid component B preheated at  $T_X$ . The thermal balance of the procedure is given by the equation

$$\Delta H_{\text{exp}} = X_B [H_B(\text{liq})_{T_E} - H_B(\text{sol})_{T_X}] + \Delta H$$

where  $\Delta H_{\text{exp}}$ ,  $[H_B(\text{liq})_{T_E} - H_B(\text{sol})_{T_X}]$  and  $\Delta H$ , referring to one mole, are, respectively, the heat evolved at constant pressure during experiment, the enthalpy variation of component B between the temperatures  $T_E$  and  $T_X$ , and the liquid-liquid enthalpy of mixing.

Salts used in this work were high grade chemicals supplied by Merck ("Suprapur" reagents). The dehydration procedure prior to their use consisted of a previous drying under vacuum at room temperature for 24 h. The temperature was gradually raised up to 500 K and the salts maintained at this temperature for another 24 h period. Finally, the anhydrous powder was melted under purified argon, in a dry-box, and the solidified melt ground to the desired particle size.

### Results

The experimental temperature selected for the investigation of the RbF–Rb<sub>2</sub>SO<sub>4</sub> system was  $T_E = 1093$  K; at this temperature only the rubidium fluoride is liquid ( $T_f = 1048$  K) whereas the rubidium sulphate is solid ( $T_f = 1347$  K). Though at 1093 K the experimental domain corresponding to a simple-phase liquid solution is somewhat restricted ( $0 < X_{\text{Rb}_2\text{SO}_4} < 0.3$  [11]), this experimental temperature had to be chosen since the vapor pressure of the liquid component was then less than 100 Pa [12]; indeed beyond this range, a very poor reproducibility of the calorimetric results can be observed.

The liquid mixture was obtained by dropping Rb<sub>2</sub>SO<sub>4</sub> samples preheated at  $T_x = 1023$  K.

Our experimental values were referred to the liquid state by calculating the enthalpy increment of rubidium sulphate from the heat content equation

TABLE 1

Experimental molar enthalpies of mixing of liquid RbF–Rb<sub>2</sub>SO<sub>4</sub> mixtures at 1093 K

| $X_{\text{Rb}_2\text{SO}_4}$ | $-\Delta H$<br>(kJ mole <sup>-1</sup> ) | $X_{\text{Rb}_2\text{SO}_4}$ | $-\Delta H$<br>(kJ mole <sup>-1</sup> ) |
|------------------------------|---|------------------------------|---|
| 0.031                        | 1.11                                    | 0.135                        | 1.61                                    |
| 0.047                        | 0.78                                    | 0.140                        | 1.97                                    |
| 0.048                        | 1.16                                    | 0.148                        | 1.75                                    |
| 0.053                        | 0.95                                    | 0.150                        | 1.66                                    |
| 0.066                        | 1.60                                    | 0.156                        | 1.89                                    |
| 0.077                        | 1.35                                    | 0.162                        | 2.05                                    |
| 0.081                        | 1.13                                    | 0.176                        | 2.04                                    |
| 0.097                        | 1.65                                    | 0.184                        | 1.87                                    |
| 0.103                        | 1.50                                    | 0.190                        | 2.21                                    |
| 0.104                        | 1.37                                    | 0.202                        | 2.16                                    |
| 0.105                        | 1.37                                    | 0.219                        | 2.46                                    |
| 0.127                        | 1.67                                    | 0.224                        | 2.51                                    |

given by Denielou [13]

$$H_{\text{Rb}_2\text{SO}_4(\text{liq})_{1093}} - H_{\text{Rb}_2\text{SO}_4(\text{sol})_{1023}} = 49.03 \text{ kJ mole}^{-1}$$

The values obtained for the liquid-liquid enthalpy of mixing,  $\Delta H$ , are reported in Table 1; they are negative over the whole concentration range.

These  $\Delta H$  values were fitted to the analytical expression

$$\Delta H = (1 + X_{\text{SO}_4}) X'_{\text{SO}_4} (1 - X'_{\text{SO}_4}) (a + bX'_{\text{SO}_4}) \quad (1)$$

where  $X_{\text{SO}_4}$  and  $X'_{\text{SO}_4}$  are the ionic fractions defined by Temkin [14] and Forland [15], respectively.

