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EVALUATION OF THE HEATS OF MIXING OF SALT SOLUTIONS FROM IONIC CHARACTERISTICS

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INTRODUCTION

The study of the laws connecting the properties of solutions and their constituent atoms is the central problem of the theory of solutions [1].

Low-temperature solutions, especially solutions of electrolytes in water and other solvents have been the subject of many papers and reviews relating to the solution of this problem. Very little light has been thrown on this question for salt melts, which have no less scientific and practical importance [2]. In what follows we will consider these systems also. Here we will restrict ourselves only to an analysis of the methods of calculating the heat ΔH or energy Q of mixing of binary solutions, assuming [2] that they are connected by the relation [3]:

$$\Delta H = Q \cdot x_1 \cdot x_2 \qquad (1)$$

where x_1 and x_2 are the mole fractions of the components.

1. COULOMBIC INTERACTION

We will deal only with solutions of salts with a common ion. Grim and Herzfeld [4] and then Tobolsky [5] used Born's method to calculate the ionic lattice energy, in order to find the heats of mixing of solid solutions of the alkali metal halides. It was assumed in this that the lattice parameters in mixed crystals (a) are the sum of those for the pure salts (a_1 and a_2), that is, Vegard's empirical rule is obeyed:

$$a = a_1 + (a_2 - a_1) \cdot x \qquad (2)$$

Then the use of Born's simple formula leads to the following expression for the heat of dissolution:

$$\Delta H \simeq -\frac{U}{2} \cdot \left(\frac{d_1 - d_2}{d_1 + d_2}\right)^2 \cdot x_1 \cdot x_2 = K_e \cdot x_1 \cdot x_2 \qquad (3)$$

where U is the lattice energy of one of the salts (or the mean for the two salts), d_1 and d_2 are the sum of the ionic radii of the first and second salts, and K_e is the energy of mixing.

The minus sign is evidence that the process is endothermic, which agrees qualitatively with the results of Delimarskii and Markov [6], according to which binary solutions of most solid salts show positive departures from Raoult's law.

As regards quantitative agreement, Table 1 shows that the energy of mixing $K_e = 4\Delta H$ calculated by Eqn. (3) is considerably less than that found experimentally (Q_{expt}).

Equation (3) is not applicable to melts, since Vegard's rule does not hold for them. A more suitable assumption here is that of Förland [7], who assumed that ions are rigid spheres and the distances between neighbours of opposite charge are unchanged on mixing the molten salts. He considers that the heat of mixing originates in the circumstance that the energy of the coulombic repulsion between the nearest cations (when the anion is common) in the solution ($X^+-Z^--Y^+$) differs from half the sum of those for the pure salts ($X^+-Z^--X^+$) and ($Y^+-Z^--Y^+$). Neglecting the

TABLE 1. Energy of mixing for solid solutions of certain salts.

System	Constituent energies of interaction		Energy of mixing		Reference
	K_e (Tobol'skii)	K_L (Lumsden)	$Q=K_e+K_L$	Q_{exp}	
KCl—RbCl	0.4	0.4	0.8	0.81	8,9
KCl—KBr	0.4	0.60	1.00	0.92	8,9
NaCl—NaBr	0.60	0.72	1.32	1.36	9,10
KBr—KI	1.00	0.40	1.40	1.56	8
NaBr—KBr	2.20	0.80	3.00	2.80	11
NaI—KI	2.00	0.60	2.60	2.50	11
NaCl—KCl	2.80	1.20	4.0	4.20	11,12
AgCl—LiCl	4.80	4.0	8.80	8.80	13
AgBr—LiBr	4.4	3.0	7.40	7.52	14
AgBr—NaBr	1.2	2.0	3.20	4.20	14
$MgCl_2$—LiCl	0	0	0	0	15
$PbBr_2$—$ZnBr_2$*	4.8	0	4.0	3.6	16
$PbBr_2$—$PbCl_2$*	0.4	0.4	0.8	—1.2	17
KBr—RbBr*	0.4	0.4	0.8	0.60	18
RbCl—RbBr*	0.4	0.4	0.8	0.8	18
KCl—KBr*	0.4	0.60	1.00	0.8	18
KCl—RbCl*	0.4	0.4	0.8	0.60	18

influence of subsequent layers, he obtained for an equimolecular melt:

$$\Delta H \simeq \frac{U}{4}\left(\frac{d_1-d_2}{d_1+d_2}\right)^2 \cdot x_1 \cdot x_2 = \frac{U}{4} \cdot \delta^2 \cdot x_1 \cdot x_2 = K_e'' \cdot x_1 \cdot x_2 . \quad (4)$$

Comparison of expressions (3) and (4) which in general are similar in form, shows that the heats of mixing in them differ in sign and also that ΔH for solid solutions is twice that for liquid solutions. Experiment shows that in accordance with Eqn. (4) heat is liberated ($Q_{expt} < 0$) in several instances, namely in the mixing of molten alkali metal halides (see Tables 2 and 3). However, the calculated energies of mixing ($K_e'' = 4\Delta H$) sometimes differ considerably from the experimental values. For molten salts with a common cation the comparison with published data [19,20] shows a still greater discrepancy in the values of Q.

True, in measuring the heats of mixing of molten alkali metal nitrates, Kleppa and Herch [26] found (see Table 4) that they are satisfactorily described by Förland's approximation:

$$\Delta H \simeq x_1 \cdot (1-x_1) \cdot U \cdot \left(\frac{d_1-d_2}{d_1+d_2}\right)^2 = x_1 \cdot x_2 \cdot U \cdot \delta^2 . \quad (5)$$

This cannot be said about solutions of silver or thallium nitrates with alkali metals nitrates, for which they [27] propose a somewhat different semi-empirical expression:

$$\Delta H = -x_1 \cdot x_2 (140 \cdot \delta^2 - U'' \cdot \delta). \quad (6)$$

In this, the first term inside the parentheses allows for the electrostatic interaction (coulombic repulsion) and the second, the presence of a covalent constituent in the lattice energy of $AgNO_3$ and $TlNO_3$.

As Table 5 shows, by a suitable choice of the parameter U'' (different for $AgNO_3$ and $TlNO_3$) satisfactory agreement was reached between the values calculated by formula (6) and the experimental data.

Blander [29] made an attempt to improve Förland's equation, by allowing for the coulombic forces being far-acting. However, he was restricted to the solution of only the linear problem for a dilute binary solution of salts with a common anion.

By considering a linear series of n cations of the solvent (at a distance r from one another), in which cations of

TABLE 2. Energies of mixing for molten alkali metal halides.

