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THERMODYNAMICS OF MOLTEN SALTS WITH A COMMON ION

A. N. Kirgintsev and E. G. Avvakumov

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1. INTRODUCTION

According to Semenchenko's classification[1], ionic salt solutions belong to the group of homoeodynamic solutions. Hence, solutions of ionic salts can be expected to show the general properties of homoeodynamic solutions.

The theory of homoeodynamic solutions relies to a great extent on statistical methods. However, at least for the time being, any kind of statistical description can give no more than a relatively crude picture of real solutions. We believe, therefore, that simple and clearly defined physical models, whose conclusions can be put to simple experimental test, should prove very valuable in this field. The regular solution model is typical of such models.

According to the theory of regular solutions, the potential energy of formation of a solution, ΔE, is given by the expression

$$\Delta E = \omega N_{AB}, \tag{1}$$

where N_{AB} and ω are respectively, the number of bonds between atoms or molecules of different kinds in the case of atomic or molecular solutions and the average potential energy of one such bond (exchange energy). For solutions of ionic salts, these quantities refer to the number of bonds between ions of different kinds and the average potential energy of one bond. If the solution, composed of the salts $A_{n_1}C_{n_2}$ and $B_{n_3}C_{n_4}$, contains n_1N_1 ions of kind A and n_3N_2 ions of kind B, we have

$$N_{AB} = \frac{n_1N_1 \cdot n_2N_2}{n_1N_1 + n_2N_2}. \tag{2}$$

Since the chemical potential of the ith salt component is given by

$$\mu_i = \mu_{i0} + \frac{\partial \Delta E}{\partial N_i} - T\frac{\partial \Delta S}{\partial N_i}, \tag{2a}$$

it can also be expressed, using Eqns. (1) and (2), in the form

$$\mu_i = \mu_{i0} + \omega\beta_i(1 - x_i)^2 - T\frac{\partial \Delta S}{\partial N_i}, \tag{3}$$

where

$$\beta_1 = \frac{n_1}{\left(x_2 + \frac{n_1}{n_2}x_1\right)^2}, \quad \beta_2 = \frac{n_2}{\left(x_1 + \frac{n_2}{n_1}x_2\right)^2}, \quad x_i = \frac{N_i}{N_1 + N_2}; \tag{4}$$

and μ_{i0} denotes the chemical potential of the ith component in its standard state (taken to be the pure compound); ΔS is the entropy of mixing. In what follows, formulae relating to the first and to the second component of a solution or of a system will be written in that order.

The present article discusses the application of regular solution theory to solutions of ionic salts having a common ion, and considers the relation between the exchange energy ω and the properties of the individual constituents. Considerable use is made of published data as well as of values calculated by the writers.

2. DISTINGUISHABILITY OF THE COMMON ION

The earliest theories of ionic solutions[2,3,4], and some of the later ones[5,6], determine the potential energy of a solution in terms of the ionic radii and the composition. The entropy of mixing is usually assumed equal to the normal entropy of mixing of ideal solutions. This approximation can be too crude when ions of different valencies are involved, since the problem of the entropy of mixing is not considered in those papers.

From the thermodynamic point of view, the formation of an ideal solution presents three independent requirements:

1. The change in potential energy resulting from formation of the solution must be zero.

2. The volume change accompanying the formation of the solution must be zero.

3. The partial entropy of mixing of the ith component must equal $-k \ln x_i$ (where k is Boltzmann's constant).

These conditions are usually assumed when dealing with molecular and atomic solutions belonging to the homoeodynamic class of solutions. The first two can also be adopted for solutions of ionic salts, but the third requires clarification.

The difference between ionic salt solutions on the one hand and atomic and molecular homoeodynamic solutions on the other is that in the former solutions the number of species (i. e. kinds of particles) is not the same as the number of solution components. For example, in a two--component KCl–RbCl solution we have three kinds of particles: potassium, rubidium, and chloride ions. The appearance of an additional species may give rise to an additional term in the entropy of mixing. Therefore, the third condition for the formation of ideal solutions of ionic salts should be formulated in the most general way, i. e. by stating that the particles (ions) in solution which determine the entropy of mixing must be distributed entirely randomly, according to the laws of chance.

The problem of ideal solutions of ionic salts appears to have been first discussed in a paper by Temkin[7], who used an ionic model of pure salts and their mixtures. The ions in pure salts and in solutions of salts are assumed to be distributed so that each cation is effectively surrounded by anions and vice versa. The electrostatic forces between ions are quite large, and therefore interchange of cations and anions must be excluded when computing the entropy of mixing. According to Temkin, the entropy of mixing is given by

$$\Delta S = \Delta S_+ + \Delta S_- ;$$
$$\Delta S_+ = k \ln W_+ ; \quad \Delta S_- = k \ln W_- ; \tag{5}$$

where W_+ and W_- are the numbers of possible interchanges between cations only and between anions only.

Temkin applied Eqn. (5) only to solutions consisting of the salts AB and CD. For solutions of other salts, Temkin introduces the concept of activity coefficient by analogy with aqueous solutions. This is hardly justifiable, however[8]. It would be desirable, therefore, to apply Eqn. (5) to ionic salt solutions of any type. In fact, the entropy of mixing, determined by the interchange between distinguishable particles (i. e. those particles whose interchange produces a new microstate of the solution), is also the parameter which determines the formation of an ideal solution. This part of the entropy is given by Eqn. (5). We should also note that whereas Temkin's paper discusses liquid solutions (melts), the conclusions are equally applicable to solid solutions of ionic salts, since the state of aggregation is not taken into consideration.

Thus, the entropy of mixing of an ideal solution of ionic salts should be calculated from Eqn. (5). In accordance with this equation, the chemical potential of the ith salt component in an ideal solution is given by

$$\mu_i = \mu_{i0} - T\left(\frac{\partial \Delta S_+}{\partial N_i} + \frac{\partial \Delta S_-}{\partial N_i}\right). \tag{6}$$

We will discuss the application of Eqn. (6) to various binary solutions having a common ion. Although the formal discussion is confined to a common anion, all theoretical conclusions are equally applicable to solutions with a common cation. The general formulae of the salts which compose the solutions are $A_{n_1}C_{n_2}$ and $B_{n_3}C_{n_4}$: we shall refer to these as the first and the second component respectively. We shall use N_1 and N_2 for the number of "molecules" of $A_{n_1}C_{n_2}$ and $B_{n_3}C_{n_4}$ in the solution.

1. The cations A and B have the same valency. The chemical formulae of the salts forming the solution are $A_{n_1}C_{n_2}$ and $B_{n_1}C_{n_2}$. A solution composed of these salts has $n_1(N_1 + N_2)$ cation sites and $n_2(N_1 + N_2)$ anion sites. We shall assume that each cation can occupy only one cation site and each anion only one anion site. The anions corresponding to the cations A and B are indistinguishable, i. e. they form a "medium", within which cation interchange can take place. Then

$$W_- = 1, \ \Delta S_- = 0. \tag{7}$$

The cations in cation sites can be distributed in more than one way: two cases are possible.

(*a*) Cations of the two kinds are distributed randomly over the cation sites in such a way that "molecules" can be distinguished in the solution:

$$A_{n_1}C_{n_2}, \ A_{n_1-1}BC_{n_2}, \ A_{n_1-2}B_2C_{n_2}, \ \ldots, \ B_{n_1}C_{n_2}.$$

In this case the individual A and B ions can interchange places. Hence

$$W_+ = \frac{n_1N_1 + n_1N_2}{(n_1N_1)!\,(n_1N_2)!}. \tag{8}$$

Substituting Eqns. (7) and (8) into (5), and differentiating Eqn. (6), we find

$$\mu_1 = \mu_{10} + n_1 kT \ln x_1;$$
$$\mu_2 = \mu_{20} + n_1 kT \ln x_2. \tag{9}$$

(*b*) The different cations in solution are distributed in groups. Assume, for example, that the solution contains only "molecules" $A_{n_1}C_{n_2}$ and $B_{n_1}C_{n_2}$. In this case, A and B ions form a group of cation sites, and interchanges in cation sites are possible only in groups of n_1 A-cations and n_1 B-cations. If we assume that these groups are randomly distributed in the solution,

$$W_+ = \frac{(N_1 + N_2)!}{N_1!N_2!}. \tag{10}$$

Substitution of Eqns. (7) and (10) into (5), and differentiation of Eqn. (6), gives

$$\mu_1 = \mu_{10} + kT \ln x_1;$$
$$\mu_2 = \mu_{20} + kT \ln x_2. \tag{11}$$

Our general solution model cannot, of course, identify the solutions in which case *a* or case *b* is realised. We may conclude, however, on general grounds, that case *a* should obtain in solid solutions, since the formation of solid solutions requires that the cations A and B should have similar properties. In liquid solutions (melts), on the other hand, case *b* is also possible.