This equation for the enthalpy of mixing was deduced from our theoretical work concerning asymmetrical molten salt mixtures of the  $\text{AB}_2\text{-A}'\text{B}$  type [16].

The assessment of the  $b$  parameter is difficult in the present case since the experiments were performed over a limited concentration range. By analogy with the  $\text{KF-K}_2\text{SO}_4$  mixture where the  $b$  coefficient in eqn. (1) was almost zero ( $b = 0.242 \text{ kJ mole}^{-1}$ ) [7], we assumed that  $b = 0$ ; then, the value of the  $a$  coefficient was found equal to  $a = -8.62 \text{ kJ mole}^{-1}$ .

We reported in Fig. 1 the curve calculated for the enthalpy of mixing from eqn. (1) and it can be noticed that it gives a correct representation of the experimental data.

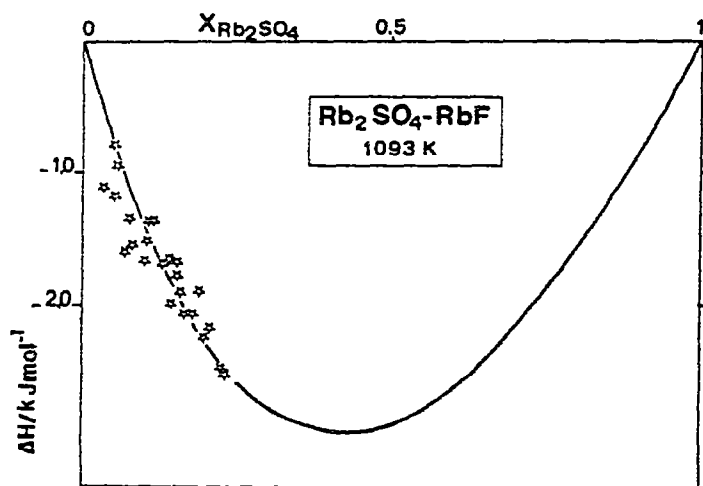


Fig. 1. Molar enthalpy of mixing  $\Delta H$  of liquid  $\text{RbF-Rb}_2\text{SO}_4$  mixture against mole fraction  $X_{\text{Rb}_2\text{SO}_4}$ . ☆, Experimental; —, calculated (eqn. 1).

ENTROPY OF MIXING OF THE RbF-Rb<sub>2</sub>SO<sub>4</sub> SYSTEM

The partial Gibbs free energy ( $\Delta\bar{G}_A$ ) of a pure solid A, in equilibrium at a temperature  $T$  with a liquid solution, referred to supercooled liquid A, may be calculated from the equation [17]

$$\begin{aligned}\Delta\bar{G}_A &= -\Delta H_f \left(1 - \frac{T}{T_f}\right) + \alpha \left[ (T_f - T) - T \ln \frac{T_f}{T} \right] + \frac{\beta}{2} (T_f - T)^2 + \frac{1}{2} \gamma T \left( \frac{1}{T_f} - \frac{1}{T} \right)^2 \\ &= \Delta\bar{H}_A - T\Delta\bar{S}_A\end{aligned}\quad (2)$$

where  $T_f$  and  $\Delta H_f$  are respectively the temperature and the enthalpy of fusion of A; the coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$  are constants in the expression for the difference in heat capacity between supercooled and solid A

$$\Delta C_p = C_p(\text{liq}) - C_p(\text{sol}) = \alpha + \beta T + \frac{\gamma}{T^2}$$

So, if the equilibrium phase diagram is known, eqn. (2) may be used in calculating the partial Gibbs free energy  $\Delta\bar{G}_A$  and therefore the partial entropy of mixing  $\Delta\bar{S}_A$ , since the partial enthalpy  $\Delta\bar{H}_A$  was also known from calorimetric investigation.

Such a calculation was already made for the three systems LiF-Li<sub>2</sub>SO<sub>4</sub> [8], NaF-Na<sub>2</sub>SO<sub>4</sub> [7] and KF-K<sub>2</sub>SO<sub>4</sub> [7], therefore only the results obtained for the RbF-Rb<sub>2</sub>SO<sub>4</sub> mixture are to be reported here.