System	Contribution of individual effects to the energy of the solution				Calculated energy of mixing, $Q=(K_P+K_L)$	Q_{exp} (Ref. 35)	Reference
	$-K_P$ (Lumsden)	K_L (Lumsden)	$-K_e'$ (Blander)	$-K_e''$ (Förland)			
LiF—NaF	1.8	0.2	0.6	1.0	—1.6		
LiF—KF	5.6	1.4	1.5	4.3	—4.2	—4.0 (—4.8)	21
LiF—RbF	7.3	2.8	2.0	5.9	—4.5	—4.2	
LiF—CsF	9.0	5.3	2.7	8.0	—3.7	—3.5	
NaF—KF	1.1	0.7	0.5	1.1	—0.4	—0.4	
NaF—RbF	1.8	1.7	1.2	2.0	—0.1	—0.2	
NaF—CsF	2.8	3.7	1.8	3.4	+0.9		
KF—RbF	0.1	0.2	0.1	0.15	+0.1		
KF—CsF	0.4	1.5	0.17	0.6	+1.1		
RbF—CsF	0.1	0.5	0.07	0.2	+0.4		
LiCl—NaCl	1.2	0.1	0.4	0.5	—1.1		
LiCl—KCl	4.4	0.4	1.2	2.4	—4.0	—3.5 (—4.0)	21
LiCl—RbCl	5.8	1.2	1.7	3.4	—4.6		
LiCl—CsCl	8.1	2.2	2.1	4.6	—5.9	—5.0	
NaCl—KCl	1.1	0.3	0.4	0.7	—0.8	—0.8	
NaCl—RbCl	1.8	0.7	1.0	1.0	—1.1		
NaCl—CsCl	3.2	1.5	1.6	2.0	—1.7		
KCl—RbCl	0.1	0.1	0.08	0.1	0.0		
KCl—CsCl	0.6	0.5	0.17	0.4	—0.1		
RbCl—CsCl	0.2	0.2	0.07	0.11	0		
LiBr—NaBr	1.0	0.0	0.35	0.46	—1.0		
LiBr—KBr	3.8	0.4	0.65	2.0	—3.4	—3.0 (—3.2)	21
LiBr—RbBr	5.3	0.9	0.85	2.9	—4.4		
LiBr—CsBr	7.7	1.8	1.1	3.9	—5.9		
NaBr—KBr	1.0	0.2	0.3	0.6	—0.8	0	
NaBr—RbBr	1.8	0.6	0.4	1.1	—1.2		
NaBr—CsBr	3.2	1.3	0.7	1.8	—1.9		
KBr—RbBr	0.1	0.1	0.1	0.008	0.0		
KBr—CsBr	0.6	0.5	0.25	0.35	—0.1		
RbBr—CsBr	0.2	0.2	0.1	0.1	0.0		
LiI—NaI	0.9	0.0	0.3	0.36	—0.9		
LiI—KI	3.5	0.3	0.5	1.6	—3.2		
LiI—RbI	5.0	0.6	0.6	2.3	—4.4		
LiI—CsI	7.1	1.2	0.9	3.2	—4.9		
NaI—KI	0.9	0.1	0.2	0.5	—0.8	—0.7	
NaI—RbI	1.7	0.4	0.3	0.9	—1.3		
NaI—CsI	3.0	0.9	0.5	1.5	—2.1		
KI—RbI	0.2	0.1	0.06	0.06	—0.1		
KI—CsI	0.6	0.3	0.2	0.3	—0.3		
RbI—CsI	0.2	0.1	0.06	0.1	—0.1		

TABLE 3. Energy of mixing for molten salt solutions with a common cation.

System	Constituent energies of mixing		Energy of reaction		Reference
	K_e'' (Förland)	K_L (Lumsden)	$Q=K_e''+K_L$	Q_{exp}	
NaCl—NaBr	—0.60	0.72	+0.12	0	22—24
NaCl—NaI	—2.40	1.60	—0.8	—0.8	25
KCl—KI	—1.60	1.20	—0.4	—0.8	25
KCl—KBr	—0.40	0.60	+0.2	0	22,24
RbCl—RbBr	—0.40	0.40	0		
AgCl—AgBr	—0.40	0.40	0	0	24
$PbBr_2$—$PbCl_2$	—0.40	0.40	0	—1.2	17
KBr—KI	—1.00	0.4	—0.60		

TABLE 4. Comparison of experimental and calculated energies of mixing, for equimolar solutions of molten alkali metal nitrates.

Melts	Contribution of individual constituents to the energy of mixing			Energy of mixing		Q_{exp} (Ref. 26)
	K_P (Lumsden)	K_L (Lumsden)	K_e'' (Förland)	$Q=K_P+K_L+K_e''$	$Q=-1405\delta^2$ (Kleppa)	
$LiNO_3$—$NaNO_3$	—0.44	0.03	—0.12	—0.53	—0.49	—0.464
$LiNO_3$—KNO_3	—1.74	0.08	—0.15	—1.81	—1.82	—1.76
$LiNO_3$—$RbNO_3$	—2.26	0.20	—0.25	—2.31	—2.5	—2.47
$LiNO_3$—$CsNO_3$	—2.94	0.40	—0.30	—2.84	—3.5	—3.0
$NaNO_3$—KNO_3	—0.39	0.04	—0.06	—0.41	—0.45	—0.41
$NaNO_3$—$RbNO_3$	—0.75	0.09	—0.08	—0.74	—0.79	—0.75
$NaNO_3$—$CsNO_3$	—1.03	0.25	—0.20	—0.98	—1.4	—1.04
KNO_3—$RbNO_3$	—0.05	0.01	—0.02	—0.06	—0.05	—0.06
KNO_3—$CsNO_3$	—0.15	0.02	—0.05	—0.18	—0.27	—0.1
$RbNO_3$—$CsNO_3$	—0.05	0.01	—0.02	—0.06	—0.10	—0.014

TABLE 5. Energy of mixing of molten alkali metal nitrates and bromides with silver and thallium salts.