2. The cations A and B have different valencies. Here, the calculation of entropy of mixing for an ideal solution presents very real difficulties. With cations of the same valency we are able to treat the anions as a "medium" for the interchange of cations, but the situation has to be more accurately defined when cations of

different valency are envisaged. Consider, for example, the solution KCl–RbCl. According to our model, this solution consists of $N_1 + N_2$ cation sites and $N_1 + N_2$ anion sites. Let the cation and anion sites in the solution be distributed in a regular pattern, forming a lattice of cations and a lattice of anions. Interchange of cations within the cation lattice is possible, independently of any interchange of anions in the anion lattice. We can visualise a hypothetical spatial separation of the two lattices, which are then spatially reunited after carrying out cation and anion interchanges. Electrical neutrality of the final solution must, of course, be preserved. The criterion for indistinguishability of the anions is that cation interchanges shall be independent of anion interchanges.

Cation interchanges in solutions with cations of different valency cause either a change in the valency of one of the cations or the appearance of vacancies in the cation or the anion sublattice. These processes are needed to compensate the excess of charge arising from the exchange of cations of different valency in solution. Since excess charge compensation most frequently involves the formation of vacancies, we shall consider only this case. It must be clearly understood that these are not the familiar Schottky or Frenkel' vacancies, but simply vacancies resulting from the presence of cations of different valency in the solution. It may be thought that the appearance of vacancies must lead to an increase in the number of microstates, and that the entropy of mixing must be larger in the present of vacancies. It should be possible to calculate the increase in the entropy of mixing by taking into account the vacancy–ion interchanges. This procedure is followed in the papers by Flood, Förland, and others[9,10], but it meets serious difficulties because vacancies cannot be transferred to ionic sites without interchanging ions as well. Consequently, we are not in a position to calculate the number of interchanges by the normal procedure. An alternative approach seems more tractable[11]. Solutions of ionic salts can be subdivided into two classes:

1. Solutions in which cations of different kinds can be interchanged without interchanging anions.

2. Solutions in which cations of different kinds cannot be interchanged without interchanging anions.

Solutions of the first class include those in which the cations have the same valency, but solutions with cations of different valency may also belong to this class. Thus, if the formation of the solution can be described by the equation

$$A_{n_1}C_{n_2} + m\,B = A_rB_mC_{n_2} + (n_1 - r)\,A, \tag{12}$$

it is evident that interchange of unlike cations can occur without interchange of anions, and solutions of this type must therefore be assigned to the first class. However, cation migration can occur also by other mechanisms. We shall consider this in the concrete case of solutions with a univalent anion.

If, in the solutions formed by the salts AC_{n_2} and BC_{n_4}, each cation occupies only one cation site, the additional anions will be located in additional anion sites. Interchange of unlike cations is impossible without anion interchange. Therefore, the anions must be treated as distinguishable species in systems of this type (with the obvious exception of AC_{n_2}–BC_{n_2} solutions), and

$$W_+ = \frac{(N_1 + N_2)!}{N_1!\,N_2!};\quad W_- = \frac{(n_2N_1 + n_4N_2)!}{n_2N_1!\,n_4N_2!}. \tag{13}$$

Consequently

$$\mu_1 = \mu_{10} + kT\left(\ln x_1 + n_2 \ln \frac{n_2x_1}{n_2x_1 + n_4x_2}\right);$$
$$\mu_2 = \mu_{20} + kT\left(\ln x_2 + n_4 \ln \frac{n_4x_2}{n_2x_1 + n_4x_2}\right). \tag{14}$$

However, a solution with vacancies in the cation sublattice can be formed in the case of AC–BC_2, AC–BC_3, AC–BC_4, and AC_2–BC_4 solutions if $N_1 > N_2$, i.e. if the solution contains a higher proportion of the salt AC_{n_2} than of BC_{n_4} – we are confining the discussion to salts in which the valency of the cation does not exceed four. Formally, this means that the cation B must occupy two cation sites. For example, when B cations are added to AC, a B cation can take the place of an A cation. If the B cation is doubly charged, charge compensation requires that a neighbouring A cation site should be unoccupied. In such a solution, a B cation can be transferred to a pair of A cation sites without disturbing the anions. Hence, the anions can be treated as indistinguishable in this case, and for these solutions we have

$$W_+ = \frac{(N_1 + N_2)!}{N_1!N_2!};\quad W_- = 1. \tag{15}$$

Therefore,

$$\mu_1 = \mu_{10} + kT \ln x_1; \tag{16}$$
$$\mu_2 = \mu_{20} + kT \ln x_2.$$

Thus, depending on the mechanism of formation of the solution, the anions can be distinguishable or indistingushable in solutions of the types AC–BC_2, AC–BC_3, AC–BC_4. and AC_2–BC_4.

We will now turn to a more complicated example. Consider solutions of the salts A_4C_3 and B_4C, in which the anion is quadrivalent. Assume that $N_1 > N_2$. The addition of B cations to A_4C_3 can be described as

$$A_4C_3 + 3B = A_3B_3C_3 + A, \tag{17}$$

a situation to which "reaction" (12) applies. We can think of the resulting solution as consisting of "molecules" of A_4C_3 and $A_3B_3C_3$. The excess of B cations in the $A_3B_3C_3$ "molecule" is located at additional cation sites. In this case the anions are, of course, indistinguishable.

The same procedure can be applied to other cases. Unfortunately, as was stated above, it is not always possible to decide unambiguously whether the anions are or are not distinguishable, but the essential features of the proposed method of evaluating the effect of the anions on the entropy of mixing are clearly illustrated by the examples given. In general, when dealing with solutions composed of the salts $A_{n_1}C_{n_2}$ and $B_{n_3}Cn_{n_4}$, we can write

$$\mu_1 = \mu_{10} + kT_{n_1} \ln \frac{n_1x_1}{n_1x_1 + n_3x_2};\quad \mu_2 = \mu_{20} + kT_{n_2} \ln \frac{n_3x_2}{n_1x_1 + n_3x_2}, \tag{18}$$

for indistinguishable anions, and

$$\mu_1 = \mu_{10} + kT\left(n_1 \ln \frac{n_1x_1}{n_1x_1 + n_3x_2} + n_2 \ln \frac{n_2x_1}{n_2x_1 + n_4x_2}\right);$$
$$\mu_2 = \mu_{20} + kT\left(n_3 \ln \frac{n_3x_2}{n_1x_1 + n_3x_2} + n_4 \ln \frac{n_4x_2}{n_2x_1 + n_4x_2}\right), \tag{19}$$

for distinguishable anions. The reader can easily verify that Eqn. (9) is a special case of Eqn. (18).

These expressions for the chemical potential in ideal solutions can be extended to real solutions in the usual way: by adding the term $kT \ln\gamma_i$ to the right-hand side of the equations, where γ_i is the activity coefficient of the ith component. For dilute solutions (and, to a first approximation, for concentrated solutions as well), the parameter γ_i can be taken to be constant. This allows the equations to be used with real solutions. Furthermore, the variation of γ_i with solution composition can be calculated from regular solution theory.

This approach to the calculation of entropies of mixing for ideal solutions of ionic salts is based on Temkin's model. The extent to which it is justified by the behaviour of real systems will be demonstrated below. At this point we should mention that a model essentially different from Temkin's is proposed in the papers of Herasimenko[12] and Bradley[13]. In this model, the interchange of cations and anions is not excluded, i. e. anions and cations are treated as equivalent from the point of view of the entropy of mixing. The model fails to take account of the most important feature of ionic solutions (namely, that ionic solutions consist of ions, not of molecules!), and is therefore a cruder approximation to real solutions than is Temkin's model.

