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STRUCTURE AND PROPERTIES OF MOLTEN SALTS

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1. INTRODUCTION

Molten salts form a large class of the liquids which exhibit electrolytic conductivity. The principal structural units in molten salts are ions, they are therefore also terms ionic liquids.

The practical importance of molten salts has increased considerably in recent years in connection with the development of new branches of metallurgy and energetics. Molten salts are widely used for the electrolytic production of various light and rare metals[1,2], used in nuclear technology as heat transfer media or reactor fuels[2,3], employed as electrolytes in fuel cells[4], etc. Recently there has been a sharp increase in the number of publications — both research papers and review articles. Reviews and monographs on various aspects of the physics and chemistry of molten salts have been published by Belyaev *et al.*[5], Voskresenskaya[6], Delimarskii and Markov[7], Morachevskii[8-10], and many other authors[2,3,11-20]. The earlier investigations have been critically discussed and reviewed[1,21].

Electrolytic conductivity and other properties of molten salts are explained if the salts are considered to be composed of charged structural units — ions. In characterising the properties of molten salts and comparing them with the properties of ionic crystals, reference is sometimes made to dissociation on melting. However, here the term "dissociation" has only conventional significance, since during fusion there is no decomposition of neutral molecules into ions. The fusion of a salt is essentially the destruction of the crystal lattice, usually accompanied by an increase in volume. The extra volume produced ensures freer movement of ions, so that it is more logical to speak of the disordering or disintegration of the crystal lattices than of dissociation. The condensation of salt vapours, which consist of neutral molecules, is accompanied by self-dissociation, as a result of which ions, earlier bound in pairs, are socialised, are collectivised, to form an ionic liquid. In this respect there is a definite analogy between salts and metals, since in the condensation of metal vapours there is the collectivisation of the electrons[22].

It is natural for properties of molten salts such as electrical conductivity, viscosity, diffusion, surface tension, heats of phase transformations, and so forth to depend on the characteristics of the ions forming the melt — their dimensions, masses, polarisability, and charge. However, in considering this dependence it is necessary to take into account that the ions in the melt form a single collective, exhibiting a definite structure. Just as the properties of ionic crystals are determined not only by the properties of the individual ions, but also by the properties of their set, that is, the crystal lattice, the properties of molten salts can be understood only by studying their structure. In turn, a study of the properties of salt melts permits assessment of their structure and makes possible their quantitative characterisation.

The development of the theory of the liquid state as applied to molten salts shows that their principal properties are due to the structural peculiarities more than to

the properties and interaction of the individual ions. This is shown especially clearly by the example of electrical conductivity of molten salts. Most of the ions in a melt are vibrating at each moment of time at definite equilibrium positions analogous to the nodes of a crystal lattice; these ions cannot participate in forward motion even in very strong fields, and consequently cannot take part in the transport of electricity. Forward motion becomes possible for a given ion only when a neighbouring equilibrium position becomes vacant, that is, as a result of fluctuations in the structure.

In the present review an attempt is made to consider the experimental data available about the properties of pure molten salts in the light of contemporary theoretical views about their structure and molecular constitution.

Until recently the ionic–molecular composition of molten salts had been studied solely by cryoscopic methods. Not long ago spectroscopy and X-ray diffraction became widely used for this purpose. The essence of the cryoscopic method lay in the use of the Raoult–van't Hoff law, according to which the freezing point depression ΔT on dissolution of a foreign salt in a given melt is

$$\Delta T_f = \nu \frac{RT_f}{L_f} \times \frac{M}{1000} \times m = \nu m k_f, \qquad (1)$$

where M is the molecular weight of the solvent, L_f its heat of fusion, m the molarity of the solution, k_f a cryoscopic constant, and ν the number of particles, foreign with respect to the solvent, which are formed from one molecule of the solute salt. Naturally, study of the freezing point depression not only permits confirmation of the ionic structure of the salt but also provides concrete information about the ionic composition of the melt.

The number of cryoscopic investigations is very large. The older works on the cryometry of molten salts were discussed by Hoenen[23] and contemporary investigations in the review of Janz *et al.*[11] The earlier works on cryometry (Zakura and others[21,23]) were not distinguished by exceptional accuracy. In later years Janz and coworkers[24,25], Kordes and coworkers[26–28], and others[29–52] made careful measurements of freezing point depressions. As an example Fig. 1 gives $\Delta T_f = f(m)$ curves for molten $AgNO_3$, and shows that Eqn. (1) is obeyed satisfactorily. Some deviations can be related to the formation of solid solutions or with the non-ideality of the system[29].

The scheme of "dissociation" of salts, as follows from the cryometric results, usually corresponds with the ionic structure of the crystals. The particles bound in the crystal, mainly by electrostatic forces, form relatively free ions in the melt, for example, Na^+, Cl^-, NO_3^-, etc. Complex ions, between the structural constituents of which covalent forces act (NO_3^-, CO_3^{2-}, SO_4^{2-}) behave as integral units and there are no signs of their decomposition into their individual constituents. In certain cases the fusion of ionic crystals leads to the formation of new, more complex ions. Thus it follows from cryoscopic measurements that in the dissolution of NaF in PbF_2 $\nu = \frac{1}{2}$, and in the dissolution of NaF in NaCl $\nu = 1$.[16] These results can be explained by assuming that a complex ion is formed during the fusion of sodium fluoride:

$$2NaF \rightleftarrows Na_2F^+ + F^-.$$

The formation of such autocomplexes during fusion is also possible in several other instances.

2. OPTICAL PROPERTIES OF MELTS

More complete information about the ionic composition of molten salts can be obtained by the study of optical properties.

Many authors have studied the absorption spectra of molten salts[53–65], and it has been shown that they usually absorb in the ultraviolet region. Their absorption spectra are essentially different from those of salt vapours. The latter usually exhibit absorption bands spaced over a rather wide range of frequencies and which consist of many closely spaced spectral lines. The molecular absorption spectra of melts consist of wide bands with one or two maxima. This diffuseness is linked with the small distance between the ions and the strong excitation of the electron clouds of the absorbing particles by the neighbour ions.

The absorption band of a molten salt is connected with the excitation of the outer electron in the anion and its transfer to an orbital in the field of neighbouring cations. Ionic crystals give similar spectra (Fig. 2).

The energy corresponding to maximum absorption is

$$\varepsilon_{max} = \varepsilon_i - h^2/8mr_0, \qquad (2)$$

where ϵ_i is the ionisation potential of the anion, m the mass of an electron, and r_0 the radius of the excited orbital, equal to the inter-ionic distance less the radius of the cation[63–65]. In the absorption band the optical density is usually very

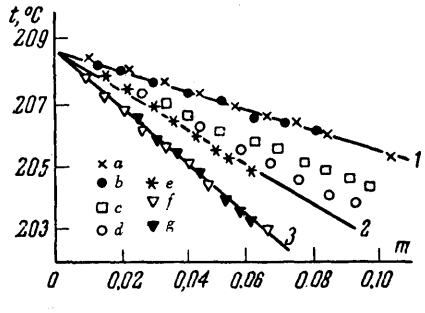


Fig. 1. Depression of the freezing point of $AgNO_3$ [26] on dissolution of: *a*) Ag_2SO_4; *b*) KNO_3; *c*) $ZnSO_4$; *d*) $PbSO_4$; *e*) $KClO_4$; *f*) $PbCl_2$; *g*) $K_2Cr_2O_7$. 1), 2), and 3) calculated curves for $\nu = 1$, 2, and 3 respectively.

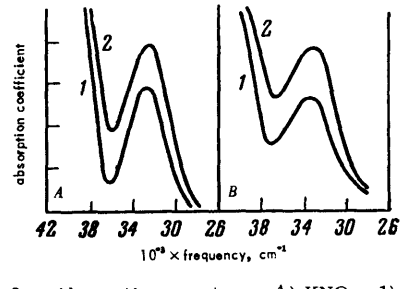


Fig. 2. Absorption spectra. *A*) KNO_3: 1) 338°, melt; 2) 333°, crystal. *B*) $NaNO_3$: 1) 308°, melt; 2) 304°, crystal.

great[59,60], so that the structure of the spectrum cannot always be established. Therefore some authors characterise the spectra by the parameters of the absorption edge (ϵ_{edge}, λ_{edge}) and not by the energy or wavelength at the absorption maximum (ϵ_{max}, λ_{max}).

There is little information about the dependence of the absorption spectrum on the nature of the salt. For the alkali metal halides, on going from Cs to Li there is a displacement of the absorption band into the violet, and on going from Cl to I, into the red side. The absorption limit of the alkali metal halides near their melting points lies at about 250–350 mμm and that of the halides of the metals of the auxiliary subgroups in the 500–600 mμm region[53,60]. A quantitative relation has been found for the alkali metal nitrates between the spectra and the cation radius:

$$\varepsilon_{max} = 3.81 + 0.33/r_+, \text{ eV}. \quad (3)$$

Probably, analogous relations exist for other salts.

A temperature dependence of the absorption spectra is predicted by Eqn. (2) and is expressed by the formula:

$$\varepsilon_{max} = \varepsilon_0 - \kappa t, \quad (4)$$

in which the coefficient κ is proportional to the coefficient of thermal expansion of the salt[55,58,60,63]. It is also noted, that for many salts the $\epsilon_{max}(t)$ curves do not have inflections near the melting point, showing that there is no complex formation[54-58,63].

There is another important parameter of molten salts — their refractive indices. Both the old work[66-68] and the more recent investigations of Bloom[13,14,69,70], Thurmond[58], and Murgulescu[71] show that the refractive indices of melts decrease linearly with rise in temperature:

$$n_t = n_0 - bt. \quad (5)$$

The dependence of the refractive indices on the nature of the salt is shown in Table 1.