The RbF-Rb<sub>2</sub>SO<sub>4</sub> equilibrium phase diagram was experimentally determined by Schmitz-Dumont [11] and Gladuschenko [18]. The general shape of these diagrams, reported in Fig. 2, is identical: only minor differences (see Table 2) appear on the coordinates of the characteristic points (two eutectics and one definite compound); on the other hand, the temperatures of fusion of the pure salts reported by the previous authors disagree and differ also from those generally selected [13,19] (see Table 3). A critical study led us to prefer the diagram proposed by Schmitz-Dumont [11].

This experimental diagram was analyzed by a least-squares optimisation technique [20] in order to obtain, via eqn. (2), the partial entropy of mixing of each component, then the integral entropy of mixing (Table 4); the data used for the thermodynamic properties of the pure salts are listed in Table 3.

The same analysis yielded the free energy of fusion of the intermediate compound; the resultant expression is

$$\Delta G_{fus}^0 = 28.20 - 0.025 T \text{ kJ mole}^{-1} \text{ of } (\text{RbF})_{0.5}(\text{Rb}_2\text{SO}_4)_{0.5}$$

The compound  $(\text{RbF})_{0.5}(\text{Rb}_2\text{SO}_4)_{0.5}$  contains 2.5 ions. The computed entropy of melting of  $25/2.5 = 10 \text{ J K}^{-1}$  per ion is therefore physically reasonable.

The calculated phase diagram is shown in Fig. 2 and has the same general

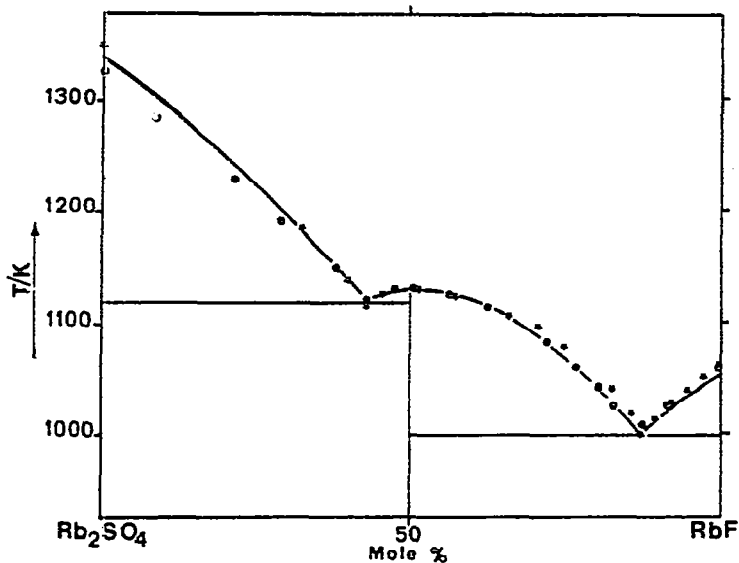


Fig. 2. Phase diagram of the RbF-Rb<sub>2</sub>SO<sub>4</sub> system. —, Calculated; ●, experimental results ref. 11; ★, experimental results ref. 18.

shape as those obtained experimentally. The coordinates of the three characteristic points

|                   |                         |                        |
|-------------------|-------------------------|------------------------|
| eutectic          | $X_{\text{RbF}} = 0.44$ | $T_f = 1118 \text{ K}$ |
| definite compound | $X_{\text{RbF}} = 0.50$ | $T_f = 1130 \text{ K}$ |
| eutectic          | $X_{\text{RbF}} = 0.87$ | $T_f = 998 \text{ K}$  |

TABLE 2

RbF-Rb<sub>2</sub>SO<sub>4</sub> System: characteristic points of the experimental equilibrium phase diagram

| $X_{\text{RbF}}$ | $T_f$ (K) | Characteristic points                     |
|------------------|-----------|---|
| 0                | 1325 [11] | Pure salt Rb <sub>2</sub> SO <sub>4</sub> |
| 0                | 1347 [18] | Pure salt Rb <sub>2</sub> SO <sub>4</sub> |
| 0.43 [11]        | 1120 [11] | Eutectic                                  |
| 0.43 [18]        | 1115 [18] | Eutectic                                  |
| 0.50 [11]        | 1129 [11] | Congruently melting                       |
| 0.50 [18]        | 1127 [18] | compound                                  |
| 0.86 [11]        | 996 [11]  | Eutectic                                  |
| 0.88 [18]        | 999 [18]  | Eutectic                                  |
| 1                | 1060 [11] | Pure salt RbF                             |
| 1                | 1063 [18] | Pure salt RbF                             |