The form of the chemical potential in liquid solutions of ionic salts can be judged from the variation of melting point with composition when the system shows a simple eutectic. Thus, the equation of the liquidus curve can be written[14]

$$\alpha_{i0} \ln\frac{T_{i0}}{T} = \ln\frac{1}{a_i}, \qquad (20)$$

where a_i is the activity of the ith component in the liquid phase, and T_{i0} is the melting point of the pure ith component. The quantity α_{i0} is simply related to the entropy of fusion of the pure ith component, ΔS_f:

$$\alpha_{i0} = \Delta S_f / kT_{i0}, \qquad (21)$$

since to a first approximation liquid salt solutions have the properties of regular solutions. Then, using Eqn. (3), we find

$$\ln a_i = \omega\beta_i (1 - x_i)^2 - T\frac{\partial\Delta S}{\partial N_i}. \qquad (22)$$

On the other hand, the entropy of mixing of a regular solution is equal to the entropy of mixing of an ideal solution. Therefore

$$(\mu_i - \mu_{i0})_{\text{ideal}} = -T\frac{\partial\Delta S}{\partial N_i}, \qquad (23)$$

where $(\mu_i - \mu_{i0})_{\text{ideal}}$ is determined by Eqns. (18) or (19).

Consider the fusion of the first component in the presence of the second component, with $x_1 > x_2$. Eqns. (18) and (19) for the chemical potential can be written, approximately, in the form

$$\mu_1 - \mu_{10} = kTn_3 \ln x_1, \qquad (24)$$

for Eqn. (18), and

$$\mu_1 - \mu_{10} = kT(n_3 + n_4)\ln x_1, \qquad (25)$$

for Eqn. (19). Substituting these expressions into Eqns. (22) and (20), we arrive at the general expression

$$Y = \alpha - KX, \qquad (26)$$

where

$$Y = \frac{\ln x_1}{\ln\frac{T}{T_{10}}}; \quad X = \frac{x_2^2}{T\ln\frac{T}{T_{10}}}. \qquad (27)$$

For indistinguishable anions

$$\alpha = \alpha_{10}/n_3, \qquad (28)$$

whereas for distinguishable anions

$$\alpha = \alpha_{10}/(n_3 + n_4). \qquad (29)$$

The quantity K in Eqn. (26) is a constant, proportional to $\omega\beta_1$. For indistinguishable anions the proportionality coefficient is $1/kn_3$, whereas for distinguishable anions it is $1/k(n_3 + n_4)$. For more exact calculations, Eqn. (26) should be replaced by

$$Y - \alpha_{10} - \frac{\omega}{k}\beta_1 X, \qquad (30)$$

where the quantity X is determined by the second Eqn. (27), and Y by the equations given below:

$$Y = \frac{n_1 \ln\frac{n_1x_1}{n_1x_1 + n_2x_2}}{\ln\frac{T}{T_{10}}} \qquad (31)$$

for indistinguishable anions, and

$$Y = \frac{n_1 \ln\frac{n_1x_1}{n_1x_1 + n_2x_2} + n_2 \ln\frac{n_2x_1}{n_2x_1 + n_4x_2}}{\ln\frac{T}{T_{10}}} \qquad (32)$$

for distinguishable anions.

Note that Eqns. (30) and (26) coincide for the case of indistinguishable anions and $n_1 = n_3$.

Table 1 gives the results of our calculations, by Eqn. (26), on 108 binary systems. The first component is taken as the major constituent. Values of α_{10} were calculated mainly from calorimetric data[15-18]. For lithium sulphate we used the calorimetric measurements of Voskresenskaya and Banashek[19]. For KSCN the values of α_{10} are taken from our calculations. Due to the large scatter in the heat of fusion values for $MgCl_2$, we were unable to choose a definite value of ΔS_f for this salt, and were again compelled to determine α_{10} from our calculations. Experimental liquidus data were taken mainly from a handbook[20]: column 9 of Table 1 gives the page references to this compilation. Other literature sources used in the calculations[21-26] are stated in column 10.

With the exception of systems 10–14 (as numbered in Table 1), we find β_1 = const for all other systems. For systems 10–14, $\beta_1 = 2/(2 + x_2)^2 \simeq 0.5 \simeq$ const. Therefore, experimental data from liquidus diagrams should give a straight line when plotted with the variables of Eqn. (26) as coordinates, and the values of α and K should be obtainable from the parameters of the linear plots. In the vast majority of cases, the experimental data do give straight lines when plotted in the coordinates of Eqn. (26). Fig. 1 shows the agreement between Eqns. (26) and (30) and experimental results for a number of systems.

Table 1 also gives the values of the parameter ω, calculated from the formula

$$\omega = \frac{n_3}{\beta_1}kK. \qquad (33)$$

For system 9, $n_3 = 2$; for all other systems, $n_3 = 1$. For system 9, $\beta_1 = 2$; for systems 10–14, $\beta_1 = 0.5$; for all other systems, $\beta_1 = 1$.

It is evident from the data of Table 1 that the systems can be divided into five groups: column 7 lists the group number of each system.

In the first group, $\alpha_{10}/\alpha = 1.02$ on the average, showing that the value of α obtained from liquidus data agrees with

TABLE 1. Results of calculations by Eqn. (26) for various binary salts systems.