It is more convenient to characterise a melt by its molecular refraction:

$$R = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{\rho}, \quad (6)$$

TABLE 1. Refractive indices of molten salts for the sodium D line[13,14].

Salt	n_0	$10^4 b$	Δt, °C
LiCl	1.590	1.60	620—750
KCl	1.667	3.50	780—810
AgCl	2.148	2.10	480—656
$CdCl_2$	1.735	0.35	590—700
$PbCl_2$	2.244	3.67	515—620

TABLE 2. Molecular refractions of salt melts (cm^3) for the sodium D line[13,70,72]

Salt	t, °C	R_{melt}	$R_{crystal}$	R for infinitely dilute solution
LiCl	650	8.20	7.59	8.42
NaCl	850	9.48	8.52	8.88
KCl	800	11.68	10.85	10.93

which for most salts is almost independent of temperature and is, to a known degree of approximation, the sum of the refractions of the individual ions. This follows, in particular, from the fact that the molecular refractions of molten salts, crystals, and infinitely dilute aqueous solutions are close to one another (Table 2).

3. RAMAN SPECTRA AND INFRARED SPECTRA OF MOLTEN SALTS

An investigation of Raman spectra and infrared spectra provides a possibility of obtaining important information about the structure of molten salts. As is well-known, in the molecular spectra produced by transitions between vibrational or rotational energy levels, there are lines which correspond to these transitions. These frequencies, which correspond to the molecular vibrational levels, determine the value of the Raman frequencies, which are equal to the sums $\nu_0 \pm \nu_i$, where ν_0 is the frequency of the exciting radiation and ν_i is that of a natural vibration of the molecule, which can be excited in scattering a beam of frequency ν_0.

Raman and infrared spectra of molten salts have been investigated only in recent years[73-81]. Bues[73-75] and Walfaren *et al.*[80] obtained Raman spectra for alkali metal nitrates, phosphates, pyrophosphates, and hydrogen sulphates, and also for zinc and cadmium chlorides, and Janz and McIntire[81] obtained those for mercury halides. Wilmshurst[76-78] and Bradbury[79] studied the vibrational spectra of various nitrates, chlorates, phosphates, and other salts with complex anions.

As an example let us consider work devoted to alkali metal nitrates. The NO_3^- ion forms a planar equilateral triangle of oxygen atoms with a nitrogen atom at the centre. Here, symmetric and antisymmetric vibrations along the bonds, giving Raman frequencies ν_1 and ν_3, two-dimensional vibrations leading to destruction of the symmetry, with frequency ν_4, and out-of-plane Raman-inactive vibrations of frequency ν_2, are possible (Fig. 3). Table 3 gives the Raman frequencies of the NO_3^- ion for crystals, aqueous solutions, and molten salts.

The values of frequencies ν_1, ν_3, and ν_4 are always very close. The spectra of melts do not contain any new frequencies. The line ν_3 for $LiNO_3$ (and $AgNO_3$) is split, which is due to the marked deformation of the NO_3^- ion. Bues[73] established that the frequency ν_1 is directly determined by

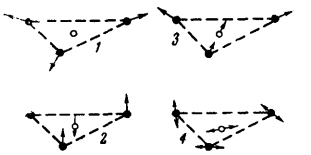


Fig. 3. Diagram of the vibrational motion of the oxygen and nitrogen atoms in the NO_3^- ion. 1) Symmetric stretching vibrations with frequency ν_1; 2) out-of-plane vibrations with frequency ν_2; 3) antisymmetric stretching vibrations with frequency ν_3; 4) bending vibrations with frequency ν_4.

TABLE 3. Combination frequencies of the NO_3^- ion.

Frequency \ Salt	$LiNO_3$			$NaNO_3$		KNO_3	
	solution	crystal	melt	crystal	melt	crystal	melt
ν_4	718	728	724	728	722	714	715
ν_3	1392	1391	1366, 1476	1387	1386	1361	1382
ν_1	1047	1086	1061	1069	1053	1050	1048

the free volume of the salt, which is calculated as the difference

$$V_f = V - \omega N, \qquad (7)$$

where N is Avogadro's number, ω the sum of the volumes of the anion and cation, and V the molar volume of the salt. The displacement of ν_1 during the fusion of the salt is explained by its expansion.

Other work on Raman and infrared spectra also showed that the structure of complex anions in a melt is analogous to their structure in crystals and aqueous solutions. The existence of complex ions in halide melts has been demonstrated[74,81].

4. SCATTERING OF X-RAYS AND NEUTRONS IN MOLTEN SALTS

During passage through a thin layer of liquid the X-rays scattered by any atom interfere with the rays scattered by its nearest neighbours, and since the number of these neighbours and the distance between them alter due to thermal motion the diffraction picture which can be observed is the result of some mean distribution of atoms and is independent of which atom was chosen at the start of the reading.

Usually the distribution of the atoms in the liquid is characterised by the function $\rho(r)$, defined as the mean number of atoms in unit volume at a distance r from the central atom. The number of atoms in the spherical layer from r to $r + dr$ equals $\rho(r)4\pi r^2 dr$.

Since in a liquid there is not a strict ordering in the position of the atoms, function $\rho(r)$ gives a continuous curve with maxima corresponding to the most probable distances. As the distance from the central atom increases, all distances become equally probable and the maxima disappear from the $\rho(r)$ curve.

Zernicke and Prins[82] and Debye[83] found a relation between the experimental scattering curve in a monatomic liquid and the radial distribution function $4\pi r^2\rho(r)$ or $\rho(r)$. This theory, which enabled an averaged picture of the distribution of particles in the liquid to be obtained from the experimental results on scattering of X-rays, was then developed by Warren *et al.*[84] for polyatomic liquids. The method of X-ray scattering was used successfully in the case of molecular liquids, particularly CCl_4 (Fig. 4). The radial distribution function for carbon tetrachloride has two narrow isolated peaks at 1.74 and 2.92 Å, corresponding to the distances between the atoms C–Cl and Cl–Cl in the CCl_4 molecule, and a series of subsequent maxima (3.5, 5.0, and 6.4 Å), corresponding to the most probable distance between the atoms of carbon and chlorine in the neighbour molecules. The form of the first two maxima shows that the CCl_4 molecule is not dissociated in the liquid. Ritter and coworkers[86-88] obtained similar results in investigating molten salts such as $AlCl_3$ and SnI_4, which are

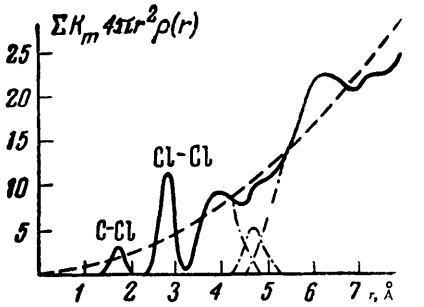


Fig. 4. Radial distribution function for CCl_4 at 25°.[85]

not electrolytes†. Experiments with molten CdI_2 showed that the coordination number 6 characteristic for the crystal‡, is retained here, but two of the iodine atoms are situated somewhat closer to the cadmium atom than are the others. This shows that CdI_2 molecules are formed in the melt as well as Cd^{2+} and I^- ions. Similarly, the distribution curve for $InCl_3$ shows that the ions In^{3+} and Cl^- and the dimer In_2Cl_6 can be formed in the melt.

In recent years there have been investigations of the scattering of X-rays in typically ionic liquids — halides, nitrates, and carbonates of the alkali metals, etc.[90-107] Fig. 5 shows a typical radial distribution curve for these melts. Despite some quantitative discrepancy between the results of different workers, they all obtained quantitatively similar results. There have been studies[89-91,96-104] devoted to the structure of alkali and alkaline earth metal halides, both with X-ray diffraction and also by neutron diffraction[102]. Alkali metal nitrates[94,95,105], molten NaOH and KOH,[93] and alkali metal carbonates and sulphates[107] have been studied. Furukawa[106] attempted to generalise the results of these investigations.

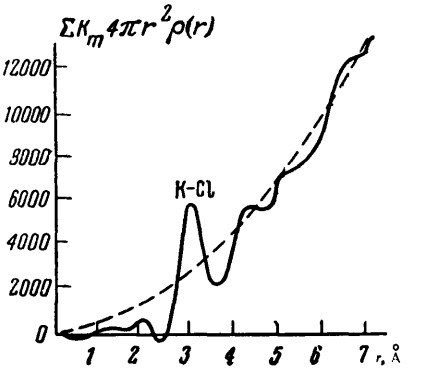


Fig. 5. Radial distribution function for molten KCl.[92]

† On fusion these salts not only give no ions but even also form dimeric molecules, for example, Al_2Cl_6.

‡ The coordination number is calculated from the area under the given peak of the radial distribution curve.

TABLE 4. Characteristics of the first coordination sphere — the M^+-X^- interaction — in melts and crystals of alkali metal halides [101,102].

Salt	Melts		Crystals		
	r'_{max}, Å	N_1	r'_{crit}, Å (t_f)	r'_{crit}, Å (20°)	N_1
LiCl	2.47	4.0	2.66	2.57	6
LiI	2.85	5.6	3.12	3.00	6
NaCl	2.88	4.7	2.95	—	6
NaI	3.15	4.0	3.35	3.23	6
KCl	3.10	3.7	3.26	3.14	6
CsCl	3.53	4.6	3.57	3.57	6(8)
CsI	3.85	4.5	3.94	3.95	6(8)

The maxima on the radial distribution curve were in all cases close to the corresponding inter-ion distances in the crystals (r_{cryst}), but the coordination numbers in the first (M^+-X^-) and second (M^+-M^+, X^-X^-) coordination spheres (N_1, N_2) are considerably less than in the crystal lattices (Table 4).