Melts	Contribution of individual constituents to the energy of the solution, calculated by formulae: K_P (19)	K_L (17)	K_e (4)	K_c (21)	$Q = K_P + K_L + K_e + K_c$	$Q = -140\delta^2 + U^{20}$	Q_{exp}	Reference
$LiNO_3$—$AgNO_3$	−0.72	0.16	−0.13	+1.50	+0.81	+0.79	+0,65	27
$NaNO_3$—$AgNO_3$	−0.12	0.09	−0.03	+0.72	+0.66	+0.55	+0.59	27
KNO_3—$AgNO_3$	−0.04	0	−0.02	−0.45	−0.51	−0.52	−0.45	27
$RbNO_3$—$AgON_3$	−0.12	0.01	−0.02	−0.85	−0.96	−1.08	−1.19	27
$CsNO_3$—$AgNO_3$	−0.3	0.07	−0.05	−1.40	−1.43	−2.0		
LiBr—AgBr	−0.75	0.18	−0.15	+2.52	+1.80	+1.72	+1.88	14,28
NaBr—AgBr	−0.12	0.10	−0.03	+1.14	+1.09	+0.98	+1.05	14
KBr—AgBr	−0.05	0	−0.02	−0.72	−0.79	−0.78	−1.48	14
RbBr—AgBr	−0.15	0	−0.03	−1.35	−1.53	−1.58	−2.58	14
CsBr—AgBr	−0.33	0.08	−0.06	−2.18	−2.49	−2.79		
$LiNO_3$—$TlNO_3$	−2.5	0	−0.2	+1.92	−0.78	−0.71	−0.88	27
$NaNO_3$—$TlNO_3$	−0.65	0	−0.07	+1.07	+0.35	+0.30	+0.256	27
KNO_3—$TlNO_3$	−0.08	0	−0.04	+0.60	+0.48	+0.38	+0.44	27
$RbNO_3$—$TlNO_3$	−0.02	0.06	−0.07	+0.27	+0.23	+0.23	+0.232	27
$CsNO_3$—$TlNO_3$	0	0.10	−0.01	−0.18	−0.1	−0.15		

another kind are distributed — at a distance $(1+\gamma)r$ from another — he finds the following expression for measurement of the energy of coulombic repulsion:

$$\Delta E = -\frac{e^2}{r}\left[2\sum_1^\infty \frac{1}{n+\gamma}\cdot(-1)^n - (1+2\gamma)\cdot\sum_1^\infty \frac{1}{n+2\gamma}(-1)^n - \left(\frac{1-\gamma}{1+\gamma}\right)\cdot\sum_1^\infty \frac{1}{n}\cdot(-1)^n\right], \quad (7)$$

where e is the charge of an electron.

ΔE is always negative and approximately 40% less in absolute value than that calculated by Förland's formula. As Table 2 shows (K'), the agreement with experiment is not improved.

2. CALCULATION OF OTHER TYPES OF INTERACTION

Some authors [10,30], following Mayer and Born [31,32], used an expression for the lattice energy allowing for the intermolecular interaction:

$$-U = -\frac{\alpha}{r} - \frac{c}{r^6} + B(r), \quad (8)$$

which includes the coulombic, van der Waals, and Born-type (repulsive) interactions. They neglected null energy and multipolar interaction. If the lattice parameters of the pure components and of the equimolecular solution are denoted r_1, r_2, and $r_{1,2}$, then the change in coulombic energy is:

$$\Delta U_{coulomb} = \frac{2\alpha\cdot e^2}{r_{1,2}} - \frac{\alpha\cdot e^2}{r_1} - \frac{\alpha\cdot e^2}{r_2}, \quad (9)$$

where α is the Madelung constant.

By assuming that the distribution of the cationic and anionic sites is random [4], Wallace finds the following relation between the constants of the van der Waals interaction ($c_{i,j}$) of the salts and the overall constant (c) for the solution:

$$c = N_1\cdot N_2\cdot c_{1,2} + N_1\cdot N_4\cdot c_{1,4} + N_2\cdot N_3\cdot c_{2,3} + \frac{1}{2}(N_1^2\cdot c_{1,1} + N_2^2\cdot c_{2,2} + N_3^2\cdot c_{3,3} + N_4^2\cdot c_{4,4} + 2N_1\cdot N_3\cdot c_{1,3} + 2N_2\cdot N_4\cdot c_{2,4}). \quad (10)$$

Here N_1 and N_3 are the ionic fractions of cations 1 and 3, and N_2 and N_4 those of the anions 2 and 4.

According to Mayer and coworkers [31,33], for the alkali metal halides:

$$B(r) = b\cdot c_{i,j}\cdot e^{\frac{r_i+r_j}{\rho}},$$

where r_i and r_j are the ionic radii, $\rho = 0.345\times10^{-8}$ cm, $b = 1\times10^{-12}$ erg; for the cations $c_{i,j} = c_1 = 1.25$; for the anions $c_{i,j} = c_2 = 0.75$, and for particles with opposite charges $c_{i,j} = c_{1,2} = 1.0$.

The potential of repulsion $B(r_0)$ for solid solutions was evaluated with allowance for the interaction of the central ion with z nearest neighbours and z' ions of the following coordination sphere:

$$B(r_0) = \beta_1\cdot e^{-r_0/\rho} + \beta_2\cdot e^{-ar_0/\rho} \quad (11)$$

where

$$\beta_1 = b\cdot z\cdot c_0\cdot\left[N_1\cdot N_2\cdot e^{\frac{r_1+r_2}{\rho}} + N_1\cdot N_4\cdot e^{\frac{r_1+r_4}{\rho}} + N_2\cdot N_3\cdot e^{\frac{r_2+r_3}{\rho}}\right] \quad (12)$$

$$\beta_2 = \frac{b\cdot z'}{2}\left[c_1\cdot\left(N_1^2\cdot e^{\frac{2r_1}{\rho}} + 2N_1\cdot N_3\cdot e^{\frac{r_1+r_3}{\rho}} + N_3^2\cdot e^{\frac{2r_3}{\rho}}\right) + c_2\left(N_2^2\cdot e^{\frac{2r_2}{\rho}} + 2N_2\cdot N_4\cdot e^{\frac{r_2+r_4}{\rho}} + N_4^2\cdot e^{\frac{2r_4}{\rho}}\right)\right] \quad (13)$$

c_0 is the van der Waals constant, taking into account the interaction between ions of opposite charge; c_1 is the same for intercationic, and c_2 that for interanionic, interactions.

The value of r_0 is the equilibrium distance between the nearest neighbours, whereas ar_0 up to the second coordination layer, and r_1, r_2 etc. are characteristic parameters of individual types of ions.

In Eqns. (11)–(13) the interaction between a given pair of ions in a solution is identical with that in the pure salts at corresponding distances.

Table 6 shows the experimental lattice parameters of solid solutions of the NaCl–NaBr, KCl–KBr, and RbCl–KCl binary systems, together with the repulsion constants β and van der Waals constants c, calculated [10] by Eqns. (11)–(13). In this, the equilibrium distances r_0 in the solid solution at 0°K were evaluated with the aid of the Born–Mayer relation:

$$r_0\left(\frac{dU(r_0)}{dr}\right) = \frac{3T}{N\cdot e}\left(\frac{dV}{dT}\right)_p, \quad (14)$$

where ϵ is the compressibility.