No.	Solvent	Solute	α_{10}	α	α_{10}/α	Group	ω, kcal	Page in Ref. 20	Ref.
1	2	3	4	5	6	7	8	9	10
1	LiF	NaF	2.90	2.95	0.98	1	—0.24		21
2	»	KF	2.90	2.50	1.16	1	—1.57		23
3	»	RbF	2.90	2.60	1.11	1	—3.10		22
4	»	CsF	2.90	3.05	0.95	1	—2.30		24
5	LiCl	KCl	2.70	2.60	1.04	1	—1.70	347	
6	»	RbCl	2.70	2.20	1.23	1	—2.00	468	
7	»	CsCl	2.70	2.10	1.28	1	—3.30	264	
8	LiBr	KBr	2.56	2.45	1.04	1	—1.70	332	
9	Li_2SO_4	K_2SO_4	0.80	0.35	2.28		6.53		25
10	»	$BaSO_4$	0.80	0.67	1.19	1	1.30		25
11	»	$PbSO_4$	0.80	0.67	1.19	1	1.36		25
12	»	$SrSO_4$	0.80	0.60	1.33	2	4.50		25
13	»	$CaSO_4$	0.80	0.60	1.33	2	7.00		25
14	»	$CdSO_4$	0.80	0.60	1.33	2	6.62		25
15	$LiNO_3$	KNO_3	5.78	4.10	1.41	2	—0.80	401	
16	»	$NaNO_3$	5.78	5.05	1.15	1	0.00	479	
17	NaF	LiF	3.12	4.38	0.72	4	—2.35		21
18	»	RbF	3.12	4.38	0.72	4	—1.95		22
19	»	CsF	3.12	4.38	0.72	4	—0.70		24
20	»	MgF_2	3.12	3.15	1.00	1	—10.30		26
21	»	CdF_2	3.12	3.11	1.01	1	—2.46	238	
22	»	CaF_2	3.12	3.11	1.01	1	—1.79		26
23	NaF	SrF_2	3.12	3.11	1.01	1	—0.37		26
24	»	BaF_2	3.12	3.11	1.01	1	0.00		26
25	NaCl	CsCl	3.25	3.25	1.00	1	—0.35	267	
26	»	RbCl	3.25	2.35	1.39	2	0.24	532	
27	»	TlCl	3.25	3.25	1.00	1	1.47	535	
28	»	$BaCl_2$	3.25	3.40	0.95	1	0.00	120	
29	»	$SrCl_2$	3.25	3.25	1.00	1	—0.46	533	
30	»	$CaCl_2$	3.25	3.25	1.00	1	—2.25	188	
31	»	$CdCl_2$	3.25	3.25	1.00	1	—6.36	228	
32	»	$MnCl_2$	3.25	2.35	1.39	2	—3.50	515	
33	»	$MgCl_2$	3.25	3.25	1.00	1	—8.74	498	
34	»	$ZnCl_2$	3.25	7.40	0.44	5	—29.30	535	
35	»	$NiCl_2$	3.25	7.40	0.44	5	—52.90	531	
36	»	$ZrCl_4$	3.25	0.16	21.25		0.75	538	
37	»	Na_2CO_3	3.25	2.35	1.39	2	1.68	735	
38	»	NaF	3.25	3.00	1.09	1	0.83	743	
39	»	Na_2SO_4	3.25	3.00	1.09	1	0.83	750	
40	»	$Na_4P_2O_7$	3.25	3.40	0.95	1	0.00	749	
41	»	CuCl	3.25	4.00	0.85	4	—2.08	292	
42	»	$SnCl_2$	3.25	4.00	0.85	4	—3.82	533	
43	»	$PbCl_2$	3.25	4.00	0.85	4	—2.08	531	
44	KF	LiF	3.00	3.80	0.79	4	—4.37		23
45	»	BaF_2	3.00	3.20	0.94	1	—1.61	129	
46	»	LaF_3	3.00	3.20	0.94	1	—16.65	274	
47	»	ThF_4	3.00	3.20	0.94	1	—26.36	388	
48	»	KCl	3.00	3.08	0.97	1	0.00	649	
49	»	KBr	3.00	2.85	1.05	1	0.41	633	
50	KF	KI	3.00	3.08	0.97	1	0.86	670	
51	»	KVO_3	3.00	3.08	0.97	1	—0.74	675	
52	KCl	AgCl	2.95	2.90	1.00	1	0.00	26	
53	»	LiCl	2.95	2.90	1.00	1	—0.88	347	
54	»	CuCl	2.95	2.10	1.39	2	—4.25	285	
55	»	$CdCl_2$	2.95	2.10	1.39	2	—14.58	224	
56	»	$MnCl_2$	2.95	2.90	1.00	1	—6.50	353	
57	»	$MgCl_2$	2.95	2.10	1.39	1	—14.58	349	
58	»	$ZnCl_2$	2.95	5.45	0.53	5	—33.40	371	
59	»	$K_2Cr_2O_7$	2.95	2.10	1.39	2	3.95	649	
60	»	K_2CrO_4	2.95	2.10	1.39	2	1.69	648	
61	»	$K_4P_2O_7$	2.95	2.90	1.00	1	4.67	658	
62	»	K_2SO_4	2.95	2.10	1.39	2	3.88	658	
63	KBr	LiBr	3.03	3.60	0.85	4	—2.90	332	
64	KNO_3	$LiNO_3$	2.32	2.10	1.10	1	—1.01	401	
65	»	$AgNO_3$	2.32	2.35	1.00	1	—4.74	51	
66	»	$Ba(NO_3)_2$	2.32	1.55	1.49	2	0.00	135	
67	»	$Pb(NO_3)_2$	2.32	2.35	1.00	1	—4.74	417	
68	»	$Sr(NO_3)_2$	2.32	1.55	1.49	2	0.74	419	
69	»	$Ca(NO_3)_2$	2.32	2.35	1.00	1	—4.23	197	
70	»	$K_2Cr_2O_7$	2.32	1.55	1.49	2	2.02	669	
71	KSCN	KCl	3.50	3.50	1.00	1	1.20	639	
72	»	KBr	3.50	»	1.00	1	1.20	631	
73	»	KI	3.50	»	1.00	1	1.20	640	
74	»	NaSCN	3.50	2.54	1.38	2	0.63	340	
75	RbF	LiF	2.88	3.05	0.95	1	—3.10		22
76	»	NaF	2.88	3.10	0.90	1	—2.10		22
77	RbCl	LiCl	2.85	2.10	1.35	2	—2.00	468	
78	RbCl	NaCl	2.85	2.12	1.35	2	1.30	532	
79	CsF	LiF	2.61	2.82	0.93	1	—3.20		24
80	»	NaF	2.61	2.75	0.95	1	2.09		24
81	CsCl	LiCl	2.63	2.70	1.00	1	—5.50	264	
82	»	RbCl	2.63	1.80	1.15	1	0.61	32	
83	AgCl	KCl	2.05	2.10	0.98	1	—1.66	26	
84	»	$PbCl_2$	2.05	2.10	0.98	1	4.17	31	
85	»	$InCl_3$	2.05	2.25	0.91	1	2.86	25	
86	»	$AgNO_3$	2.05	2.60	0.77	4	—0.32	585	
87	»	Ag_2SO_4	2.05	1.85	1.11	1	1.60	587	
88	AgBr	RbBr	1.60	1.80	0.90	1	—2.07	16	
89	$AgNO_3$	$LiNO_3$	2.85	2.50	1.14	1	1.40	53	
90	»	KNO_3	2.85	2.90	1.00	1	0.00	51	
91	»	$CsNO_3$	2.85	2.60	0.92	1	—0.90	50	
92	MgF_2	BaF_2	4.53	4.90	0.93	1	—0.46	130	
93	»	KF	4.53	4.90	0.93	1	—10.76	380	
94	»	RbF	4.53	2.40	1.89	3	—2.48	506	
95	$MgCl_2$	$CaCl_2$	7.40	7.40	1.00	1	—9.89	184	
96	»	$SrCl_2$	7.40	7.40	1.00	1	—11.15	504	
97	»	$BaCl_2$	7.40	7.40	1.00	1	—8.88	117	
98	»	NaCl	7.40	3.60	2.05	3	—1.50	498	
99	»	KCl	7.40	3.60	2.05	3	—3.50	349	
100	$MgCl_2$	RbCl	7.40	3.60	2.05	3	—4.69	502	
101	»	CsCl	7.40	3.60	2.05	3	—6.37	266	
102	BaF_2	MgF_2	1.42	1.50	0.95	1	0.78	130	
103	»	LiF	1.42	0.70	2.03	3	1.38	129	
104	»	NaF	1.42	0.70	2.03	3	2.67	128	
105	»	KF	1.42	0.70	2.03	3	4.00	132	
106	»	RbF	1.42	0.70	2.03	3	4.14	133	
107	»	$BaCl_2$	1.42	1.50	0.95	1	—2.12	595	
108	»	$Ba_3(PO_4)_2$	1.42	1.50	0.95	1	—7.66	600	

the value derived from calorimetric experiments. This is observed in the majority of systems (66 out of 108). For all these systems $n_3 = 1$. We may conclude from the observed agreement that in these systems the common ions are indistinguishable.

In the second group of systems $\alpha_{10}/\alpha = 1.39$ on the average: this is fairly close to unity, and there would be grounds for assigning these systems to the first group. However, the departure from unity can hardly be ascribed to experimental error, since it is found in an appreciable number of systems (19 out of 108). Evidently, we are dealing with a rather "subtle" anomaly in the entropy of mixing.

The third group, which includes the systems MgF_2–RbF; $MgCl_2$–NaCl, $MgCl_2$–KCl, $MgCl_2$–RbCl, $MgCl_2$–CsCl; BaF_2–LiF, BaF_2–NaF, BaF_2–KF, BaF_2–RbF (in all of which $n_3 = 1$), gives $\alpha_{10}/\alpha = 2$. We conclude that these systems form solutions in which the anions are distinguishable, since Eqn. (29) requires just this value of α_{10}/α for systems with distinguishable anions. The lower part of Fig. 1 shows the results of our calculations by Eqn. (26) for BaF_2 containing additions of LiF, NaF, KF, and RbF. The upper part of the diagram illustrates our calculations by Eqn. (30) for BaF_2 containing LiF, NaF, KF, and RbF, and our calculations by Eqn. (26) for BaF_2 containing MgF_2, $BaCl_2$, and $Ba_3(PO_4)_2$. It can be seen that the straight lines of all the solutes meet at a common point when corrected for the distinguishability of the anions.