It is interesting that the values of r'_{max} for melts are usually somewhat less than in crystals close to the melting point — the ions in melts are more closely packed on account of the break-down of the symmetry of the field. The considerable breadth of the first peak shows that the true distance between the ions M^+-X^- can be also much greater and less than r'_{max}. The closest possible distance between ions in melts is close to the M^+-X^- distance in gaseous molecules.

The absence of accurately determined values of the inter-ion distances in melts implies that the ions associate in separate groups, between which are distributed unoccupied voids and vacancies. In the small groups the ions are more closely packed, as in gaseous molecules; the coarse groups represent as it were fragments of the crystal lattice. These groups are in dynamic equilibrium, continuously forming and decomposing.

The second peak on the radial distribution curves is still more diffuse than the first. The sharpest second peak, that is, the greatest indication of uniformity in M^+-M^+ and X^-X^- distances and the degree of ordering of the melt structure are observed for salts with a small cation (lithium and sodium halides). In potassium and caesium salts the second peak is very diffuse, which is evidence of a less regular structure.

There are interesting prospects in studying the structure of molten salts, not only by the methods considered above, but also by γ-radiation absorption [108] and nuclear magnetic resonance [79,109]. However, there has not yet been proper development in these directions.

5. DENSITY AND MOLAR VOLUME

Investigation of the nature of molten salts and their practical application necessitate a knowledge of their physical properties, including density.

Melt densities are measured either pyknometrically or by hydrostatic weighing [5,2]. The results obtained before 1939 — and particularly the work of Jaeger [110,111], Klemm [112,113], and others [114-119] cannot now be considered sufficiently reliable. The most reliable data on densities of the alkali metal halides have been published by Yaffe and van Artsdalen [120]; they fit (see Table 5) Mendeleev's linear equation:

TABLE 5. Densities of molten alkali metal halides in g cm^{-3} — parameters of Eqn. (8).

Salt	a	$10^3 b$	Salt	a	$10^3 b$	Salt	a	$10^3 b$
LiCl	1.7660	0.4328	NaI	3.3683	0.9191	RbBr	3.4464	1.0718
LiBr	2.8878	0.6520	KCl	1.9767	0.5831	RbI	3.6377	1.1435
LiI	3.5397	0.9176	KBr	2.7333	0.8252	CsCl	3.4782	1.0650
NaCl	1.9911	0.5430	KI	3.0985	0.9557	CsBr	3.9109	1.2234
NaBr	2.9518	0.8169	RbCl	2.8799	0.8832	CsI	3.9179	1.1834

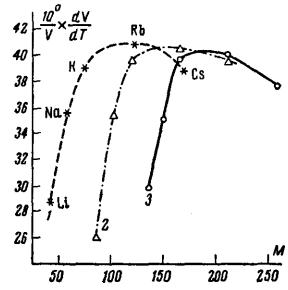


Fig. 6. Dependence of the volume coefficient of expansion of molten salts at the melting point on the molecular weight [120]: 1) chlorides; 2) bromides; 3) iodides.

$$\rho = a - bt. \qquad (8)$$

Careful measurements have been made [121,122,130,131] of the density of alkali metal nitrates and carbonates. There is less systematic information about the density of salts of the alkaline earth metals and the metals of the auxiliary subgroups, particularly $MgCl_2$, [123,124] $CaCl_2$, [125] and $BaCl_2$, [126] mercury halides [81,128], alkaline earth fluorides [127], and various other salts [132-135]. In all cases Eqn. (8) is obeyed.

The volume coefficients of thermal expansion of molten salts:

$$\alpha = \frac{1}{V}\times\frac{dV}{dt} = -\frac{1}{\rho}\times\frac{d\rho}{dt} = \frac{b}{\rho}, \qquad (9)$$

and their molar volumes:

$$V = M/\rho. \qquad (10)$$

are entirely determined by their internal structure. In particular, it is characteristic of the alkali metal halides that the coefficients of thermal expansion of the lithium and sodium salts are relatively small, whereas those of the potassium, rubidium, and caesium salts are relatively large and almost independent of the nature of the salt (Fig. 6). This difference is probably connected with the above-mentioned expanded structure for salts with a large cation.

Comparison of the molar volumes of molten salts [5,16,21] shows that those of typically ionic melts are relatively small, whereas those of molecular liquids (CCl_4, $SiCl_4$, etc.) are large. It is also noted that salts formed by metals of auxiliary subgroups have smaller molar volumes than are usually associated with complex formation on melting.

6. COMPRESSIBILITY

The compressibility of molten salts has been determined in practice from measurements of the velocity of ultrasonic waves (u_L), which is related with the adiabatic compressibility by the relation:

$$\beta_s = -1/V(\partial v/\partial p)_s = \rho^{-1}u_L^{-2}. \quad (11)$$

To calculate the isothermal compressibility information about the isobaric (C_p) and isochoric (C_V) heat capacities of the melt:

$$\beta_T = -\frac{1}{V}\left(\frac{dV}{dp}\right)_T = \beta_s \times \frac{C_p}{C_V}, \quad (12)$$

is required.

There have been several measurements of ultrasonic velocity in molten salts[136,142] and it has been shown that melt compressibilities depend on temperature and increase with it (Table 6). For salts of a given type the compressibility also increases with the molecular weight.

The information about compressibility and ultrasonic velocity in salt melts obtained by Bockris and Richards[136] and other authors[139-141] differ considerably. In particular,

TABLE 6. Isothermal compressibility of alkali metal halides, 10^{12} cm^2 dyn^{-1}.[136]

Salt	700°	800°	900°	1000°	Salt	700°	800°	900°	1000°
LiCl	21.1	24.7	28.6	33.0	KCl	—	38.4	45.7	54.7
LiBr	25.8	29.4	33.6	38.4	KBr	—	43.8	52.1	62.1
NaCl	—	28.7	33.8	40.0	KI	49.9	59.9	72.0	87.3
NaBr	—	33.6	38.6	44.9	CsCl	42.9	51.2	62.7	76.3
NaI	40.0	47.3	65.6	65.6	CsBr	55.8	67.1	82.7	103.1

Bockris and Richards[136] state that the ultrasonic velocity is a linear function of $T^{\frac{1}{2}}$, whereas others[139,140] give T. The reason for this discrepancy is unexplained.

7. SURFACE TENSION

The surface tension of molten salts at their phase boundary with a vacuum or inert gas has been measured by the methods of lifting a ring, maximum bubble pressure, etc.[143]. The temperature dependence of surface tension is usually expressed by the linear equation[111]:

$$\sigma = a - bt, \quad (13)$$

although in some cases a quadratic interpolation formula has to be used. The measurements of the surface tension of molten salts made between 1900 and 1930 (for example, Jaeger[111], Arndt and Löwenstein[114]) are inaccurate, since the methods used in these works are not completely reliable. However, the results of later investigations often differ considerably from one another. Of work in recent years, reference may be made to measurements of the surface tension of halides[145-157,161], carbonates[122], and nitrates[145,158-160]. Table 7 summarises the most reliable results and shows that the surface tension depends greatly on the nature of the salt. According to Semenchenko's

TABLE 7. Surface tension of molten salts — coefficients of Eqn. (13).

Salt	a	b	Reference	Salt	a	b	Reference
NaCl	168.4	0.068	147	$CaBr_2$	153.1	0.0459	154
NaBr	140.9	0.056	153	CaI_2	98.7	0.0174	154
NaI	147.4	0.090	145	$SrBr_2$	178.0	0.0439	154
KCl	156.3	0.075	147	SrI_2	134.8	0.0383	154
KBr	142.2	0.072	145	$BaCl_2$	225.0	0.078	156
KI	138.7	0.087	145	$PbCl_2$	192.1	0.110	145
$MgCl_2$	74.0	0.01	147	$CdCl_2$	95.6	0.021	153
$CaCl_2$	178.0	0.038	149	AgCl	202.2	0.052	153

theory, the surface tension of melts should be determined by the electrostatic interaction of the particles, that is, in the final reckoning, on their generalised moment $\mu = z/r$.[162,163] This probably explains the decrease in the surface tension of the alkali metal halides with increasing radii of cation and anion[163,164]. Salts of the alkaline earth metals show the reverse relation, which is thought[163] to be usually explained by the formation of autocomplexes on melting. However, this explanation cannot be considered exhaustive.

The parachor, the equation for which is given by Bachinskii[165]:

$$\Pi = \frac{M}{\rho_{liq} - \rho_{solid}}\sigma^{1/4}, \quad (14)$$

for molten salts usually varies only slightly with temperature. The problem whether the parachors of salts are the sums of the parachors of the individual ions has not been studied.

8. HEAT CAPACITY

The molar heat capacities of molten salts at constant pressure are almost independent of temperature. Values of C_p have been tabulated by Kubaschewski and Evans[166] and elsewhere; more recent values are available[167-169]. Table 8 gives values of C_p and the change of heat capacity on melting:

$$\Delta C_p = (C_p^{liq})_f - (C_p^{solid})_f. \quad (15)$$

It is seen that the heat capacity of molten salts is (within an accuracy of 5–10%):

$$C_p \approx 8\nu \text{ cal deg}^{-1} \text{ mole}^{-1}, \quad (16)$$

where ν is the number of ions formed by one molecule of salt.

However, this rule is inapplicable to salts with polyatomic anions. At the same time it is valid for salts such as $MgCl_2$, $PbCl_2$, etc., and this does not agree with the assumptions about the formation of autocomplexes in these melts.