Furthermore, the values of r_0 were calculated by the additivity rule and appeared (see Table 6) quite close to the experimental values.

The heat of mixing ΔH is expressed by the lattice energies U_1, U_2, and U of the pure salts and solid solution:

$$\Delta H = U - x_1\cdot U_1 - x_2\cdot U_2. \quad (15)$$

TABLE 6. Lattice parameters of solid solutions of alkali halides, repulsion constants (β_1 and β_2), and van der Waals forces (c) after Wallace [10].

System	Mole fraction, N_1	$10^8 r_0$, cm (298°K) expt.	by the rule of mixing	deviation	$10^8 r_0$, cm (0°K) expt.	by the rule of mixing	deviation	$10^{60} c$, erg cm	$10^{12}\beta_1$, erg	$10^{12}\beta_2$, erg
NaCl—NaBr	1.0	2.8144	—	—	2.79	—	—	180	5498	24880
	0.75	2.8588	2.8560	0.0028	2.837	2.831	0.006	201	6081	30170
	0.50	2.9017	2.8977	0.040	2.88	2.872	0.008	223	6664	35990
	0.25	2.9411	2.9393	0.038	2.919	2.913	0.006	247	7247	42340
	0.0	2.9809	—	—	2.954	—	—	271	7830	49230
KCl—KBr	1.0	3.1362	—	—	3.105	—	—	451	13380	30480
	0.75	3.176	3.176	0.000	3.151	3.146	0.006	488	14840	35840
	0.50	3.217	3.216	0.001	3.192	3.184	0.008	325	16300	41730
	0.25	3.257	3.256	0.001	3.229	3.224	0.005	564	17760	48240
	0.0	3.2952	—	—	3.263	—	—	604	19220	55240
KCl—RbCl	1.0	3.1362	—	—	3.105	—	—	451	13380	30480
	0.5	3.216	3.211	0.005	3.185	3.178	0.07	570	16590	34360
	0.0	3.286	—	—	3.251	—	—	692	19790	39060

TABLE 7. Comparison of the lattice energies and heats of mixing, and also of their constituents for solutions of salts which form solid solutions (kcal mole^{-1}).

System	N_1	Repulsion potential $B(r_0)$ 298°K abs.	298°K rel.	0°K abs.	0°K rel.	Coulombic energy $-\frac{ae^2}{r_0}$ 298°K abs.	298°K rel.	0°K abs.	0°K rel.	Intermolecular interaction $-\frac{c}{r^6}$ 298°K	298°K rel.	0°K	0°K rel.	Lattice energy, $-U$ 298°K	0°K	Heat of mixing 298°K	0°K	298°K	0°K
														absolute values		Refs. 9 and 10		calculated (Ref. 34)	
NaCl—NaBr	1.0	26.22		28.21		200.7		202.5		5.23		5.52		179.71	179.81				
	0.5	24.88	0.04	26.53	—0.331	194.7	0.4	196.2	0.7	5.37	0.015	5.64	0.05	175.19	175.31	0.34	0.54	0.45	0.42
	0.5	(25.18)	(0.34)	(27.20)	(0.32)	(195.6)	(0.1)	(196.7)	(0.2)	(5.35)	(0.035)	(5.64)	(0.05)	(175.17)	(175.14)			(0.47)	(0.57)
	0	23.46		25.54		189.5		191.3		5.54		5.86		171.58	171.62				
KCl—KBr	1.0	22.90		25.08		180.3		182.0		6.89		7.25		164.29	164.17				
	0.5	22.07	0.27	23.74	—0.2	177.0	0.2	177.0	0.6	6.85	0	7.225	0.086	160.48	160.48	0.23	0.45	0.47	0.49
	0.5	(22.12)	(0.32)	(24.31)	(0.36)	(177.4)	(0.1)	(177.4)	(0.2)	(6.84)	(0.01)	(7.20)	(0)	(160.52)	(160.29)			(0.43)	(0.56)
	0	20.71		22.83		173.2		173.2		6.81		7.152		157.68	157.52				
KCl—RbCl	1.0	22.90		25.08		180.3		182.0		6.89		7.25		164.29	164.17				
	0.5	22.29	0.04	24.44	0	177.4	0.35	177.4	0.5	7.4	—0.005	7.92	—0.06	160.91	160.88	0.20	0.40	0.39	0.44
	0.5	(22.67)	(0.42)	(24.95)	(0.50)	(177.8)	(0.1)	(177.8)	(0.1)	(7.39)	(0.005)	(7.85)	(0.01)	(160.22)	(160.7)			(0.57)	(0.61)
	0	21.60		23.93		173.8		173.8		7.9		8.46		158.3	158.33				

In the opinion of Wallace, the change in $B(r)$ is approximately two-thirds of the energy of mixing; the change in the coulombic energy covers most of the rest, and the van der Waals force makes a small contribution.

Table 7 gives the lattice energies, the values of the individual constituents, and their contributions to the heat of mixing, calculated[34] by Eqns. (8)–(15). The calculated values of ΔH are compared with those found experimentally. Although our calculated values do not differ too much from Wallace's values, the relative significance of the various types of interaction is different. The main source of ΔH is the change in the coulombic interaction and not the repulsion forces. Both types of energy are very sensitive to the departure of the lattice parameters from additivity. Values calculated assuming that Vegard's law is applicable are given in parentheses. Here the relative significance of the change in the Born repulsion has increased to about three-quarters of the total energy of mixing. However, in all the systems there are positive departures from Vegard's law. This leads to a relative decrease in the energy of coulombic interaction, and consequently an increase in the positive contribution to the heat of mixing. On the other hand, the Born potential here falls, its contribution decreases, and even the sign changes to positive (at 0°K).

It is interesting to note that the results of the calculation are almost independent of whether we use the equilibrium values of the lattice parameters or assume the applicability of the additivity rule. However, this is correct only when allowance is made not only for the coulombic interaction but also the potential of repulsion.

Comparison with experiment shows a systematic increase in the calculated values of ΔH. Allowance for only one coulombic interaction at 298°K gives the best agreement with experiment, which cannot be said of the data for 0°K.

Wallace's method is apparently not applicable to liquid salts, since there is no long-range order in them. Lumsden[35] considered solutions of molten alkali metal halides with a common anion. He assumes that the energy of mixing is due above all to the asymmetry of the electric field of cations of different kind. The main negative contribution is therefore introduced by the polarisation energy; the increase in van der Waals interaction is a positive term.