In the fourth group we find $\alpha_{10}/\alpha = 0.76$ on the average. This group comprises nine systems. It can be shown that the formation of limited solid solutions can account for an α_{10}/α ratio below unity, but only small departures from unity can be expected.

In the fifth group of systems the ratio α_{10}/α is close to 0.5, a value which can be explained by the formation of dimers of the solute in the melt. This group includes only three systems.

The NaCl–$ZrCl_4$ system, for which the ratio α_{10}/α is anomalously high, is quite unique.

Calculations by Eqn. (26) give a value of 2.28 for the ratio α_{10}/α of the system Li_2SO_4–K_2SO_4. But $n_3 = 2$ for this system, and the theoretical value of α_{10}/α is 2 if the chemical potential is described by Eqn. (9). This agrees with the experimental value. We should point out that our calculations support Grjotheim and Urnes' view[27] that Temkin's ionic model is applicable to the Li_2SO_4–K_2SO_4 system. Grjotheim and Urnes' calculations have been questioned by Kordes[28], who put forward an explanation of the cryoscopic results in terms of complex formation, but, as we have seen, the criticism is unjustified.

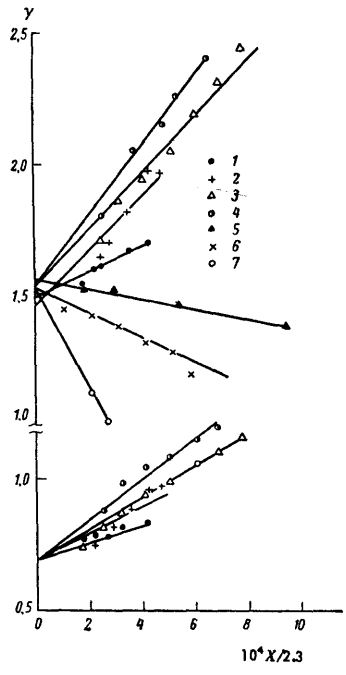


Fig. 1. Comparison of Eqns. (26) and (30) with experimental data for BaF_2 containing the following solutes:
1) LiF; 2) NaF; 3) KF; 4) RbF; 5) MgF_2; 6) $BaCl_2$; 7) $Ba_3(PO_4)_2$.

TABLE 2. Results of calculations by Eqn. (30) for a number of systems.

No.	Solvent	Solute	α_{10} from Table 1	α_{10} from Eqn. (30)	ω, kcal
1	BaF_2	LiF	1.42	1.50	2.30
2	»	NaF	1.42	1.50	5.52
3	»	KF	1.42	1.50	6.16
4	»	RbF	1.42	1.50	6.72
5	$MgCl_2$	NaCl	7.40	7.40	—3.36
6	»	KCl	7.40	7.40	—5.52
7	»	RbCl	7.40	7.40	—9.43
8	»	CsCl	7.40	7.40	—14.54
9	MgF_2	RbF	4.53	4.90	—6.67

Since the anion is distinguishable in systems 98–101 and 103–106, the value of ω should be calculated from the formula

$$\omega = \frac{n_3 + n_4}{\beta_1} kK, \qquad (34)$$

rather than from formula (33). However, this parameter was calculated even more precisely by using Eqn. (30). The results are set out in Table 2.

Returning to the data of Table 1, we see that the systems AC_2–BC exhibit anion distinguishability, as required by the theoretical considerations presented above. The MgF_2–KF system is exceptional in this respect, and does not have distinguishable anions. On the other hand, in the opposite type of system (AC–BC_2) anion distinguishability (and in some cases even cation distinguishability) is not observed. The possibility of loss of anion distinguishability in systems of this type has been discussed at the beginning of the present Section. Thus, the experimental information from liquidus diagrams which has been examined is in keeping, on the whole, with the theoretical considerations of anion distinguishability presented above. The proposition of anion distinguishability is supported also by data on crystallisation from aqueous solutions[29].

3. RELATION BETWEEN THE EXCHANGE ENERGY AND THE PROPERTIES OF THE CONSTITUENTS OF THE SOLUTION

The quantity ω reflects the change in interionic bond energy for the various components, and depends on the properties of the individual ions (charge, radius, structure of the electronic shell, etc.). The search for a relation between the value of ω and these properties is one of the major problems of the theory of ionic solutions.

Hildebrand and Salstrom[30] were the first to show that some binary mixtures of fused salts exhibit regular solution behaviour. These workers provided a theoretical basis for Eqn. (1) by a statistical procedure previously applied by Heitler[31] to non-electrolyte solutions. Among the systems examined by Hildebrand and his coworkers, those consisting of alkali metal bromides with silver bromide, and of lead halides with zinc halides, had the properties of regular solutions. The system were studied by an e. m. f. method, based on reactions between an electrode and the melt. Most of the experimental data now available for the activity of components in molten salts have been obtained by this method (see Table 3).

Data on heats of mixing are of the utmost importance in the thermodynamics of fused salts. Kleppa and coworkers[37,39,53] have undertaken a series of calorimetric measurements of the heats of mixing for the nitrates of metals in Groups I and II of the Periodic Table, and obtained some very interesting results, which show that these mixtures are regular solutions and have negative heats of mixing. Solid solutions of these salts have positive heats of mixing. The authors ascribe this difference to the fact that in solid solutions there is a loss of lattice energy due to the change in the distance between nearest neighbours, whereas in a melt the most important interactions are those between second nearest neighbours. They have shown[37] that the exchange energy for molten alkali metal nitrates is described by the empirical relation

$$\omega = -E\left(\frac{d_1 - d_2}{d_1 + d_2}\right)^2, \qquad (35)$$

where E is the crystal lattice energy of the mixture, and d_1 and d_2 are the distances between the centres of the ions in the pure first and second component respectively.

We have already discussed calculations based on Eqn. (20). An alternative approach is to use the familiar form of Schröder's equation:

$$\ln a_i = \alpha_{i0}\left(\frac{T_{i0}}{T} - 1\right). \qquad (36)$$

Aukrust *et al.*[23] determined the activity of the components in the systems LiF–KF, LiCl–KCl, and LiBr–KBr from liquidus data by using Eqn. (36) in conjunction with the heat capacities of the components in the liquid and in the solid phase, and showed that solutions of these salts depart relatively little from regular solution behaviour.

TABLE 3. Experimental values of ω for various systems.