TABLE 3  
Free energies, temperatures and enthalpies of fusion of the compounds used in the phase diagram analysis

| Salt                            | $\Delta G_f^0 = A + BT + CT^2 + FT \ln T + G/T$ (kJ mole <sup>-1</sup> ); $T$ (K) |           |                     | $T_{\text{fus}}$<br>(K) | $\Delta H_{\text{fus}}$<br>(kJ mole <sup>-1</sup> ) | Ref. |                |
|---------------------------------|---|-----------|---------------------|-------------------------|---|------|----------------|
|                                 | A   | B         | C × 10 <sup>5</sup> |                         |   |      | F              |
| RbF                             | 266.1785  | -0.766495 | 1.742424            | 0.080640                | 0.731266  | 1048 | 22.975<br>[19] |
| Rb <sub>2</sub> SO <sub>4</sub> | -19.61999   | 0.712341  | 4.645266            | -0.105544               | 0   | 1339 | 38.418<br>[13] |

TABLE 4

Calculated molar entropy of mixing of the liquid RbF-Rb<sub>2</sub>SO<sub>4</sub> mixture

| $X_{\text{Rb}_2\text{SO}_4}$ | $\Delta S$ (J mole <sup>-1</sup> K <sup>-1</sup> ) |
|------------------------------|--|
| 0.1                          | -2.88  |
| 0.2                          | -3.97  |
| 0.3                          | -4.31  |
| 0.4                          | -4.14  |
| 0.5                          | -3.72  |
| 0.6                          | -3.13  |
| 0.7                          | -2.42  |
| 0.8                          | -1.63  |
| 0.9                          | -0.83  |

are in good agreement with the data reported by Schmitz-Dumont [11]. The only differences appear in regions close to the pure components since we preferred in this calculation the temperatures of fusion generally accepted (Table 3) instead of those reported [13,19] which differ by 12 and 14 K, respectively.

#### DISCUSSION

We stated previously [21] that the variation of the equivalent interaction parameter  $\lambda' = \Delta H / (1 + X_{\text{SO}_4})X'_{\text{SO}_4}(1 - X'_{\text{SO}_4})$  against the equivalent ionic fraction  $X'$ , is representative of the interactions in the solution.

Therefore, the concentration dependence  $\lambda' = f(X'_{\text{SO}_4})$  of the equivalent interaction parameter was plotted in Fig. 3 for the four AF-A<sub>2</sub>SO<sub>4</sub> mixtures (A = Li [8], Na [7], K [7], Rb).

It can be pointed out that  $\lambda'$ , or  $\Delta H$ , varies over the whole concentration range in the sequence  $\Delta H(\text{Na}) > \Delta H(\text{K}) > \Delta H(\text{Rb})$  and that  $\Delta H(\text{Li}) < \Delta H(\text{Na})$ .

These results can be explained as follows: when the cation radius is small compared with those of the anions, the London-van der Waals interactions prevail on those interactions due to Coulombic repulsions resulting in a positive excess enthalpy. The greater the cation radius, the greater the absolute value of this Coulombic term; so, the enthalpy of mixing decreases so as to become negative just like the systems investigated. The ionic radius of sodium (0.96 Å [22]) is small compared with those of F<sup>-</sup> (1.36 Å [22]) and SO<sub>4</sub><sup>2-</sup> (2.30 Å [23]) and the enthalpy of mixing of NaF-Na<sub>2</sub>SO<sub>4</sub> is positive. For the KF-K<sub>2</sub>SO<sub>4</sub> and RbF-Rb<sub>2</sub>SO<sub>4</sub> mixtures, the situation is different