Lumsden neglects the change in coulombic energy, which is scarcely proved. The method of calculation proposed by him is scarcely applicable to solutions of salts with a common cation.

The non-polar London forces which act between ions give an energy contribution which is inversely proportional to the distance raised to the sixth power. The forces are short-range, therefore in a mixture with a common anion they can be restricted to the interaction between the nearest cations.

Starting from the simplest geometrical relations, Lumsden finds an expression for the change in the energy of the non-polar interaction for mixing:

$$E_L = K_L \cdot \frac{x \cdot y}{x + y} \qquad (16)$$

Here x and y are the number of moles of the salts X^+Z^- and Y^+Z^-; but the quantity K_L is connected with the constants $c_{i,i}$ by the relation:

$$K_L = 86.5 \cdot \left[\frac{c_{X,X}}{(2r^2_{X,Z})^3} + \frac{c_{Y,Y}}{(2r^2_{Y,Z})^3} - \frac{2\sqrt{c_{X,X} \cdot c_{Y,Y}}}{(r^2_{X,Z} + r^2_{Y,Z})^3} \right] \qquad (17)$$

We note that the values E_L calculated by Wallace's formulae are considerably less than those for the same salts by Eqn. (17). The main reason for this is the different definition of the constant $c_{i,j}$ for the mixture of salts. Whereas Lumsden assumes that $c^2_{X,Y} = c_{X,X}\, c_{Y,Y}$, the quantity $c_{X,Y}$ found by formula (10), differs little from the arithmetic mean.

The rule of the geometric mean, true under definite conditions for a series of simple mixtures of dielectrics cannot be unconditionally applicable to ionic solutions. The introduction of formula (10) here is more reasonable.

As is well-known, the geometric mean is always less than the arithmetic mean or equal to it. Therefore the results of the calculations by Eqns. (16) and (17) should

give an increased positive departure in the heat of mixing. Allowance for the asymmetry of the electric field in mixtures with a common anion leads to the following expression for the polarisation energy:

$$E_P = K_P \cdot \frac{x \cdot y}{x + y} \qquad (18)$$

$$K_P = -1060 \cdot N \cdot \alpha \left(\frac{1}{r^3_{X,Z}} - \frac{1}{r^3_{Y,Z}} \right)^2 \qquad (19)$$

In this the molar polarisability $N\alpha$ is expressed in cm^3 but the inter-ion distance $r_{i,j}$ in ångströms (10^{-8} cm).

Table 2 gives the values of the constants K_L and K_P calculated by Lumsden for mixtures of alkali halides with a common anion. In this, the inter-ionic distances were taken from Wyckoff[36], the constants $c_{i,j}$ from Mayer[32], and the data on polarisabilities from Kordes[37]. According to Lumsden, the quantities he obtained agree with the thermal analyses for several binary systems.

Lumsden evidently overestimates the size of the contribution of polarisation in the energy of mixing. The linear model of the solution can hardly be transferred to the three-dimensional without some restrictions†.

It is necessary to consider also the possible revaluation of the role of the London interaction. Use of the geometric mean rule for the constants $c_{i,j}$ leads, evidently, to too high results. On the other hand, allowance for the non-polar interaction, although small, is very important, especially in mixtures with a common cation. In several instances the London forces are the only ones making a positive contribution to the heat of mixing.

As the electron clouds of the ions can be deformed and partially overlap one another, a considerable part of the contribution to the excess energy of the mixture is due not only to the repulsion of particles with charges of the same sign, but also to the change in the interaction of the cation with the anion. The mean distance between them is determined by the minimum free energy — see Eqn. (14) — and should change on mixing.

We will restrict discussion to the formulae mentioned and will not consider those in which the energies of mixing are linked with macroscopic characteristics. This refers in particular to Shimoji's equation[38], in which molecular volumes are introduced instead of the ionic distances.

3. COMPARISON WITH EXPERIMENTAL DATA

To calculate the energies of mixing we used the usual values of the ionic radii, which are compromises between those recommended by various authors. Where possible, directly measured inter-ionic distances were used.

a. Solid Solutions

To calculate the energy by the Wallace method the lattice parameters of the solid solutions must be known. Furthermore, use of this method leads to values of ΔH which are too high (see Table 7). We therefore calculated[34] the energy of mixing with an allowance for the electrostatic interaction after Tobolsky, Eqn. (3), and for the London forces after Lumsden, Eqn. (17). Comparison of values of Q thus calculated with the experimental values (see Table 1) shows very good agreement. For six binary systems marked with asterisks there are only the heats of mixing of the liquid phases. The values of Q in five of these are close to those calculated for the solid solutions. An exception is the $PbBr_2$–$PbCl_2$ system, for which even the signs of the thermal effect are different. As Delimarskii and Markov show[6], this system is a rare exception among solid solutions. They explain[6] the negative departures observed here by the formation of the compound PbClBr.

b. Fused Alkali Metal Halides and Nitrates

Unfortunately, heats of mixing of liquid solutions of alkali halides have not been studied calorimetrically; electrometric data are quite scanty. For comparison there are limited results obtained from the fusion diagrams[35] and from vapour pressures[25,39].

Table 2 contains the values of the contributions of the individual effects to the energy of mixing of salts with a common anion, calculated from Eqns. (4), (7), (17), and (19). The quantities Q found by Lumsden ($K_P + K_L$) do not agree very well with the experimental values. The Förland formula (4) gives a large deviation.

For salts with a common cation the main contribution to Q comes from the coulombic interaction, which decreases the energy of the system, and the dispersion interaction, which increases the potential of the solution. As Table 3 shows, these contributions are approximately the same and compensate one another. As a result the solutions are characterised by small departures from ideality ($\Delta H \simeq 0$). The results of the calculations are close to the available experimental data (see Table 3).

In solutions of salts with a common anion considerable negative departures are observed (see Table 2), connected mainly with the polarisation effect. On the other hand, the role of this effect is small for salts with a common cation.

Precision calorimetric investigations of the thermal effects of mixing of molten nitrates, made at 345–450°C by Kleppa[26] are of special interest for testing the various methods of calculation. Heats calculated with allowance for coulombic (4), non-polar (17), and polarisation (19) effects, and also found by Eqn. (5) are compared with experimental data in Table 4. The best agreement with experiment is obtained if we are restricted only to the polarisation effect. Somewhat worse results are given by the sum of all three constituents (coulombic, London, and polarisation). Eqn. (5) gives approximately the same deviations.