TABLE 8. Heat capacity C_p^{liq} and change in heat capacity during fusion ΔC_p for salts (cal deg^{-1} mole^{-1}).[166-169]

Salt	C_p	ΔC_p	Salt	C_p	ΔC_p	Salt	C_p	ΔC_p
LiCl	15.5	1.5	$MgCl_2$	22.1	2.0	$PbCl_2$	24.9	2.6
NaCl	15.9	0.6	$CaCl_2$	24.7	4.35	$PbBr_2$	26.3	5.6
KCl	16 0	1.35	$SrCl_2$	26.2	5.1	PbI_2	32.3	11.7
RbCl	15.3	1.3	$CdCl_2$	26.7	4.9	$BiCl_3$	34.3	8.2

For salts of one type there is also some increase in heat capacity with molecular weight. There is only approximate information about the jumps in heat capacity on melting. It must also be taken into account that the rise starts much below the melting point of the salt[170].

9. HEATS OF VAPORISATION AND VAPOUR PRESSURE

Usually the heat of vaporisation and boiling point of salts are known only approximately. The heat of vaporisation is determined either calorimetrically or by measuring the temperature dependence of vapour pressure[171]. Heats of vaporisation of salt melts have been published[166,172-176].

Salts with a strongly ionic type of bond (alkali metal halides) are typified by a higher boiling point and heat of vaporisation, and those with a considerable covalent bond fraction (for example, $BeCl_2$, $ZnCl_2$) by a lower one.

The alkali metal halides have been most fully studied. The entropy of vaporisation of these salts ($\Delta S^\circ_{vap} = L^\circ_{vap}/T_{boil}$) is 25-30 cal deg^{-1} mole^{-1}, which is evidence that they have similar degrees of ordering. Pauling[177] showed that the heats of vaporisation and melting and the melting and boiling points of the alkali metal halides should exhibit a regular dependence on the inter-ionic distance in the crystals, since all these properties are associated with the lattice energy and this is determined by the sum of the ionic radii. However, the properties of real salts depart considerably from the expected relation. Pauling considers that these anomalies are due to the mutual repulsion of large anions which play a considerable part in lattices with small cations (Li and Na salts).

Investigations of the vapour pressure of molten salts have been reviewed[166,173,178], but recently new results about the composition of the vapours of inorganic salts have been obtained which compel critical consideration of the earlier measurements. Thus it was shown[179-185] that in alkali metal halide vapours there is a large proportion of dimers $(MX)_2$ and trimers $(MX)_3$. Formation of polymers was also found in ThF_4,[176] $FeCl_2$,[186] CuCl,[187] AgCl,[188] and other salt vapours. The heats of dissociation of the polymeric molecules are comparable with the heats of vaporisation.

The polymerisation in the salt vapours leads to a change in their molecular weight, a knowledge of which is necessary if the vapour pressure is determined by the vaporisation method, the effusion method, etc. Therefore the old data obtained by such methods[189,190] are incorrect. The most reliable absolute methods of determining vapour pressure — the static and the boiling point[171,191] methods — were used in references 192-203 and 174, 176 respectively.

TABLE 9. Vapour pressures of molten salts in mmHg[166,179,198].

Salt	$-A$	$-B$	D	Salt	$-A$	$-B$	D	Salt	$-A$	$-B$	D
LiF	14500	4.02	23.56	KCl	11023	3.526	20.80	CsBr	10270	3.52	20.65
LiCl	10760	4.02	22.30	KBr	10050	3.0	18.67	CsI	10230	3.52	20.70
LiBr	10170	3.52	20.55	KI	14560	3.52	20.41	$BeCl_2$	6340	—	10.64
LiI	11110	3.52	21.70	RbF	11190	3.52	20.90	$MgCl_2$	10840	5.03	25.53
NaF	13260	3.52	21.31	RbCl	10300	3.0	18.77	$ZnCl_2$	8440	1.50	16.61
NaCl	11495	3.52	20.93	RbBr	10220	3.52	18.80	$CdCl_2$	9183	5.04	25.91
NaBr	10500	3.0	18.81	RbI	10280	3.52	20.64	$PbCl_2$	10168	6.65	31.73
NaI	10740	3.52	20.96	CsF	9850	3.52	20.52	$FeCl_2$	9476	5.23	23.65
KF	11150	3.52	20.60	CsCl	10770	3.52	18.14	$BiCl_3$	5980	7.04	31.38

Applying the Clausius-Clapeyron equation under conditions far from the critical, and assuming that the vapour will behave as an ideal gas, but that the temperature dependence of the heat of vaporisation is expressed by the relation $dL_{vap}/dT = \Delta C_p$, it is easy to obtain

$$\log p = \frac{A}{T} + B \log T + D, \qquad (17)$$

where $A = -L_{vap}/4.575$, $B = \Delta C_p/R$, ΔC_p is the difference between the heat capacities of liquid and vapour, L°_{vap} is the heat of vaporisation at the boiling point, and D a constant. In some instances the term $B \log T$ can be neglected§.

Eqn. (17) is usually employed to express the experimental results, the coefficients A, B, and D being determined empirically. Table 9 gives their values for several salts.

In certain cases[179] attempts have been made to calculate theoretically the coefficient $B = \Delta C_p/R$ from the experimental values of C_p^{liq} and the calculated C_p^{vap}. In this, the values of B should evidently be close within a particular series of salts. As Table 9 shows this requirement is fulfilled in many instances.

10. HEATS OF FUSION OF IONIC CRYSTALS

The fusion of crystals and the thermodynamic parameters of this process (T_f, L_f) are determined by the lattice energy, and thus in the end by the radii, polarisability, ionic charges, and the structure of the electron clouds of the ions. Heats of fusion are determined by calorimetric and cryoscopic methods and by measurement of the temperature coefficients of the e.m.f. of chemical cells[166,205,206]. The melting points and heats of fusion of salts are given in various reviews[166,172,207,208]. Recently these quantities have been determined[167,169,192,209-215], but the results obtained are often quite contradictory.

Table 10 gives the parameters for the fusion of alkali metal halides. An analysis of it and of the other available data suggests the following conclusions[5]:

TABLE 10. Heats (kcal mole^{-1}) and entropies (e.u.) of fusion of alkali metal halides[209].

Salt	L_f	ΔS_f	Salt	L_f	ΔS_f	Salt	L_f	ΔS_f
LiF	6.47	5.77	NaBr	6.24	6.12	RbF	6.15	5.76
LiCl	4.76	5.39	NaI	5.64	6.04	RbCl	5.67	5.70
LiBr	4.22	5.13	KF	6.75	5.97	RbBr	5.57	5.77
LiI	3.50	4.72	KCl	6.34	6.08	RbI	5.27	5.73
NaF	7.78	6.14	KBr	6.10	6.06	CsF	5.19	5.23
NaCl	6.69	6.23	KI	5.74	5.02	CsCl	4.84	5.27
						CsBr	5.64	6.20
						CsI	5.64	6.27

§ Eqn. (17) can be derived from kinetic considerations[204]. Since the number of vacancies in a crystal[22] is $N = \alpha n_0 \exp(-L^\circ_{vap}/RT)$, where n_0 is the number of pairs of ions in 1 cm^3 and α a constant, we obtain for the density of the vapour

$$\rho = NM/N_A = \alpha \rho_{crit} \exp(-L^\circ_{vap}/RT),$$

where $\rho_{crit} = n_0 M/N_A$. And since $p = \rho_n RT/M$ and $\rho/M = 1/V$, then $\ln p = \ln \alpha RT - \ln V - L^\circ_{vap}/RT$, where p is expressed in bars and R in J mole^{-1} deg^{-1}.[204]

1. Crystals with doubly-charged ions melt at a higher temperature than those formed by similar singly-charged ions.

2. In a series of salts with the same cation, the melting point falls as the anion radius increases.

3. The melting points of crystals containing cations with 18-electron and incomplete clouds are lower than those of crystals with ions of similar radii but having inert gas shells.

4. As the bond covalency increases the melting point of the salt decreases. In particular, crystals with layer lattices (CdI_2, $MgCl_2$, $ZnCl_2$) have low melting points. The fall in melting point on going from the fluorides to the iodides of the alkaline earth metals is also explained by the increase in the degree of covalency of the bond.

5. Salts with molecular lattices have very low melting points and are not electrolytes, for example $SiCl_4$(t_f = 68°), $TiCl_4$ (-30°), $PbCl_4$ (-15°), etc. However, the same elements in a lower oxidation state give ionic salts with high melting points: $TiCl_2$ (400°), $PbCl_2$ (501°), etc.

6. The melting point of salts is greatly dependent on the crystal lattice structure. Pauling[117] noted that the low melting points of lithium salts are explained by the small radius of the Li^+ ion, as a result of which anion–anion contact occurs in the lattice and the mutual repulsion of the anions reduces the lattice energy. A linear relationship between the melting point and the ratio of the radii of the ions has been reported[216] for alkali metal halides.

The entropies of fusion for the alkali metal halides $\Delta S_f = L_f/T_f$ are close to 6 e.u. mole^{-1}, which corresponds to 3 e.u. g-ion^{-1}. Remembering that the entropy of fusion of the monatomic noble gases is also close to 3 e.u. × × g-atom^{-1}, this can be considered as confirmation of the purely ionic structure of the melts. The marked departure from this value for some salts is usually considered as an argument in support of the hypothesis concerning the formation of autocomplexes in the fusion of the salts.

11. VISCOSITY

The viscosity of molten salts has been determined by use of both static (falling sphere[217,218]) methods, the capillary flow method[217,219], and also dynamic methods (for example, measurement of the damping of harmonic oscillations of a body of rotation suspended in the melt by an elastic filament[217-220]). Dynamic methods usually introduce errors on account of the impossibility of allowing for all the factors which affect the measurement[217]. Static methods are generally more reliable but serious difficulties are encountered when working with melts. Hence completely reliable and systematic data on the viscosity of molten salts are still lacking.