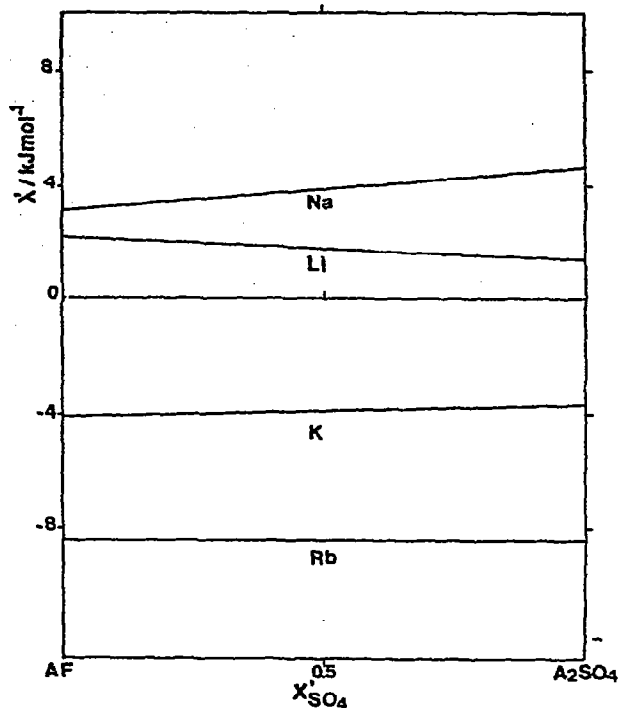


Fig. 3. Variation of the equivalent interaction parameter  $\lambda'$  against equivalent ionic fraction  $X'_{SO_4}$  in AF-A<sub>2</sub>SO<sub>4</sub> mixtures.

since the ionic radii of K<sup>+</sup> (1.34 Å [22]) and Rb<sup>+</sup> (1.48 Å [22]), though greater than that of SO<sub>4</sub><sup>2-</sup>, are to be compared with that of F<sup>-</sup>; and we obtain  $0 > \Delta H(K) > \Delta H(Rb)$ .

Contrary to Julsrud and Kleppa's conclusions [24], this difference in the thermodynamic behaviour of the NaF-Na<sub>2</sub>SO<sub>4</sub> and KF-K<sub>2</sub>SO<sub>4</sub> mixtures seems therefore plausible.

The abnormal behaviour of mixtures containing the lithium ion has been already evidenced in the systematic investigation of common alkali cation halides A(Cl-Br), A(Cl-I) and A(Br-I) with A = Li, Na, K, Rb, Cs [2]; this could only be interpreted with relation to the very small size of the lithium ion. Besides, this singularity of the lithium ion is general since in common anion mixtures too, the systems concerned behave differently from the mixtures containing the other alkali ions [25].

The limiting partial enthalpy of each component of a mixture can be deduced from the equivalent interaction parameter  $\lambda'$  [21]

$$\lim_{X'_{SO_4} \rightarrow 0} (\lambda') = \lambda'(0) = \Delta \bar{H}_{A_2SO_4}^{\infty} / 2$$

$$\lim_{X'_{SO_4} \rightarrow 1} (\lambda') = \lambda'(1) = \Delta \bar{H}_{AF}^{\infty}$$

For each of the four investigated systems, we reported the values deduced for the limiting partial enthalpy of the components (Table 5); it can be noticed that the limiting partial enthalpy of the sulphate always has a larger absolute value than that of the fluoride.

This is physically equivalent to saying that the introduction of one sulphate ion in the quasi-lattice of fluoride ions induces a larger energetic perturbation than the inverse process (introduction of one fluoride ion in the quasi-lattice of sulphate ions). This statement seems reasonable since the radius of the sulphate ion is much larger than that of the fluoride ion. Therefore it could be interesting to confirm this fact by investigating similar systems in which a larger ion would substitute for the sulphate ion.

As already shown [21], expression (1) for the enthalpy of mixing  $\Delta H$  provides a good representation of the experimental data obtained for many asymmetrical  $AB_2-A'B$  systems. It should be mentioned that no particular problem arises in defining the enthalpy of mixing since  $\Delta H$  is a direct excess function.

The definition of the other excess functions is less obvious in relation to the choice of a reference state of ideality of the  $AB_2-A'B$  mixtures. Accordingly many analytical expressions were proposed in the literature for the entropy of the ideal reference solution. Indeed, a statistical definition of this reference state is ambiguous due to the asymmetry in ionic charges; the aim of the following discussion is to bring out a criterion able to direct the choice of this reference state.