It is unfortunately difficult to solve the problem of the nature of the energy of mixing in molten nitrates, since even allowance for only the coulombic interaction between the nearest cations (5) gives approximately the same thermal effect as the polarisation of anions (ΔH_P).

c. Solutions of Alkali Metal Nitrates and Bromides with Silver and Thallium Salts

In solutions of $AgNO_3$ with alkali metal nitrates (MNO_3) it is observed[27] that there is a gradual change from positive departures (melts with $LiNO_3$ and $NaNO_3$) to negative

† Presumably the author means that the overestimate of the contribution of polarisation is supported only when a two-dimensional model is applied to the (three-dimensional) system (Ed. of Translation).

(KNO_3, $RbNO_3$). Here, as in AgBr–MBr melts [14], the increase in the radius of the M^+ cation leads to an increase in the negative departures from Raoult's law. An analogous dependence was found [27] in $TlNO_3$–MNO_3 melts.

Kleppa and Hersh [27] connect these phenomena with the fact that the lattices of the silver and thallium salts are only partly ionic. The non-coulombic contribution to the lattice energy is thought by them to be ~ 25 kcal for $AgNO_3$ and 15 kcal for $TlNO_3$.

The small changes in volume and energy (entropy) during fusion [40–45] are due to the asymmetric distribution of the electron density around the Ag^+ nucleus. Such a picture also holds true for SiO_2, where the bond between the silicon and the oxygen is very strong and the heat of fusion is small [46].

Förland thinks [40] that the change in energy during mixing is here due to the difference in structure of AgBr and MBr melts. Therefore during mixing one of the compounds or both changes its structure, which promotes an increase in energy. On the other hand, the energy of the solution should decrease, since the Ag^+ polarises Br^- more strongly than the alkali metal cations. Evidence of this is given by the lattice energy of AgBr being greater than that of MBr [47,48]. The absorption of heat during the mixing of AgBr with LiBr and NaBr is due mainly to the structural effects, and the liberation of heat in melts of AgBr with KBr and RbBr is mainly determined by the change in polarisation. It must also be taken into consideration that the tendency of silver salts to complex formation is evidence of the considerable relative significance of the directed bonds.

According to Markov and Delimarskii [6], here the complex-former is usually itself associated. When it passes into the solution, energy is expended in destroying these associates and is liberated as a result of the formation of new complexes with the second component.

The relative influence of these opposing effects is determined in an equimolecular solution of AgBr and MBr by the electrostatic field of the M^+ cation. With strong cations (Li^+) the breakdown of the associate predominates and heat is absorbed. The amount of the latter is determined to a first approximation by the quantity:

$$\delta = \frac{d_{Ag^+} - d_{M^+}}{d_{Ag^+} + d_{M^+}} \qquad (20)$$

On the other hand, with a weak partner (Rb^+) complex formation mainly occurs. The degree to which it takes place also depends on ratio (20), but with the opposite sign.

What has been stated allows the contribution of the directed bonds to the heat of mixing to be represented by the relation:

$$K_c = \Delta U \cdot \left(\frac{d_{M^+} - d_{Ag^+}}{d_{M^+} + d_{Ag^+}}\right) \qquad (21)$$

In this ΔU is the energy due to the existence of directed bonds in the complex-forming salt.

Hence the heat of mixing of salt melts containing strongly polarisable ions has contributions from at least four effects: coulombic, polarisation, intermolecular, and that due to complex formation and the breakdown of the initial associates.

Table 5 compares the heats of mixing calculated by the formula:

$$Q = K_P + K_L + K_e^* + K_c \qquad (22)$$

with those found experimentally [14,27] and also with those calculated by the formula (6). The values of ΔU for nitrates (Ag^+ and Tl^+) were taken as -21 and -16 kcal. [27] As for bromides, we found the quantity $\Delta U \simeq$ -33 kcal from the difference between the experimental and calculated values of the lattice energy. As Table 5 shows, formula (6) and Eqn. (22) allow the thermal effects of mixing to be evaluated with known accuracy.

d. Energy of Mixing of Halides with Cations of Different Valency

In recent years there have been studies [15,49–62] of the properties of solutions formed by molten $PbCl_2$, $CdCl_2$, $ZnCl_2$, $MgCl_2$, and alkali metal chlorides MCl, and also $PbBr_2$ and $CdBr_2$ with MBr. Some of these results are given in Table 8.

$PbCl_2$–LiCl solutions show small positive departures from Raoult's law. In $PbCl_2$–NaCl melts there are moderate negative departures which increase considerably on going to solutions with KCl or RbCl. The latter are due to the formation of complex ions, as is confirmed by the investigation of electrical conductivity [64–66], surface tension [67,68], viscosity [69], transport number [70,71], and specific and molar volumes [72].

The same regularity is observed in solutions of $CdCl_2$ and $ZnCl_2$ with MCl as in $PbCl_2$ melts.

On going from chloride solutions to the corresponding solutions of bromides there is an increase in the negative departures.

The relationships quoted earlier for evaluating the energy of mixing were developed for solutions of uni-univalent salts, having, for example, a common anion. For melts containing cations of different valency, Eqns. (3), (4), (15), (17) and (19) are inapplicable.

TABLE 8. Heats of mixing of halides in equimolar amounts with cations of different valencies.

System	Heat of mixing, kcal mole^{-1} calculated by the formulae: (23)	(5) $\Delta H = -140 \cdot \delta_1^2$	(24) $\Delta H = -15 \cdot \delta_1$	experimental	Reference
$PbCl_2$–LiCl	−0 65	−0.04	−0.24	+0.05	49
				+0.10	50
$PbCl_2$–NaCl	−1.05	−0.43	−0.84	−0.25	50
				−0.75	49
$PbCl_2$–KCl	−2.48	−1.65	−1.60	−1.25	49
				−1.50	50
$PbCl_2$–RbCl	−2.7	−2.2	−1.9	−1.4	50
				−2.2	49
$PbBr_2$–LiBr	−0.9	−0.05	−0.2		
$PbBr_2$–NaBr	−1.74	−0.4	−0.8	−0.5	50
				−1.0	63
$PbBr_2$–KBr	−2.8	−1.5	−1.5	−3.0	50
				−2.5	63
$PbBr_2$–RbBr	−3.45	−2.0	−1.8		
$CdCl_2$–LiCl	−2.0	−0.25	−0.64		
$CdCl_2$–NaCl	−3.1	−1.0	−1.2	−0.8	51
				−0.9	53
$CdCl_2$–KCl	−4.6	−2.65	−2.1	−2.5	51
$CdCl_2$–RbCl	−5.0	−3.2	−2.35		
$CdBr_2$–LiBr	−2.15	−0.22	−0.6		
$CdBr_2$–NaBr	−3.3	−0.9	−1.2	−0.25	52
$CdBr_2$–KBr	−4.6	−2.4	−1.9	−3.25	52
$CdBr_2$–RbBr	−8.4	−3.1	−2.2		
$ZnCl_2$–LiCl	−3.7	−0.42	−0.9		
$ZnCl_2$–NaCl	−5.4	−1.6	−1.6	−2.3	53
$ZnCl_2$–KCl	−7.3	−3.6	−2.5	−3.0	53
$ZnCl_2$–RbCl	−7.8	−4.4	−2.7	−4.6	53
$MgCl_2$–LiCl	−4.4	−0.65	−1.0	+0.1	15
$MgCl_2$–NaCl	−6.3	−1.7	−1.7	−1.5	15
$MgCl_2$–KCl	−8.2	−4.1	−2.5	−4.0	15
$MgCl_2$–RbCl	−8.8	−4.7	−2.9	−6.0	15