The temperature dependence of viscosity is usually expressed by the equation[22,221-223]:

$$\eta = A_\eta \exp(E_\eta/RT). \qquad (18)$$

In the theory of absolute reaction rates[221,224] the preexponential factor is given by:

$$A_\eta = 1.09 \times 10^{-3} \rho^{2/3} T^{3/2} / M^{1/6} \Delta E_{vap}, \qquad (19)$$

where $\Delta E_{vap} = L_{vap} - RT$ is the energy of vaporisation, and M the molecular weight. Panchenkov[225,226], starting from the assumption that the transfer of momentum between the particles of the liquid takes place during separation of the particles from one another, deduced the equation:

$$\eta = A\rho^{4/3} T^{1/2} \exp(2\Delta E_{vap}/\gamma RT)[1 - \exp(-2\Delta E_{vap}/\gamma RT)], \qquad (20)$$

where γ is the coordination number and A a constant.

Panchenkov's equation was applied successfully to the viscosity of melts of NaCl and $NaNO_3$, the constants γ and A being determined empirically[225].

Equation (18) is usually employed in practice[19,227], the coefficients being found empirically. Table 11 gives values of the viscosity at $1.1T_f$ °K and the parameters $A\eta$ and $E\eta$, calculated for various salts from published results.

TABLE 11. Viscosity of molten salts.

Salt	$10^4 A_\eta$, P	E_η, kcal × × mole^{-1}	$10^2 \eta_{1.1T_f}$, P	Reference	Salt	$10^4 A_\eta$, P	E_η, kcal × × mole^{-1}	$10^2 \eta_{1.1T_f}$, P	Reference
LiCl	1.64	8.35	1.27	274	AgI	15.8	5.13	2.90	230
NaCl	2.11	9.10	1.02	228	$MgCl_2$	35.5	5.25	4.08	233
KCl	4.29	7.40	1.10	228	$CaCl_2$	86.3	3.70	4.34	150
LiBr	7.07	5.30	1.38	227	$CdCl_2$	22.9	3.98	2.04	231
NaBr	2.85	8.00	1.06	229	$CdBr_2$	21.9	4.30	2.30	232
KBr	2.92	7.96	1.14	229	$PbCl_2$	5.37	6.77	3.05	231
RbBr	12.07	4.73	1.15	227	$PbBr_2$	7.95	6.25	3.47	232
AgCl	7.64	5.30	2.13	230	$AgNO_3$	18.2	3.08	2.06	234
AgBr	11.7	4.85	2.71	220		—	—	—	—

Equation (18) is usually employed in practice[19,227], the coefficients being found empirically. Table 11 gives values of the viscosity at $1.1T_f$ °K and the parameters $A\eta$ and $E\eta$, calculated for various salts from published results.

The relation between viscosity and the nature of the salt has been insufficiently studied. Several investigators[223,235] note a relation between the activation energy for viscous flow $E\eta$ and the melting point. In particular, for alkali metal halides the ratio $E\eta/L_f$ is close to 1.2. Melts of the halides of bivalent metals have a much greater viscosity, which is probably due to the appreciable fractions of covalent and van-der-Waals interactions. Bachinskii[236] considers that viscosity is not a direct function of temperature but is connected with the molar volume of the liquid:

$$\eta = \frac{C}{V - \omega}, \qquad (21)$$

where C and ω are constants, $V - \omega$ having the physical interpretation of the volume available for the motion of the particles in the liquid, that is, the free volume. The applicability of Eqn. (21) to molten salts has been demonstrated[19,237], the difference $V - \omega$ usually being 2–6 cm^3 × × mole^{-1}, and ω always considerably exceeding the volume of the solid at the melting point. The constant C depends on the radii of the ions[19]. Ideas about the relation between viscosity and the free volume of a molten salt have also been developed elsewhere[139,140].

12. DIFFUSION

Information about coefficients of self-diffusion in molten salts have only been obtained in recent years thanks to the use of radioactive isotopes. Table 12 gives the values of the empirical coefficients of the exponential equation:

$$\Delta = \Delta_0 \exp\left(-\frac{E_\Delta}{RT}\right), \qquad (22)$$

calculated from the experimental results of various authors. Many investigators[238-240,242,248] have tried to apply to salts the Stokes–Einstein equation:

$$\Delta = \frac{kT}{6\pi\eta r_i}, \qquad (23)$$

TABLE 12. Coefficients of self-diffusion of ions in molten salts.

Salt	$10^3\Delta_0^+$, $cm^2\ s^{-1}$	E_Δ^+, kcal $mole^{-1}$	$10^3\Delta_0^-$, $cm^2\ s^{-1}$	E_Δ^-, kcal $mole^{-1}$	Reference
NaCl	3.36	7.65	3.02	8.37	238, 239
RbCl	2.51	8.00	1.67	7.42	238
CsCl	1.73	7.30	2.46	7.82	238
NaI	0.63	4.00	0.43	4.41	238
TlCl	0.76	4.60	—	—	244
$ZnBr_2$	79.0	16.0	—	—	243
$PbCl_2$	0.773	6.75	0.895	7.10	241, 242
$LiNO_3$	2.47	5.50	1.95	6.32	246
$NaNO_3$	1.29	4.96	0.90	5.07	245, 246
KNO_3	1.32	5.52	1.42	5.75	246
$CsNO_3$	1.13	5.60	1.78	6.27	246
$AgNO_3$	0.49	3.72	0.31	3.84	246
Na_2CO_3	0.192	(900°)	0.279	(900°)	247

where r_i is the ionic radius. However, comparison of Tables 12 and 11 shows that Eqn. (23) is scarcely applicable, owing to the absence of the required equality between the activation energies for the diffusion of cations and anions and a regular connection between Δ_0 and the radii of the ions¶.

The Nernst–Einstein equation:

$$\Lambda = \frac{F^2}{RT}(\Delta^+ + \Delta^-), \qquad (24)$$

where Λ is the molar conductivity, is also probably inapplicable to melts. This question has been studied[238-240,248] and the inapplicability of Eqn. (24) was attributed to the interaction of ions in the diffusion of ion pairs.

Recently Panchenkov[249] derived an equation connecting the diffusion coefficients with the molar volume, heat of vaporisation, and coordination number of the liquid. The possibility of using this equation for molten salts has not been verified.

Several investigators[22,250-252] link the coefficients for the diffusion of ions with the free volume of the liquid. In particular, Cohen and Turnbull[250] derive the equation:

$$\Delta = gau\exp(-\gamma V/V_f), \qquad (25)$$

where g and γ are constants, a is the diameter of the molecule, u the gas kinetic velocity, V the molar volume, and V_f the free volume. This equation has been verified for melts[238,251], but the results of various authors contradict one another. Bockris[238] considers that the Fürth–Frenkel' vacancy theory is more applicable to salts (see below).

13. ELECTRICAL CONDUCTIVITY

There have been many papers devoted to the electrical conductivity of molten salts; a review of the early investigations was given in monograph by Lorenz[253]. The later works, including those of Jaeger and Kapma[254], Sandonini[117], Goodwin and Mailey[255], and Arndt[256,257], were discussed by Biltz and Klemm[258] and then by Drossbach[259] and Antipin *et al.*[21] The results of these workers can now be considered only as approximate.

The method of measuring the electrical conductivity of salt melts has been described[120,125,260-268]. The most important point here is the necessity of using a very sensitive a.c. bridge which permits the compensation of both ohmic and capacitative components of the cell impedance over a wide range of frequencies. The electrical conductivity of the alkali metal halides was determined[120,149,150,254,258,261,269-278], but the results often do not agree with one another. The most reliable values have been given[120]. The electrical conductivity of the alkaline earth halides has been measured[123,126,149,150,279-283] and the halides of the auxiliary subgroup metals[81,125,130,279,284-288] have been studied. Bockris *et al.* give the most reliable data[279]. The electrical conductivity of nitrates[130,131,134,268,285,289-292], carbonates[122], pyrophosphates[133], etc. have also been studied.

The temperature dependence of the electrical conductivity of molten salts is usually expressed by Kohlraush's formula[293]:

$$\kappa = a + bt + ct^2, \qquad (26)$$

which usually fits the experimental data well, often without the quadratic term (that is, with $c = 0$). However, this formula has no physical basis.

Frenkel'[22] showed that the equation:

$$\Lambda = \kappa M/\rho = A_\Lambda \exp(-E_\Lambda/RT), \qquad (27)$$

should hold for molar conductance. This idea was developed by Eyring, who used the theory of absolute reaction rates to derive the relationship[120]:

$$\Lambda = 5.18\times10^{18}(D+d)d_i^2\exp(\Delta S^*/R)\exp(-\Delta H^*/RT), \qquad (28)$$

where D is the dielectric constant of the melt, d_i half the inter-ion distance, and ΔS^* and ΔH^* the entropy and heat of activation of the migration. For the alkali metal halides ΔS^* is 6.0–8.5 cal $mole^{-1}\ deg^{-1}$. Formula (26) corresponds to the conductance of a single ion. In the general case, according to Frenkel'[22]:

$$\Lambda = a_1\exp(-E_1/RT) + a_2\exp(-E_2/RT), \qquad (29)$$

and this transforms into (26) when $E_1 \simeq E_2$, $E_1 \gg E_2$, or $E_1 \ll E_2$. Analogously to (26) we can write:

$$\kappa = A_\kappa\exp(-E_\kappa/RT), \qquad (30)$$

in which[294]:

$$E_\Lambda = E_\kappa + RT^2\alpha. \qquad (31)$$

The measurements of Yaffe and van Artsdalen[120] showed that at least for the alkali metal halides $\Delta H^* = f(T)$ and Eqns. (26) and (30) are not obeyed. For example, the true relations are:

for LiBr,

$$\Lambda = \exp(5.5709 - 694.83/T + 0.43261\times10^{-3}T),$$

and for CsBr,

$$\Lambda = \exp(9.4173 - 3980.3/T + 1.1528\times10^{-3}T),$$

etc., but these have no theoretical basis. At the same time many authors consider that Eqns. (26) and (30) are obeyed by most molten salts, at least in the range of temperatures studied[122,131,284].