No.	System	Temperature, °C	Method of measurement	ω, kcal	Ref.
1	AgCl—LiCl	500	e.m.f.	2.16	32,8,33
	ditto	600	ditto	2.14	32,8,33
2	AgCl—NaCl	900	»	0.75—1.10	34
3	AgCl—KCl	800	»	—1.00—1.20	35
4	AgBr—LiBr	500	»	1.92	30,33
	ditto	550	»	1.86	30
	»	600	»	1.82	30
5	AgBr—NaBr	550	»	0.96	30
	ditto	600	»	0.94	30
6	AgBr—KBr	500	»	—1.56	30
	ditto	550	»	—1.58	30
	»	600	»	—1.60	30
7	AgBr—RbBr	500	»	—2.54	30
	ditto	550	»	—2.58	30
	»	600	»	—2.62	30
8	$AgNO_3$—$LiNO_3$	209.6	cryoscopy	0.12	36
	ditto	350	calorimetry	0.65	37
9	$AgNO_3$—$NaNO_3$	320	e.m.f.	1.06	38
	ditto	350	calorimetry	0.59	37
10	$AgNO_3$—KNO_3	209.6	cryoscopy	—0.92	36
	ditto	350	calorimetry	—0.45	37
11	$AgNO_3$—$RbNO_3$	209.6	cryoscopy	—1.08	36
	ditto	350	calorimetry	—1.20	37
12	$AgNO_3$—$CsNO_3$	209.6	cryoscopy	1.38	36
13	$AgNO_3$—$TlNO_3$	209.6	»	1.79	36
14	LiF—KF	775	»	—1.20	23
15	LiCl—KCl	775	»	—0.9—1.0	23
16	LiBr—KBr	775	»	—0.8	23
17	$LiNO_3$—$NaNO_3$	345	calorimetry	—0.46	39
18	$LiNO_3$—KNO_3	345	»	—1.76	39
19	$LiNO_3$—$RbNO_3$	345	»	—2.47	39
20	$LiNO_3$—$CsNO_3$	450	»	—3.00	39
21	$NaNO_3$—KNO_3	345—450	»	—0.41	39
22	$NaNO_3$—$RbNO_3$	345	»	—0.74	39
23	$NaNO_3$—$CsNO_3$	450	»	—0.06	39
24	KNO_3—$RbNO_3$	345	»	—0.06	39
25	KNO_3—$CsNO_3$	450	»	—0.09	39
26	$RbNO_3$—$CsNO_3$	450	»	0.02	39
27	Li_2CO_3—$CaCO_3$	20—1100	measurement of CO_2 pressure	—2.40	40
28	Na_2CO_3—$CaCO_3$	20—1100		—5.50	40
29	K_2CO_3—$CaCO_3$	20—1100		—11.50	40
30	K_2CrO_4—$K_2Cr_2O_7$	650	not stated	+0.5	41
31	Na_2CrO_4—$Na_2Cr_2O_7$	450	ditto	+0.3	41
32	NaCl—KCl	25	calorimetry	+4.20	42
33	KCl—RbCl	50	»	+0.85	43
34	$PbCl_2$—$ZnCl_2$	500	e.m.f.	—2.40	8,44
	ditto	600	ditto	—2.80	8,44
35	$PbBr_2$—$ZnBr_2$	400	»	0.80	8,45
	ditto	450	»	0.50	8,45
	»	500	»	0.30	8,45
36	KCl—$PbCl_2$	550	»	—12.40	8,46
	ditto	600	»	—12.40	8,46
37	KCl—$MgCl_2$	650	»	—11.80	8,47,48
	ditto	750	»	—13.10	8,47,48
	»	850	»	—13.60	8,47,48
	»	950	»	—14.30	8,47,48
38	AgCl—AgBr	500	»	2.25	49
39	LiCl—LiBr	800	not stated	+0.15	41
40	KCl—KBr	50	calorimetry	0.93	43
	ditto	800	not stated	0.53	41
41	NaCl—NaBr	50	calorimetry	1.32	43
	ditto	800	not stated	0.35	41
42	CsCl—CsBr	25	calorimetry	1.05	50
43	TlCl—TlBr	25	»	0.64	51
44	$MgCl_2$—$MgBr_2$	800	not stated	—0.32	41
45	$PbCl_2$—$PbBr_2$	450	e.m.f.	0.87	8,52
	ditto	500	ditto	0.83	8,52
	»	550	»	0.77	8,52

Margulescu and Sternberg[54,55], using the equations

$$kT_1 \ln \gamma_1 = \omega x_2^2; \quad kT_2 \ln \gamma_1 = \omega x_2^2, \tag{37}$$

written explicitly for the two temperatures T_1 and T_2, arrived at the expression

$$\ln a_1(T_2) = \frac{T_1}{T_2} \ln a_1(T_1) + \frac{T_2 - T_1}{T_2} \ln x_1. \tag{38}$$

They used this equation to compare activity values obtained from liquidus diagrams with the values obtained at higher temperatures by the e.m.f. method. The results were satisfactory.

Sinistry proposed[36,38,56] the use of the equation

$$\frac{\Delta T}{1 - x_l} = fK_0 + b(1 - x_l). \tag{39}$$

for determining the value of ω, where ΔT is the depression of the freezing point caused by addition of the solute, K_0 is the cryoscopic constant, f is the number of particles into which the solute dissociates, and b is a constant. Eqn. (39) was derived by Haaze[57]; unlike the van't Hoff equation[58]

$$\frac{\Delta T}{1 - x_l} = fK_0, \tag{40}$$

it can be applied to moderately concentrated solutions. According to Sinistry[38],

$$\omega = -\frac{b}{fK_0}. \tag{41}$$

The values of ω obtained by Sinistry from cryoscopic data and Eqn. (41) are sometimes in serious disagreement with Kleppa's calorimetric results. It should be noted that Eqn. (39) can be derived from Eqn. (20) for the case of dilute solutions with unlike ions of the same valency.

Flood *et al.*[40] measured the activity of $CaCO_3$ in $CaCO_3$–M_2CO_3 mixtures (where M is an alkali metal) by measuring the amount of carbon dioxide evolved in the decomposition of the mixture. These mixtures were found to behave like regular solutions.

Published experimental values of ω for various molten salts with a common ion are listed in Table 3. Data relating to the solid solutions NaCl–NaBr, KCl–KBr, CsCl–CsBr, and TlCl–TlBr are also tabulated. A comparison of the data of Tables 1 and 3 clearly shows that one of the two values of ω obtained from Eqn. (26) agrees satisfactorily with the corresponding value in Table 3 (systems LiF–KF, LiCl–KCl, KCl–AgCl, AgBr–LiBr, and KCl–$MgCl_2$). It is interesting to note, in this connection, that the value of ω determined in the crystallisation region of the first salt does not agree numerically with the ω value determined in the crystallisation region of the second salt for the same system (see Table 1). Yet, these two values should be identical if a regular solution treatment is strictly applicable. The discrepancy may be due to a difference in properties between the crystallisation regions of the first and the second salt. In particular, this behaviour has been reported[65] for the composition–property curves close to the eutectic temperature.

As already pointed out, the value of ω depends on the individual properties of the ions. Using available data we have tried to identify the functional relation between ω and the radii of the cations and anions present in the solution. The value of ω is plotted against the radius of the common ion in Fig. 2 for six families of salts with a common ion. It is obvious that the straight-line plots for salts with a common cation and those for salts with a common anion respectively converge to a point: this means that the salt solutions achieve ideality when the anion (for the case of salts with a common anion) or the cation (for the case of salts with a common cation) reaches a certain size. It is also found that the slope of the straight lines of Fig. 2 is proportional to the difference between the radii of the non-common ions present in the solution. The general equation for families of salts with a common ion is

$$\omega = 31 \left(\frac{r_1 - r_2}{r_1 + r_2}\right)\left(1 - \frac{r}{r_0}\right), \tag{42}$$

where r_1 and r_2 are the radii of the non-common ions of the first and second component, r is the radius of the common ion, and $r_0 = r$ for $\omega = 0$. The value of r_0 is 3.06 for the particular family of salts with a common anion examined

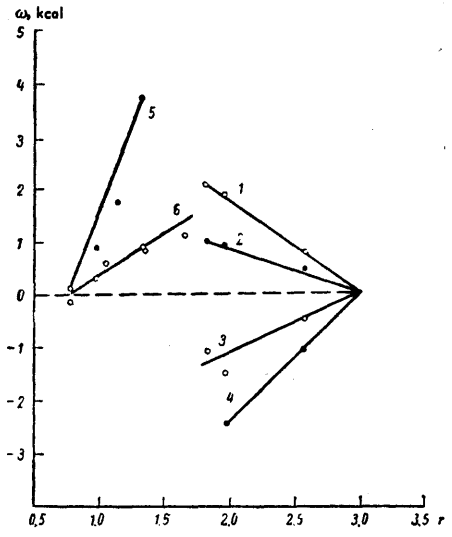


Fig. 2. Variation of the exchange energy in binary systems with radius of the common ion:
1) AgX–LiX; 2) AgX–NaX; 3) AgX–KX; 4) AgX–RbX (where X = Cl, Br, NO_3); 5) MCl–M_2SO_4; 6) MCl–MBr (where M = Li, Mg, Na, Tl, Ag, Pb, K, Cs).

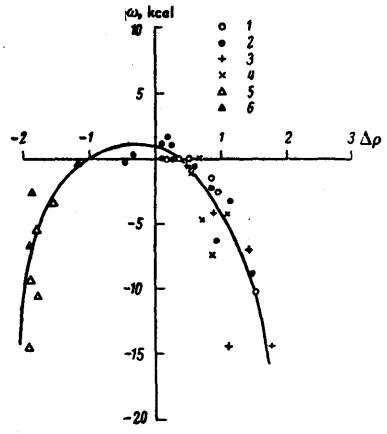


Fig. 3. Variation of exchange energy with difference in generalised moments:
1) NaF (with additions of Ba, Sr, Ca, Cd, Mg fluorides);
2) NaCl (with additions of Cs, Rb, Ba, Sr, Ca, Mn, Mg chlorides);
3) KCl (with additions of Ag, Li, Cu, Mn, Mg chlorides);
4) KNO_3 (with additions of Ba, Sr, Ca nitrates);
5) $MgCl_2$ (with additions of Cs, Rb, K, Na chlorides);
6) MgF_2 (with additions of Rb, Ba, Ca fluorides).

in Fig. 2, and 0.78 for the family of salts with a common cation.