When allowance is made for the difference in the charges of the cations in the derivation of the expression for the contribution from the change in polarisation Eqn. (19) becomes, to a first approximation:

$$K'_P = -1060 \cdot N \cdot \alpha \cdot \left[\frac{2}{(r^{2+})^3} - \frac{1}{(r^+)^3}\right]^2 . \qquad (23)$$

The energy of mixing found by this formula truly gives the change in Q in AX_2–BX melts. An increase in the radius of the M^+ ion increases the negative departures, whereas an increase in the dimensions of M^{2+} decreases it. The negative departures in bromides under conditions otherwise equal are stronger than in chlorides, since the polarisability of Br is greater than that of Cl. However, the size of the calculated heats of mixing is much higher (see Table 8) than that found experimentally. As the heat of mixing is determined now not by the difference $(r_1 - r_2)$ but by the relation $(\frac{1}{2}r^{2+} - r^+)$, then Eqn. (5) can be used as an empirical formula:

$$\Delta H = -U \cdot \delta_1^2 \qquad (24)$$

in which:

$$\delta_1 = \frac{\frac{r^{2+}}{2} - r^+}{d_1 + d_2}$$

Unlike formula (5), it is not based on any physical model of the solution. The quantity U essentially should be close to the arithmetic mean of the lattice energies of the salts. The closest results to experiment are obtained (see Table 8) on taking U = -140 kcal, which is much less than $\frac{1}{2}(U_{AX_2} + U_{BX})$.

An equation analogous to (21) in which the ratio $\delta = \frac{d_1 - d_2}{d_1 + d_2}$ is used instead of $\delta_1 = \frac{\frac{r_1}{2} - r_2}{d_1 + d_2}$ is less convenient. The expression

$$\Delta H = -15 \cdot \delta_1 \qquad (25)$$

also, like formulae (23) and (24), does not give (see Table 8) the change in sign of the departures of the solutions from the ideal.

Table 9 gives the experimental results on the thermochemistry of solutions of alkali metal nitrates[27] and carbonates[62] with the corresponding calcium salts. The use of empirical equations (24) and (25) gives somewhat better results than the more well-founded formula (23).

Expressions (22), (5), and (6) poorly describe the experimental results for solutions of the alkaline earth metals (see Table 10). This cannot be said about the chlorides and bromides of other metals.

TABLE 9. Heats of mixing of molten alkali metal nitrates and carbonates with calcium salts (for equimolar compositions).

System	Heat of mixing, kcal mole^{-1} calculated by the formulae: (23) K'_P	(24) $-225 \cdot \delta_1^2$	(21) $-20 \cdot \delta_1$	experimental	Reference
$Ca(NO_3)_2$–$LiNO_3$	−0.6	−0.3	−0.74	+0.4	27
$Ca(NO_3)_2$–$NaNO_3$	−1.1	−1.2	−1.5	−1.1	27
$Ca(NO_3)_2$–KNO_3	−1.4	−3.2	−2.4	−3.0	27
$Ca(NO_3)_2$–$RbNO_3$	−1.8	−4.2	−2.8	−4.35	27
$CaCO_3$–Li_2CO_3	−0.8	−0.3	−0.75	−0.6	73
$CaCO_3$–Na_2CO_3	−1.47	−1.23	−1.50	−1.4	73
$CaCO_3$–K_2CO_3	−2.0	−3.2	−2.5	−2.9	73
$CaCO_3$–Rb_2CO_3	−2.6	−4.3	−2.9		

TABLE 10. Heats of mixing in molten chlorides and bromides of bivalent metals (for equimolar compositions).

Melts	Heat of mixing, kcal mole^{-1} found by the formulae: (22)	(5) $-600 \cdot \delta^2$	(6) $-80 \cdot \delta$	experimental	Reference
$PbCl_2$–$CaCl_2$	+1.3	−1.2	+1.1	+1.8	50
$PbCl_2$–$SrCl_2$	+0.9	−0.4	+0.8	+0.1	50
$PbCl_2$–$BaCl_2$	−0.7	−0.1	−0.8	−0.4	50
$CdCl_2$–$CaCl_2$	0	0	0		
$CdCl_2$–$SrCl_2$	−0.3	−0.35	−0.35		
$CdCl_2$–$BaCl_2$	−1.7	−2.2	−2.2	−1.6	50
$ZnCl_2$–$CaCl_2$	−1.2	−1.0	−1.0		
$ZnCl_2$–$SrCl_2$	−2.5	−2.2	−2.2		
$ZnCl_2$–$BaCl_2$	−5.6	−5.8	−5.8	−4.5	53
$MgCl_2$–$CaCl_2$	−2.2	−1.0	−1.0		
$MgCl_2$–$SrCl_2$	−3.9	−3.3	−3.3		
$MgCl_2$–$BaCl_2$	−7.5	−6.9	−6.9		
$PbCl_2$–$CdCl_2$	−1.1	−1.4			
$PbCl_2$–$ZnCl_2$	−5.0	−4.3		−9.0	74
$PbCl_2$–$MgCl_2$	−5.7	−5.3			
$CdCl_2$–$ZnCl_2$	−1.1	−0.9			
$CdCl_2$–$MgCl_2$	−1.5	−1.3			
$ZnCl_2$–$MgCl_2$	~0	~0			
$PbBr_2$–$ZnBr_2$	−2.2	−3.8		+0.9	16
$PbCl_2$–$PbBr_2$	−0.2	−0.4		⩽0	17

It is also interesting to note that for oxides and silicates the comparison of calculated values of Q with the published information gives reasonable agreement in general (see Tables 11 and 12).

e. Melts of Reciprocal Salt Systems

Voskresenskaya[78-80] confirmed Kablukov's prediction that the stable pair of salts will be that which corresponds to the liberation of heat during the double decomposition in the solid state. The determination of the direction of the double decomposition from the thermal effects is permissible here, since the sign of ΔZ for the reaction usually changes at temperatures higher than the liquidus. A recommendation has been made[78] for the calculation of the heat of reaction by the lattice energies (U) of the individual salts, found by Kapustinskii's formula:

$$U = 256 \cdot \frac{n \cdot z_1 \cdot z_2}{r_1 + r_2}, \qquad (26)$$

where z_1 and z_2 are the charges of the ions.