The relation between Λ or κ and viscosity is interesting. Walden's well-known rule[295]:

$$\Lambda\eta = \text{const}, \qquad (32)$$

evidently does not apply to molten salts. This was shown, for example, by Erdey-Gruz[296], who attributed the inapplicability of Eqn. (32) to the possibility of a Grotthus mechanism of migration. Such an explanation cannot withstand criticism, since the electrical conductivity of a molten salt

¶ It is possible, however, that this discrepancy is due to experimental errors (for example, see Bockris and coworkers[238-240]).

calculated by the Nernst–Einstein equation (24) is always greater than the actual value. For the same reason the hypothesis of Abraham and Brenet[297] about the existence of considerable electronic conductivity in pure molten salts cannot be accepted.

Barzakovskii[21] considers that since the Stokes–Einstein equation (23) forms the basis of the Walden formula, the inapplicability of formula (32) is explained by the inapplicability of (23) for melts. Actually the matter is complicated because the mechanisms of viscous flow and migration in molten salts are not identical. As Frenkel' notes, in the first case the large ions play the chief part, and in the second the smaller ions.

Several investigators have discussed the applicability to melts of the formula[275,298-301]:

$$\Lambda^n\eta = \text{const}, \qquad (33)$$

but as Delimarskii and Markov showed[7], Eqn. (33) is the simple consequence of the exponential temperature dependence of Λ and η and completely fails to reveal a connection between these quantities.

Comparison of the data shown in Tables 14 and 13 shows a significant relation between the conductivity of melts and the nature of the salt. Biltz and Klemm[258] associate the value of Λ at an appropriate temperature (for example, at a temperature equal to 1.1 T_f, °K) with the position of the cation of the salt in Mendeleev's table. The electrical conductivity of the melt increases with the ionic nature of the bond. On the other hand, salts with a high fraction of covalent bonding (such as the mercury halides) are poor conductors. Biltz[302] noted that the temperature coefficient of conductivity also increases with the covalency of the bond.

TABLE 13. Coefficients of the electrical conductivity equation, Eqn. (26).[120]

Salt	a	10^2b	$10^{4.6}c$	Salt	a	10^2b	$10^{4.6}c$
LiCl	+0.5285	1.1250	4.554	KI	−1.7100	0.6408	1.965
LiBr	+1.0095	0.7834	2.057	RbCl	−1.8097	0.6176	2.1985
LiI	−0.5780	1.348	9.695	RbBr	−3.0505	0.9104	4.510
NaCl	−0.1697	0.6259	1.953	RbI	−1.0798	0.4055	1.6305
NaBr	−0.4392	0.5632	1.572	CsCl	−1.8023	0.5628	1.765
NaI	−0.8202	0.5940	1.976	CsBr	−1.4137	0.4255	1.228
KCl	−1.7491	0.738	3.000	CsI	−1.3313	0.3958	1.305
KBr	−3.2261	1.0124	4.828	—	—	—	—

TABLE 14. Electrical conductivity of molten halides from published results[130,260,279,281].

Salt	$\chi_{t,t}T_f$	a	10^2b	Salt	$\chi_{t,t}T_f$	a	10^2b	10^6c
$BeCl_2$	0.0095	−0.0385	0.01	BaI_2	0.896 *	−0.932	0.229	—
$MgCl_2$	1.196	−0.424	0.200	$ZnCl_2$	0.035	0.550	−0.292	4.0
$MgBr_2$	0.869	−0.690	0.925	$ZnBr_2$	0.050	0.550	−0.293	4.0
MgI_2	0.671*	−0.735	0.1765	ZnI_2	0.105 *	0.302	−0.202	3.26
$CaCl_2$	2.480	−1.450	0.445	$CdCl_2$	2.075	0.510	0.240	—
$CaBr_2$	1.467	−0.896	0.309	$CdBr_2$	1.220	−0.080	0.200	—
CaI	1.392*	−0.350	0.193	CdI_2	0.325	−0.660	0.215	—
$SrCl_2$	2.410	−1.360	0.384	$HgCl_2$	$5.12\cdot10^{-5}$	$-7.32\cdot10^{-5}$	$3.75\cdot10^{-7}$	—
$SrBr_2$	1.091	−1.150	0.309	$HgBr_2$	$2.27\cdot10^{-4}$	$-3.31\cdot10^{-4}$	$1.95\cdot10^{-6}$	—
SrI_2	0.864	−0.725	0.227	HgI_2	$2.41\cdot10^{-3}$	$5.82\cdot10^{-3}$	$1.1\cdot10^{-4}$	—
$BaCl_2$	2.452	−1.378	0.355	$PbCl_2$	1.819	−0.889	0.470	—
$BaBr_2$	1.488	−1.120	0.270	AgCl	4.074	2.154	0.366	—

* χ is given for MgI_2 at 800°, CaI_2 at 900°, SrI_2 at 700°, BaI_2 at 800°, and ZnI_2 at 490°.

The low electrical conductivity of molten salts is often considered as an index of the formation in the melt of low-mobility autocomplexes and neutral molecules. However, this type of hypothesis requires confirmation by analysis of all the properties of the molten salt.

14. TRANSPORT NUMBERS

Various methods based on the use of radioactive isotopes are employed in determining the transport numbers of the ions in molten salts, but the analysis of the results thus obtained presents difficulties if one is speaking of the transport numbers in the pure salt. The transport numbers in an inert solvent are determined as the ratios:

$$\left.\begin{aligned} t_+ &= \frac{\Lambda^+}{\Lambda_+ + \Lambda_-} = \frac{u_+}{u_+ + u_-} \\ t_- &= \frac{\Lambda_-}{\Lambda_+ + \Lambda_-} = \frac{u_-}{u_+ + u_-} \end{aligned}\right\}, \qquad (34)$$

where Λ_i are the ionic conductivities, u_i the mobilities, that is, the rates of movement of the ions under unit potential gradient. In aqueous solutions the rate of motion of the ions is considered relative to the immovable mass of solvent. Understandably, it is more difficult to determine the rate in a melt. In this connection several authors[303-305] have generally denied the possibility of determining transport numbers in molten salts on account of the absence of a "coordinate system", whose part in solvents and crystals is played by the solvent or the lattice. Sundheim[304], starting from the principle of conservation of momentum and applying it to the electrolysis process, derived a formula relating the transport numbers to the masses of the ions:

$$t_- = \frac{M_+}{M_+ + M_-}, \quad t_+ = \frac{M_-}{M_+ + M_-}. \qquad (35)$$

This theory was supported by various investigators[306-308] but disputed in other papers[11,309]. Esin *et al.*[310] showed the fallibility in Sundheim's theory, pointing out that in molten salts the change in momentum is not zero[311] because of internal friction. Esin showed further that in the melt the transport of charges is effected not by the whole mass of the ions, but only by the small fraction of them which have sufficient energy (the activation energy of migration). These ions at any particular moment move relative to the melt, which acts as the same "coordinate system" as the crystal lattice in solid salts. Laity[312] developed a formal theory of migration and diffusion in molten salts based on a consideration of the inter-ion coefficients of friction.

Mulcahy and Heymann[313] proposed an empirical equation for the molar conductance of alkali metal halides close to the melting point†:

$$\Lambda = 105(1/r_+ + 1/r_-), \qquad (36)$$

where r_i is the ionic radius. From this equation the relationship found by Duke[314,315]‡ can be easily obtained:

$$t_- = \frac{r_+}{r_+ + r_-}; \quad t_+ = \frac{r_-}{r_+ + r_-}, \qquad (37)$$

which often agrees well with experiment.

† Markov and Delimarskii[316] showed that another relationship is more accurate:

$$\Lambda = \text{const}\,(1/r_+^2 + 1/r_-^2).$$

‡ Duke obtained his equations by comparing the force of internal friction and the electric field $zeE = kr_i u_i$, whence $r_+/r_- = u_-/u_+$.

TABLE 15. Transport numbers in molten salts.

Salt	$\frac{r_+}{r_+ + r_-}$	t_-	Reference	Salt	$\frac{r_+}{r_+ + r_-}$	t_-	Reference	Salt	$\frac{r_+}{r_+ + r_-}$	t_-	Reference
LiCl	0.25	0.25	323	TlCl	0.47	0.50	314 } 315 }	$LiNO_3$	0.18	0.16	314
NaCl	0.34	0.38	323	$ZnCl_2$	0.28	0.40	328	$NaNO_3$	0.29	0.29	314
KCl	0.42	0.38	323	$CdCl_2$	0.35	0.34	321	KNO_3	0.37	0.40	314
RbCl	0.45	0.42	323	$PbCl_2$	0.42	0.78	318	$CsNO_3$	0.55	0.60	327
CsCl	0.48	0.36	323			0.75	320	$TlNO_3$	0.55	0.69	326
AgCl	0.42	0.46	325			0.39	321	$AgNO_3$	0.35	0.28	314
		0.17	329	$PbBr_2$	0.40	0.83	319			0.25	330
	—	—	—		0.40	0.92	319				

There have been several investigations of transport numbers in salt melts[317-336]. The methods of measurement have been discussed[337]. Almost all the investigators used a cell with a diaphragm separating the electrode spaces, and the decrease in volume of the melt in one of the compartments during electrolysis was compensated for by the constant addition of salt to it. The absence of a flow of salt under the action of gravity is usually verified by the position of a bubble in a capillary joining the two parts of the vessel, or by some other means.