The configurational ideal entropy of mixing  $\Delta S^{\text{id}}$  of the system  $AF-A_2SO_4$  can be calculated in a classical way from the basic equation

$$\Delta S^{\text{id}} = k \ln \Omega^*$$

Many expressions were proposed which depend on the model adopted in describing the solution and therefore on the maximal number of configurations  $\Omega^*$ .

TABLE 5  
Limiting partial enthalpies in  $AF-A_2SO_4$  mixtures

| Mixture                             | $\overline{\Delta H_{A_2SO_4}^\infty}$<br>(kJ mole <sup>-1</sup> ) | $\overline{\Delta H_{AF}^\infty}$<br>(kJ mole <sup>-1</sup> ) |
|-------------------------------------|--|---|
| LiF-Li <sub>2</sub> SO <sub>4</sub> | 4.18   | 1.38  |
| NaF-Na <sub>2</sub> SO <sub>4</sub> | 6.28   | 4.68  |
| KF-K <sub>2</sub> SO <sub>4</sub>   | -8.06  | -3.79   |
| RbF-Rb <sub>2</sub> SO <sub>4</sub> | -17.24   | -8.62   |

(a) The classical description of an ionic liquid as two interlocking anionic and cationic quasi-lattices, as proposed by Temkin [14], gives the following equation for one mole of solution

$$\Delta S^{\text{id}} = -R(X_{\text{F}^-} \ln X_{\text{F}^-} + X_{\text{SO}_4^{2-}} \ln X_{\text{SO}_4^{2-}})$$

where  $X_i$  are Temkin's ionic fractions.

This equation is strictly identical to that obtained for a symmetrical system since in the previous description of the liquid the charge asymmetry was not accounted for.

(b) Forland [15] considered that the substitution of one monovalent ion ( $\text{F}^-$ ) by one divalent ion ( $\text{SO}_4^{2-}$ ) induces one excess negative charge; the electroneutrality of the assembly can be preserved in considering that a vacant site or anionic vacancy is created. The entropy of mixing is given by the expression

$$\Delta S^{\text{id}} = -R(X_{\text{F}^-} \ln X'_{\text{F}^-} + 2X_{\text{SO}_4^{2-}} \ln X'_{\text{SO}_4^{2-}}) \quad (4)$$

where  $X'_i$  are Forland's ionic equivalent fractions.

Identical results were obtained by Lumsden [24]—one divalent ion  $\text{SO}_4^{2-}$  is fictitiously assimilated to two monovalent ions  $(\text{SO}_4)_{0.5}^-$ —and by ourselves using the “surrounded ion” concept [21]—vacancies are considered as interstitial next-nearest neighbours of a given ion.

(c) When the vacancy is assumed to be closely attached to the divalent ion, as a true dimer, the Flory's equation [27] can be used to obtain

$$\Delta S^{\text{id}} = -R(X_{\text{F}^-} \ln X'_{\text{F}^-} + X_{\text{SO}_4^{2-}} \ln X'_{\text{SO}_4^{2-}}) \quad (5)$$

Since  $\Omega^*$  is the *maximum* number of configurations, the excess entropy of the solution, in so far as entropy results only from configuration, should be negative or zero. This remark must be taken into account for the choice of the ideal reference state.

The entropy of mixing of the  $\text{RbF-Rb}_2\text{SO}_4$  system was obtained in the present work; that of  $\text{AF-A}_2\text{SO}_4$  systems ( $A = \text{Li, Na, K}$ ) was already determined [7,8] using the same method.

We plotted for these four systems the entropy of mixing against the mole fraction, together with the three expressions proposed for the ideal entropy (Fig. 4). It can be seen that only expression (4) gives excess terms which are all negative (Fig. 5) except for the  $\text{LiF-Li}_2\text{SO}_4$  system which will be discussed separately. Therefore, this expression seems the more adequate in describing the ideality of these solutions. Here again the  $\text{LiF-Li}_2\text{SO}_4$  system behaves differently from the other alkali systems: its excess entropy has only a small negative part and is positive on the concentration range  $0.25 < X_{\text{Li}_2\text{SO}_4} < 1$ .