TABLE 11. Energy of mixing of molten oxides.

Melts	Constituent energies of mixing, calculated by the formulae: (19) K_P	(17) K_L	(7) K'_e	Energy of mixing $Q=-800 \cdot \delta^2$	$Q=K_P+K_L+K'_e$	Q_{exp}	reference
FeO–MnO	−0.08			−0.04	−0.08		
FeO–CaO	−2.0		−0.2	−2.4	−2.2	−6.8	22
FeO–MgO	0	0.15		0	+0.15		
FeO–NiO	−0.07			−0.16	−0.07		
FeO–CoO	0			0	0		
FeO–ZnO	−0.08			−0.05	−0.08	0	23
FeO–PbO	−6.5	0.20	−0.9	−8.0	−7.2		
FeO–BaO	−7.6		−0.9	−11.5	−8.5		
MnO–CaO	−1.3		−0.2	−1.8	−1.5		
MnO–MgO	−0.1	0.20		−0.1	+0.1		
MnO–NiO	−0.3			−0.3	−0.3	>0	24,75
MnO–CoO	−0.1			−0.1	−0.1		
MnO–ZnO	0			0	0		
MnO–PbO	−4.9	0.15	−0.6	−8.0	−5.4		
MnO–BaO	−6.1		−0.8	−10.0	−6.9		
CaO–MgO	−2.1		−0.2	−2.8	−2.3		
CaO–NiO	−2.8		−0.2	−2.9	−3.0		
CaO–ZnO	−1.3		−0.2	−2.0	−1.5		
CaO–PbO	−1.2	0.2	−0.2	−2.3	−1.2		
CaO–BaO	−1.8		−0.2	−3.9	−2.0		
MgO–NiO	−0.1		−0.1	−0.1	−0.2	~0	24,75
MgO–ZnO	−0.1			−0.1	−0.1		
MgO–PbO	−6.4	0.6	−0.8	−9.6	−6.6		

TABLE 12. Energy of mixing of certain molten silicate solutions.

Melts	Constituent energies of mixing		Energy of mixing found by the formulae:			Reference
	K_P' (Lumsden) (23)	K_e'' (Förland)	$Q=K_P'+K_e''$	$Q=-4\cdot\delta_1^2$	expt.	
FeO—SiO_2	—10.2	—0.7	—10.9	—13.3	—10.0	76
CaO—SiO_2	—20.3	—1.3	—21.6	—28.8	—27.0	77
MnO—SiO_2	—11.5	—0.9	—12.4	—14.0	—10.0	77
MgO—SiO_2	—9.6	—0.8	—10.4	—12.6	—27.0	77
PbO—SiO_2	—30.4	—2.1	—32.5	—48.5		
ZnO—SiO_2	—11.6	—0.9	—12.6	—14.0	—14.3	76
Na_2O—SiO_2	—17.7	—1.2	—18.9	—24.0		

As our calculations showed, the best agreement is obtained by using the lattice energies found experimentally.

Comparison of the thermal effects of the double decompositions ΔH_R with the heats of mixing of the solutions ΔH with a common ion shows that the former are appreciably greater than the latter. Thus, for LiF–CsF melts the quantity ΔH is 5 kcal, but the heats ΔH_R for the reciprocal systems LiCl + CsF, LiBr + CsF, and LiI + CsF are respectively -9, -13, -15 kcal per mole solution.

To a first approximation the energy of mixing Q of the reciprocal system AX + BY = AY + BX is equal to the sum of those for four systems with a common ion: AX + BX, AY + BY, AX + AY, and BX + BY. Thus Q_R for the system LiI + CsF = LiF + CsI is 15.5 kcal, and the sum of quantities Q for the solutions LiF + CsF, LiF + LiI, LiI + + CsI, and CsF + CsI is 14.8 kcal.

In reactions with ions of different valency the energies of mixing are greater. The differences between the quantities calculated by the Kapustinskii formula and those found experimentally are more significant. As has been shown[78], the experimental values are usually much less than those calculated.

The great difference between calculation and experiment is partly connected with the increase in the fraction of directed bonds in salts of higher valency. It therefore seems desirable to use data on heats of formation. However, there still remains an indeterminacy, connected with the departure of the heat capacity of the components from the Kopp–Neumann law.

It is interesting to note that here also there is a link between the quantities ΔH_R for reciprocal systems and the values of ΔH for their consistuent solutions with a common ion.

All the above shows that the calculation of the energy of mixing from the properties of the individual particles is still in its earliest stages even for such simple systems as ionic melts. We thought it desirable to review these publications in order to draw the attention of investigators to future developments in this important problem.

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REARRANGEMENTS INVOLVING THE CLEAVAGE OF N–N OR N–O BONDS AND FORMATION OF A NITRILE GROUP

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1. INTRODUCTION

There has been much recent work on rearrangements in which an N–N or N–O bond is broken and a nitrile group formed.

Compounds which can undergo this conversion include substituted aldehyde hydrazones, their cyclic analogues, the 3-unsubstituted pyrazolines and indazoles, and their cyclic and acyclic oxygen analogues, that is, aldoximes and 3-unsubstituted isoxazoles.

The nitrile fission of N–N or N–O bonds is observed under diverse experimental conditions: by the action of salts of complex-forming metals or platinum group metals; in the pyrolysis of hydrochlorides or quaternary salts; in the Hofmann degradation of quaternary ammonium bases; and by the action of nucleophilic reagents. The lack of data on the mechanism of the reaction and the variety of conditions, despite the external similarity of the processes, often hinder their comparison and generalisation.

2. NITRILE FISSION OF N–N OR N–O BONDS BY ELECTROPHILIC REAGENTS OR METAL CATALYSTS†

In 1910 Arbuzov observed[1,2] that heating aliphatic aldehyde phenylhydrazones to 180–200° with catalytic

† Metal catalysts are only formally included in this section, in view of the lack of knowledge of the mechanism of their action and the paucity of experimental material.