The value of ω in Eqn. (42) is expressed in kcal. Ionic radii, here and elsewhere in the present paper, are the Goldschmidt values for the crystalline state[69], expressed in Ångström units.

Table 4 gives the numerical values of the crystal lattice energy for the salts to which Eqn. (42) applies. E_1 and E_2 are the crystal lattice energies of the first and second salt component, taken from a handbook[69]. The quantity ΔE is the difference $E_1 - E_2$. The mean value of ΔE for all the salts listed in Table 4 is 23.1, i.e. of the same order of magnitude as the constant coefficient in Eqn. (42).

Semenchenko[59] proposed the use of generalised moments for characterising the properties of particles such as ions, atoms, and molecules. The physical significance of the generalised moment is quite simple: it corresponds to the force due to the charge on the particle. For ions, the generalised moment gives the potential at the surface of the ion, considered as a sphere of radius r.

Using the concept of generalised moments, Semenchenko developed a general approach[68] to solubility phenomena. According to his theory, the mutual solubility of substances is higher, the smaller the absolute difference between their generalised moments. Thus, plots of $\Delta\rho$ against solubility (where $\Delta\rho$ is the difference in generalised moments between solvent and solute) give a curve with a maximum at $\Delta\rho = 0$.

Our results for the variation of ω with $\Delta\rho$ give a curve similar to that of Semenchenko (Fig. 3). In these calculations, the salt present in solution at the lower concentration is treated as the solute. The generalised moment is found by dividing the charge on the ion by the ionic radius.

The relation between ω and the difference in generalised moments shown in Fig. 3 refers to salts with a common anion. An analogous relation for salts with a common cation does not appear to exist, at least judging from the data of Table 1. This is not surprising, since generalised moments are not a very accurate way of characterising the energetics of anions.

TABLE 4. Crystal lattice energies of various salts.

System	E_1, kcal	E_2, kcal	ΔE, kcal	System	E_1, kcal	E_2, kcal	ΔE, kcal
LiCl—LiBr	195.6	185.2	10.4	AgBr—LiBr	210.0	185.20	24.8
NaCl—NaBr	181.9	172.5	9.4	AgCl—NaCl	213.7	182.0	31.7
KCl—KBr	166.6	159.0	7.6	AgBr—NaBr	210.0	173.0	37.0
$MgCl_2$—$MgBr_2$	592	568.5	11.6	AgCl—KCl	213.7	167	46.7
$PbCl_2$—$PbBr_2$	524.7	511	6.8	AgBr—KBr	210.0	160	50.0
AgCl—LiCl	213.7	196.0	17.8				

4. CALCULATION OF EXCHANGE ENERGIES

In theory, the exchange energy can be calculated if a procedure for calculating the crystal lattice energy of the solution is available. The energy of a crystal lattice is calculated most simply by means of Born's formula[60]

$$E = \frac{ANe^2z_1z_2}{d}\left(1 - \frac{1}{u}\right), \qquad (43)$$

where A is Madelung's constant, N is Avogadro's number, e is the electronic charge, z_1 and z_2 are the numbers of electronic charges on the cation and the anion, and u is a quantity which characterises the repulsive forces.

X-Ray diffraction experiments have shown that the average distance between oppositely charged ions in a

solution varies in the simplest case (Vegard's law) according to the expression

$$d = d_1x_1 + d_2x_2. \quad (44)$$

Various attempts have been made[2,3,4] to substitute an expression of this type into the Born formula. The result is that the energy of formation of the solution, which should be identified with the potential energy of formation of the solution, is always positive: this is, of course, contrary to experience. In subsequent papers the energy of the solution is calculated more exactly.

Lumsden[5] treats the excess energy ΔE of a solution as the sum of two terms:

$$\Delta E = \Delta E_1 + \Delta E_p, \quad (45)$$

where ΔE_1 is the interaction energy of ions of a given kind in the immediate neighbourhood of an arbitrarily chosen ion, and ΔE_p the polarisation energy of the anions.

The quantity ΔE_1 is calculated by the London formula

$$E_1 = -\frac{P}{d^6}, \quad (46)$$

where P is a constant. In an ionic solution of the type AC–BC (the theory is concerned only with solutions of alkali metal halides) each cation is effectively surrounded only by anions, and each anion only by cations. Hence, in the immediate surroundings of any cation the energy of the C–C bond has to be considered, and in the immediate surroundings of any anion the energy of the A–A, B–B, and A–B bonds is relevant. The bond energy of cations is small in comparison with the bond energy of anions, and it is legitimate to consider only the energy of the C–C bonds. The C–C distance in the pure salts AC and BC is $2^{0.5}d_{AC}$ and $2^{0.5}d_{BC}$ respectively, where d_{AC} and d_{BC} are the distances A–C and B–C. In the solution, this distance has the value $(d_{AC}^2 + d_{BC}^2)^{0.5}$. Hence the energy of the solution due to London forces is

$$E_1 = -\left[\frac{P_{AA}}{(2d_{AC}^2)^3}N_{AA} + \frac{P_{BB}}{(2d_{BC}^2)^3}N_{BB} + \frac{P_{AB}}{(d_{AC}^2 + d_{BC}^2)^3}N_{AB}\right], \quad (47)$$

where P_{AA}, P_{BB}, and P_{AB} are the constants of Eqn. (46) for the appropriate bonds; N_{AA}, N_{BB}, and N_{AB} are the numbers of A–A, B–B, and A–B bonds in the solution. For a regular solution

$$N_{AA} = \frac{Z}{2}x_1^2(N_1 + N_2); \quad N_{BB} = \frac{Z}{2}x_2^2(N_1 + N_2);$$
$$N_{AB} = Zx_1x_2(N_1 + N_2), \quad (48)$$

where Z is the coordination number. Substituting (48) into (47), and after some rearrangement, we obtain

$$\Delta E_1 = \omega_1 x_1 x_2 (N_1 + N_2), \quad (49)$$

where

$$\omega_1 = \frac{Z}{2}\left[\frac{P_{AA}}{(2d_{AC}^2)^3} + \frac{P_{BB}}{(2d_{BC}^2)^3} + \frac{2P_{AB}}{(d_{AC}^2 + d_{BC}^2)^3}\right]. \quad (50)$$

If the anion is surrounded by cations of different size it becomes polarised. The force F_0 of the field acting on an anion surrounded by oppositely distributed A and B cations is

$$F_0 = e\left(\frac{1}{d_{AC}^2} - \frac{1}{d_{BC}^2}\right). \quad (51)$$

The energy due to polarisation of the anions in solution is

$$\Delta E_p = \frac{mF_0^2}{2}N_{AB}, \quad (52)$$

where m is the polarisability of the anion. Substituting (51) into (52), and using (48), we obtain

$$\Delta E_p = \omega_p x_1 x_2 (N_1 + N_2), \quad (53)$$

where

$$\omega_p = \frac{Z}{2}me^2\left(\frac{1}{d_{AC}^2} - \frac{1}{d_{BC}^2}\right)^2. \quad (54)$$

Lumsden[5] allowed also for the polarisation of the anion due to the second layer of cations, when Eqn. (54) becomes

$$\omega_p = \left(\frac{4}{5}\right)^2\frac{Z}{2}me^2\left(\frac{1}{d_{AC}^2} - \frac{1}{d_{BC}^2}\right). \quad (55)$$

However, the occupancy of the second layer of cations is rather indeterminate: this causes inaccuracies in the computed second-layer polarisation, which is therefore best ignored.