As already discussed for the enthalpy of mixing, this anomaly may be

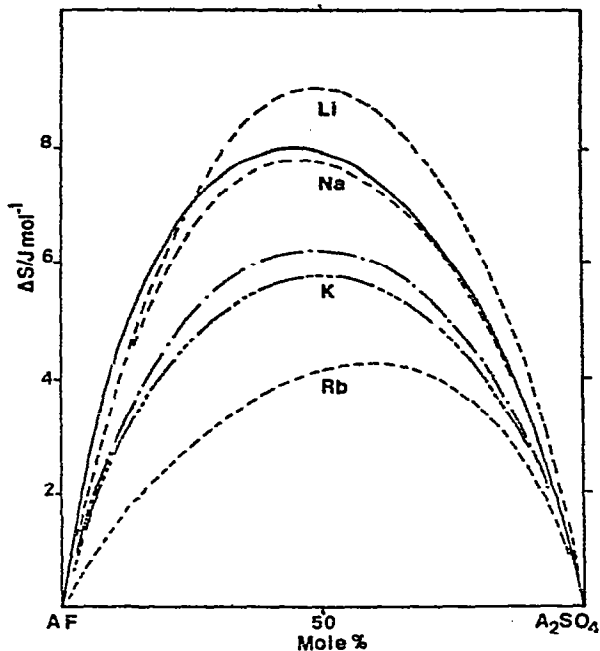


Fig. 4. Variation of the molar entropy of mixing against the mole fraction  $X_{SO_4}$  for AF- $A_2SO_4$  mixtures. — — —, Ideal (Temkin); ———, ideal (Førland); - · - · -, ideal (Flory).

attributed to the particular feature of the lithium ion; furthermore, as underlined by Kleppa [25],  $Li^+$  has a higher ionic potential ( $Z/r = 1.75 \text{ \AA}^{-1}$ ) than the other alkali ions ( $Z/r = 1.04, 0.75, 0.67 \text{ \AA}^{-1}$  for  $Na^+, K^+, Rb^+$ , respectively) which may influence the organisation of the structure of

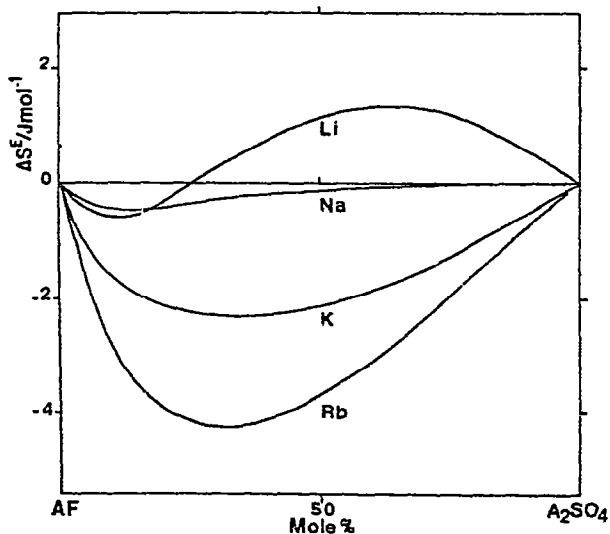


Fig. 5. Molar excess entropy calculated from Førland's ideality in AF- $A_2SO_4$  systems.

the mixture. The evolution of the excess entropy of the other alkali mixtures is regular in the sequence

$$\Delta S^E(\text{Na}) > \Delta S^E(\text{K}) > \Delta S^E(\text{Rb}) \text{ and } \Delta \bar{S}_{\text{AF}}^{\text{E},\infty} < \Delta \bar{S}_{\text{A}_2\text{SO}_4}^{\text{E},\infty}.$$

Therefore, since the charge asymmetry effect was accounted for in the choice of the ideal reference state, the same remarks already made for the enthalpy of mixing stand also for the excess entropy.

#### ACKNOWLEDGMENTS

The authors wish to thank Dr. A. Pelton and Dr. C. Bale (Ecole Polytechnique, Montreal, Canada) for their very valuable assistance. Financial aid from the Centre National de la Recherche Scientifique is gratefully acknowledged.

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