The most reliable results of the measurements of transport numbers are given in Table 15.

Most authors consider that transport numbers are almost independent of temperature but Duke *et al.*[329] have found a considerable increase in t_- for AgCl on raising the temperature from 650° to 925°. An analysis of the results given in Table 15 shows that in many instances Eqn. (37) agrees well with experiment. There are considerable deviations only for lead and zinc halides and for silver and thallium nitrates.

Characteristically, most solid states exhibit unipolar conductivity. Thus, the transport numbers of the cation in NaCl and KCl decrease from 1.00 to 0.93 and 0.88 respectively as the temperature is raised from 400° to 600°, whereas in the melt t_+ for both salts is 0.38. Lead chloride exhibits anionic conductivity in the solid state ($t_- = 1.0$) but in the melt $t_- \simeq 0.70$. Hence, fusion changes the mechanism of electrical conductivity, and the widely-held opinion that the conductivity of molten salts is also unipolar is incorrect.

15. THERMAL CONDUCTIVITY

Bloom[13], Gambill[338], and Turnbull[339] have investigated the thermal conductivity of molten salts. The thermal conductivity of potassium and sodium nitrates is 11.25×10^{-4} and 13.50×10^{-4} cal cm^{-1} s^{-1} deg^{-1} respectively. According to Turnbull, the thermal conductivity of molten salts is made up of vibrational μ_{vib} and diffusion μ_{dif} constituents:

$$\mu_{vib} = 2.85 \times 10^{-3} (T_f \nu / M)^{1/2} (V_{solid}/\nu)^{2/3}, \quad (38)$$

$$\mu_{dif} = 2\Delta C_V / V, \quad (39)$$

where C_V is the heat capacity and ν the number of ions in a salt molecule.

To a first approximation thermal conductivity can be calculated by Vargaftik's formula[340]:

$$\mu = 4.28 \times 10^{-3} C_p \rho^{4/3} / M^{1/3}, \quad (40)$$

where M is the molecular weight of the salt.

16. VOLUME CHANGE DURING FUSION OF IONIC CRYSTALS

The fusion of ionic crystals is characterised by the following features:

1. The volume of the salt increases sharply during melting.

2. The anisotropy of the properties of the crystals disappears during fusion, this being the direct consequence of the disappearance of ordering in the position of the particles. As X-ray analysis shows, in the liquid state ordering is retained only in the nearest surrounding particles (short-range order). There is no order at greater distances (long-range order).

3. During fusion there is a marked change in electrical conductivity, heat capacity, diffusion coefficients, and other properties of the salt[18,234,341], which is evidence of the break-down of structure. It is characteristic that these changes start below the melting point (premelting effect) and are greatly dependent on the nature of the salt.

All these features permit a liquid to be considered as a disordered crystal and the melting process as one of partial breakdown of the crystal lattice. In crystals of the inert gases, alkali metal halides, and similar materials, there is probably a single possible means of breakdown of the lattice — the transfer of ions from the lattice positions into the interstices and to the surface of the crystal. For more complicated crystals with polyatomic complex anions or ions with easily distorted shells the destruction of order can proceed by a change in the orientation of the complex ions, the formation of new types of molecular packing, and also the formation of autocomplexes owing to the degeneration of the ionic bond and the increase in polarisation interactions[342-347].

The most important characteristic of the fusion process is the volume change. The increase in molar volume during fusion can be termed the surplus volume of the melt, and this has been measured in several studies[347-355]. Table 16 gives Schinke and Sauerwald's results[348], recalculated with allowance for other data[120], and calculated values of ΔV, derived using the latest data on the coefficients of linear expansion of crystals[356] at room temperature (in parentheses).

Table 16 shows that the surplus volume depends markedly on the nature of the salt. For alkali metal halides, as for crystals of inert gases, it is 20–25%; for Ca, Sr, and Ba

TABLE 16. Excess volume of molten salts (cm^3 $mole^{-1}$).

Salt	ΔV	$\frac{\Delta V}{V_{solid}}$, %	Salt	ΔV	$\frac{\Delta V}{V_{solid}}$, %	Salt	ΔV	$\frac{\Delta V}{V_{solid}}$, %	Salt	ΔV	$\frac{\Delta V}{V_{solid}}$, %
LiF	3.27	29.4	NaBr	8.09	22.5	KI	9.34	16.0	CsI[a]	18.0	28.3
LiCl	5.84	26.1		(8.90)	(25.3)		(10.20)	(17.7)	$AgCl^b$	2.41	8.9
	(6.16)	(27.9)	NaI	8.42	18.3	RbCl	6.81	14.5	$AgBr^b$	2.54	8.2
LiBr	6.89	25.1		(9.98)	(22.5)		(6.79)	(14.5)	$CaCl_2$	0.49	0.9
	(7.24)	(26.7)	KF	4.45	17.2	RbBr	7.11	13.3	$SrCl_2$	2.35	4.2
LiI	(7.60)	(22.1)	KCl	7.30	17.6		(7.81)	(14.7)	$BaCl_2$	2.27	3.5
NaF	4.64	27.4		(8.10)	(19.9)	RbI	(8.55)	(13.2)	$LiNO_3^c$		28.2
NaCl	7.36	24.4	KBr	7.77	16.2	CsCl	6.16	11.4	$NaNO_3^c$		11.0
	(8.05)	27.3		(8.82)	(18.8)	CsBr[a]	14.3	26.8	KNO_3^c	—	1.0

[a] See Johnson *et al.*[352]; [b] see Strelkov[353]; [c] see Davis *et al.*[234] and Landon and Ubbelohde[347].

halides it is only a few per cent, just as for nitrates, and this is due to the degeneration of the ionic bond and reorientation.

The "surplus" volume is in general not the "free volume of the liquid", if by this term we understand that part of the volume available for the translational and vibrational motion of the ions, since part of the surplus volume is screened by the force fields of the neighbour particles[357]. The value of the "free volume" of the liquid can be determined as follows[358]. It is known that the statistical partition fnnction of a system with particles oscillating in closed micro-cells which they cannot vacate has the form:

$$\Phi_m = \left[\frac{(2\pi mkT)^{3/2}}{h^3} \times \frac{V_f}{N}\right]^N [\Phi_{int} \exp(-E/RT)]^N, \quad (41)$$

where V_f is the total free volume, N Avogadro's number, m the mass of the particle, h Planck's constant, Φ_{int} the internal partition function, and E the potential energy, determinable as the energy for the transformation of the system into ideal gas at 0°K.

Virtually, this partition function corresponds to a crystal expanded to the volume of the liquid. The difference between the crystal and the liquid is that in the latter the particles are not localised in their cells and therefore:

$$\Phi_{liq} = \frac{1}{N!}\left[\frac{(2\pi mkT)^{3/2}}{h^3} \times V_f\right]^N [\Phi_{int} \exp(-E/RT)]^N. \quad (42)$$

When this equation is combined with the known relation:

$$p = RT(\partial \ln \Phi/\partial V), \quad (43)$$

an equation of state of the liquid, similar to the van der Waals equation, is obtained

$$V_f[p + (\partial E/\partial V)_T] = RT, \quad (44)$$

where the derivative $\partial E/\partial V$ has the significance of the internal pressure of the system. To calculate the free volume, another well-known relationship can be used:

$$(\partial E/\partial V)_T = T\frac{\alpha}{\beta} - p, \quad (45)$$

which in combination with (44) gives:

$$V_f = R\beta/\alpha. \quad (46)$$

Another method of calculating the free volume involves the determination of the entropy of vaporisation of the liquid, which equals[359,360]

$$\Delta S_{vap} = R \ln(V_{gas}/V_f), \quad (47)$$

and

$$L_{vap} = -RT \ln(V_b/V_{gas}), \quad (48)$$

but since for a gas $V_{gas} = RT/P$, then:

$$V_f = \frac{RT}{p} \exp\left(-\frac{L_{vap}}{RT}\right) = \frac{RT}{P_b} \exp\left(-\frac{L^\circ_{vap}}{RT_b}\right). \quad (49)$$

TABLE 17. Free volumes of alkali metal halides at 800°, $cm^3\ mole^{-1}$.

Salt	V_f (Ref. 46)
LiCl	6.84
NaCl	6.84
KCl	8.26
CsCl	10.50

However, the results of calculations by Eqns. (46) and (49) usually differ by an order of magnitude.

We note that the physical significance of the concept of free volume has not been finally determined and is still the subject of discussion, so that some authors understand other quantities as free volume[360-362].