Adding (49) and (53) we obtain

$$\Delta E = (\omega_1 + \omega_p)x_1x_2(N_1 + N_2). \quad (56)$$

This equation can be used to calculate the properties of real solutions. The constants P_{AA} and P_{BB} for alkali halides have been calculated by Mayer[61]. For the constant P_{AB}, Lumsden assumes

$$P_{AB}^2 = P_{AA} \times P_{BB}. \quad (57)$$

Values of m for the anions F^-, Cl^-, Br^-, and I^- have been determined by Kordes[62]: they are 0.462, 1.63, 2.29, and 3.56 cm³ respectively. The parameters d_{AC} and d_{BC} are equal to the anion–cation distances in the crystal. Values of ω obtained by Lumsden for a number of systems are reproduced in Table 5. A comparison between experimental liquidus curves and similar curves calculated from theoretical values of ω is given in Lumsden's paper[5]. On the whole, the calculated values agree with experiment. It should be noted, however, that whereas one branch of the liquidus curve coincides with the experimental data, the other branch usually shows some departure. This is further confirmation that the ω values for different components in a given binary system with simple eutectic are different.

The excess free energy can also be calculated with the help of the theory proposed by Vasastjerna[6] for solid

TABLE 5. Comparison of ω values obtained according to Lumsden and to Vasastjerna with the values derived from the liquidus diagram data by Eqns. (26) and (30).

No.	System	ω_1, kcal (after Lumsden)	ω_1, kcal (after Vasastjerna)	From Eqns. (26) and (30)		
				ω_1, kcal	ω_2, kcal	$\bar{\omega}$, kcal
1	LiF–NaF	–1.60	+0.96	–0.24	–2.35	–1.30
2	LiF–KF	–4.20	+3.10	–1.57	–4.37	–2.97
3	LiF–RBF	–4.50	—	–3.10	–4.00	–3.55
4	LiF–CsF	–4.70	—	–2.30	–3.20	–2.75
5	NaF–KF	–0.40	+0.85	—	—	—
6	NaF–RbF	–0.10	—	–2.00	–2.10	–2.05
7	NaF–CsF	+0.90	—	–0.70	+2.09	+0.70
8	LiCl–NaCl	–1.10	+0.99	—	—	—
9	LiCl–KCl	–4.00	+2.20	–1.70	–0.88	–1.30
10	LiCl–RbCl	–4.60	—	–2.00	–2.00	–2.00
11	LiCl–CsCl	–5.90	+4.60	–3.30	–5.50	–4.40
12	NaCl–KCl	–0.80	+0.25	—	—	—
13	NaCl–RbCl	–1.10	+0.83	+0.24	+1.30	+0.77
14	NaCl–CsCl	–1.70	+1.40	–0.35	–1.06	–0.70
15	KCl–CsCl	–0.10	—	—	—	—
16	LiBr–KBr	–3.40	—	–1.70	–2.90	–2.30
17	LiBr–CsBr	–5.90	+2.70	—	—	—
18	LiI–NaI	–0.90	+0.89	—	—	—
19	LiI–CsI	–5.90	+2.84	—	—	—
20	NaI–CsI	–2.10	+1.22	—	—	—
21	$LiNO_3$–KNO_3	–1.90	—	–0.80	–1.01	–0.90

solutions of ionic salts. According to this theory, the excess energy of mixing and the entropy of mixing are given by the expressions

$$\Delta E = \frac{Ae^2}{d}\left(\frac{\Delta d}{d}\right) x_1 \quad x_2 (N_1 + N_2)\left\{\frac{\theta_1}{8}[1 + \sigma(1 - 4x_2)] + \right.$$
$$\left. + \frac{\theta_2}{8}[1 + \sigma(1 - 4x_1)] + \frac{1}{2}(1 + \sigma)\right\}; \quad (58)$$

$$\Delta S = -k(N_1 \ln x_1 + N_2 \ln x_2) - k(\varkappa \ln \varkappa + \lambda \ln \lambda + \mu \ln \mu + \nu \ln \nu). \quad (59)$$

In these expressions

$$\theta_i = \frac{3 + 4Tv}{\frac{eAe^2}{6d_i^4 - Tv}}; \quad \varkappa = \frac{x_1}{x_1 - x_2\sigma};$$
$$\lambda = x_1 x_2 (1 + \sigma); \quad \mu = \frac{x_1 x_2}{x_2 - x_1\sigma}; \quad \nu = \frac{x_2}{x_2 - x_1\sigma}, \quad (60)$$

where the degree of short-range order, σ, is defined by

$$\sigma = \frac{1 - 2x_1 \quad x_2 l - \sqrt{1 - 4x_1 x_2 l}}{2x_1 \quad x_2 l};$$
$$l = 1 - \exp\left\{\frac{Ae^2}{d}\left(\frac{\Delta d}{d}\right)^2 \frac{\theta_1(1 - 4x_2) + \theta_2(1 - 4x_1) + 4}{8kT}\right\}, \quad (61)$$

$\Delta d = d_1 - d_2$, v is the coefficient of thermal expansion, and ϵ the compressibility coefficient. The quantity d in Eqn. (58) denotes the distance between cation and anion, which can be calculated by Vegard's law. The quantity d_i refers to the distance between cation and anion in the corresponding pure salt.

In Hovi's papers[51,52,63] the theory of Vasastjerna is used to calculate the free energy of solid solutions, thus making it possible to predict critical separation temperatures. Unfortunately, these calculated results lack direct experimental confirmation. Heats of mixing calculated by Eqn. (58) for solid solutions are in tolerably good agreement with experiment[42,51,52,63].

Vasastjerna's theory can also be applied to molten salts. Margulescu and Sternberg[64] have applied it to the systems AgBr–LiBr, AgBr–NaBr, AgCl–NaCl, and AgBr–AgCl. The excess energies of mixing derived from experimental data are in general agreement with the calculated values.

The present writers have evaluated Eqn. (58) for a number of systems, using d values taken from Levy *et al.*[66] and ϵ and v values taken from Bockris and Richard[67]. The calculations were made for the composition $x_1 = x_2 = 0.5$. The value of ω was found from the relation

$$\omega = \frac{1}{x_1 \quad x_2} \quad \Delta E = 4\Delta E.$$

It should be noted that ω is required by Eqn. (57), to be a function of solution composition, but in a rough comparison with experiment it may be taken as constant.

The results of this calculation are entered in Table 5. For comparison, the table gives also the values of ω_1, which relate to crystallisation of the first component, and of ω_2, which relate to the region of crystallisation of the second component. These values are taken from Table 1, i.e. they were calculated by Eqns. (26) and (33). The arithmetic mean of ω_1 and ω_2 is tabulated as $\bar{\omega}$. Inspection of Table 5 shows that Lumsden's theory agrees, on the whole, with values taken from liquidus diagrams. In some cases, however, there is serious discrepancy. Thus, in the NaF–CsF system, $\omega_1 < 0$ and $\omega_2 > 0$, whereas Lumsden gives $\omega > 0$. For the NaCl–RbCl system ω_1 and ω_2 are positive, but according to Lumdsen $\omega < 0$. In the other systems the value of ω calculated by Lumsden's method is close to $\bar{\omega}$. On the other hand, the theory of Vasastjerna does not lead to satisfactory results.

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The results presented in this review provide evidence that the theory of regular solutions is applicable to molten salts. A collection of exchange energy data more comprehensive than any hitherto available[41,54] is also presented. The data of Table 3 show that the absolute value of ω decreases or increases with increasing temperature according to whether ω is positive or negative, respectively. These changes are small, however, and the assumption made when using Eqns. (26) and (30) that ω is independent of temperature is, on the whole, justified. Hence, these equations can be used to interpret experimental data from liquidus diagrams. Furthermore, analysis of the liquidus curves in systems with a simple eutectic can provide information on the entropy of mixing of ionic salt solutions.

We have stated that Lumsden's theory is in agreement with experiment. However, its conclusions are still only applicable to solutions of uni-univalent salts. The variation of the exchange energy with difference of generalised moments can be used to give an approximate estimate of this quantity in solutions of salts with different cations and a common anion.

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Institute of Inorganic Chemistry,
Siberian Section of the Academy
of Sciences of the USSR