17. THEORY OF THE FUSION OF IONIC CRYSTALS

The important theories of fusion can be classified into a few groups. The vibrational theories of fusion link the crystal → liquid change with the vibrational motion of the particles[363-376]. The basis of the vibrational theories is the idea of the mechanical instability of the crystal lattice, which appears with increase in the amplitude of the vibrations of the ions. Lindemann[363], by considering the collision of the vibrating particles as a criterion of fusion, obtained a formula for the melting point:

$$T_f = \text{const}\, V/\beta. \quad (50)$$

In later works Born[367,368], Fürth[370-373], Patrushev[376], and Thompson[369] also developed different variants of the vibrational theory. As Mott showed[374,375] Born's concept of the melting point as the temperature for the disappearance of the elastic properties of a crystal due to the vibration of the atoms is erroneous. However, there is also a grain of truth in the vibrational theories. In particular, this applies to Patrushev's theory which connects the increase in volume during fusion with the heats of fusion and sublimation:

$$L_f/L_s = \text{const} \times \Delta V/V_{solid}. \quad (51)$$

The theory of disordering is seen as the basis of the melting process in the disappearance of the order peculiar to the crystal. Frenkel'[22] and Bresler[377] have considered this question most fully. To characterise the order in the system they introduce the concepts of degree of short- and long-range order. In a crystal MX the long-range order is expressed by the cations and anions occupying completely determined ("cationic and anionic") positions, and short-range order by each ion M^+ being surrounded by six X^- ions and vice versa. The breakdown of long-range order signifies that a fraction N''_+ of the cationic places, out of the total number $N_+ = N'_+ + N''_+$, is occupied by anions. The Bragg–Williams criterion[378]

$$\gamma = \frac{N'_+ - N''_+}{N'_+ + N''_+} = \frac{2N'_+ - N_+}{N_+} \quad (52)$$

serves as a measure of the long-range order. For the ideal crystal $N'_+ = N_+$, $N''_+ = 0$, $\gamma = 1$. With complete disorder, $N'_+ = N''_+$, $\gamma = 0$. When out of the total number p of nearest neighbours the mean number of neighbours of the same kind is n, and that of the other kind is m, then the degree of short-range order can be characterised by Bethe's criterion[379]:

$$\xi = \frac{m-n}{p} = \frac{m-n}{m+n} = \frac{2m-p}{p}. \quad (53)$$

For the ideal crystal $n = 0$, $m = p$, and $\xi = 1$; with complete disorder, $m = n = p/2$, and $\xi = 0$.

Frenkel' gives[22] the following assumptions: (a) melting corresponds to complete disappearance of long-range order; (b) the probability of transfer of an ion to a "foreign" site is determined by the Boltzmann relation, that is,

$$N''_+ = N'_+ \exp(-\varepsilon/kT), \quad (54)$$

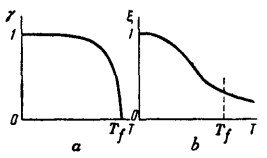


Fig. 7. Change in the degrees of long-range (γ) and close-range (ξ) order with rise in temperature[22].

in which $\epsilon = \gamma\epsilon_0$; (c) the probability of differently charged ions occupying neighbouring positions is determined by the relation:

$$n = m\exp(-\Delta\varepsilon/kT), \quad (55)$$

where $\Delta\epsilon$ is the mean difference in energies of interaction of the pairs M^+-M^+, X^--X^-. In this case we can obtain:

$$\gamma = \tanh(\varepsilon_0\gamma/2kT), \quad (56)$$

$$\xi = \tanh(\Delta\varepsilon/2kT). \quad (57)$$

Graphs of these functions (Fig. 7) show that long-range order disappears by a sharp jump at a definite temperature T_f, at which an appreciable fraction of short-range order is retained.

Despite the qualitative agreement with experiment, this theory is not completely accurate since the change in volume during melting is not taken into account, that is, in the final reckoning the part played by "holes" in the destruction of order§ is not considered. An attempt to allow for this feature was made by Bresler[377], who determined the degree of short-range order as the probability of the coordination number p and of disorder as reduction in the coordination number to $(p - 1)$, which gives:

$$\xi = [1 + p\exp(-\varepsilon/kT)]^{-1}, \quad (58)$$

where ϵ is the energy of the system.

A more detailed statistical theory of fusion has been developed[383-389]. Kurosawa[390] and Karpachev and Karasik[391] attempted to create a quantitative theory of fusion of ionic crystals. The former considered the liquid as a solution of holes in an ionic medium and the application of the Debye–Hückel theory to the interaction of holes enabled several properties of molten salts to be calculated (melting point, etc.). The entropy of fusion of ionic crystals has been calculated[391] as the result of the expansion of the crystal and the appearance in it of unoccupied sites (vacancies). The relation finally obtained was:

$$\Delta S_f = -\frac{\alpha}{\beta}\Delta V + 4.6R[\log(1 + \Delta V/V_{solid}) + (\Delta V/V_{solid})\log(1 + V_{solid}/\Delta V)]. \quad (59)$$

18. THEORY OF MOLTEN SALTS

The theory of ionic liquids has been developed in the last few years as part of the general theory of the liquid state. Its first considerable success was connected with the development of the hole theory (Frenkel'[22], Fürth[392,393] and others[394,395]) which is based on the concept of a liquid as a quasi-crystal with a large number of vacant sites – the holes. The holes are attributed with the ability to migrate and a spherical form, and the liquid itself is regarded as a continuous medium. The energy of formation of a hole of radius r is[393]:

$$\varepsilon_g = 4\pi r^2\sigma, \quad (60)$$

and the mean volume of a hole is:

$$v_g = 0.68(kT/\sigma)^{3/2}. \quad (61)$$

Frenkel'[22] and Kurosawa used the idea of hole theory to explain the diffusion and viscosity of molten salts. Bockris and coworkers[136,238] used the same viewpoint in handling their experimental results on diffusion and ultrasonic velocity in melts.

One of the first theories of the liquid state[396] considered a liquid as a dynamic combination of microregions with an ordered structure (sibotaxic group), situated in mobile equilibrium internally and with the molecules forming irregular transition regions. A development of this theory is the theory of significant structures[397-400], according to which in a liquid there coexist regions with a crystal lattice structure, regions containing "gaslike" molecules, and also dislocations, vacancies, holes, and other defect structures. The degree of bonding of the molecules in the liquid is characterised by the ratio V_{solid}/V_{liq}, and the statistical sum of states is determined as the product of the partition functions of the "gaslike" and "solidlike" particles. By applying the theory of significant structures to molten alkali metal halides, Eyring and others[399,400] found for the partition function:

$$\Phi = \left\{\frac{\exp(E/2RT)(V_{liq}/V_{solid})^{1/3}}{[1-\exp(-\theta/T)]^3}\left[1 + N_g\exp\left(-\frac{aE}{2N_gRT}\left(\frac{V_{liq}}{V_{solid}}\right)^{1/3}\right)\right]\right\}^{2NV_{solid}/V_{liq}} \times$$

$$\times\left\{\frac{(2\pi mkT)^{3/2}}{Nh^3}eV_{liq}\frac{8\pi^2IkT}{h^2}[1-\exp(-h\nu/kT)]^{-1}\right\}^{(1-V_{solid}/V_{liq})N}, \quad (62)$$

where E is the potential energy of the salt at T_f, θ is the Einstein characteristic temperature, m, I, and ν are the mass, moment of inertia, and fundamental vibration frequency of the halide molecule, a is an empirical parameter, N Avogadro's number, and $N_g \simeq 10(V_{liq} - V_{solid})/V_{solid}$ the concentration of holes. A comparison of the fusion parameters, calculated by Eqn. (62), with the experimental values shows good agreement (Table 18). However, unfortunately Eqn. (62) contains the empirical coefficient a.

Eyring[383] and Lennard-Jones and Devonshire[384] developed a theory representing a liquid as an expansion of a crystal in which each molecule can move freely in a certain volume, equal to ω/N, where ω is the total free volume of the cell. Assuming it to be equal to the free volume of the liquid and using Eqns. (40), (41), and

$$S = k\{\ln\Phi + T(\partial\ln\Phi/\partial T)_V\}, \quad (63)$$

TABLE 18. Comparison of theory of significant structures with experiment[399].

Salt	T_f, °K		ΔS_f, cal deg^{-1} mole^{-1}		V_{liq}, cm^3 mole^{-1}	
	calc.	expt.	calc.	expt.	calc.	expt.
NaCl	1070	1073	7.75	6.21	38.1	37.6
KCl	1023	1043	5.40	6.06	49.1	48.9
NaBr	1023	1020	6.14	6.12	43.8	49.6
KBr	1008	1007	4.83	6.06	56.1	55.8

§ Samoilov[380-382] considered the decrease in coordination number during fusion.

we can obtain the change in entropy due to the removal of the prohibition for movement of a molecule from one cell to another:

$$\Delta S^{\circ} = k \ln (N^N/N!) \simeq kN = R. \quad (64)$$

This quantity was termed the communal entropy of the liquid and identified with the entropy of fusion. The latter, of course, is incorrect, since Eqn. (40) relates to a conventional crystal and the complete freedom of mixing of the particles is reached only in vaporisation of the liquid[385].

The quantity ω in the Eyring-Lennard-Jones and Devonshire theories is determined as follows[401]. In a three-dimensional cubic lattice let only a central molecule move and six of its neighbours be immovably fixed; the volume bounded by these neighbours for all N molecules is

$$\omega = 8N[v^{1/3} - \sigma]^3, \quad (65)$$

where σ is the diameter of the molecule, and $v^{\frac{1}{3}} = (V/N)^{\frac{1}{3}}$ is the distance between the centres of neighbouring molecules. The quantity ω, calculated for molten salts[136], is 0.5–1.0 cm^3 mole^{-1} for alkali metal halides, which is much smaller than the actual free volume (compare Table 18).

The ideas of Lennard-Jones and Devonshire were applied to salt melts and developed by McQuarrie[402] who obtained, in particular, an equation for vapour pressure:

$$\log p = \frac{0.434\,(D_0 - \alpha\epsilon^2/a)}{kT} + 0.217 \log T + \log \left\{ \frac{\left(\frac{M}{M_+ M_-}\right)^{\frac{3}{2}} (8\pi k)^{\frac{1}{2}} hI \times 7.6 \times 10^4}{V_f^2 \epsilon^2} \right\}, \quad (66)$$

where M is the mass of diatomic molecules, M_+ and M_- are the masses of the cation and anion, I is the moment of inertia, ϵ the charge of the ions, D_0 the energy for the decomposition of the molecule into ions, and α the Madelung constant. The values of V_f obtained from Eqn. (66) were of the order of 0.05 cm^3 mole^{-1} for the alkali metal halides. However, McQuarrie's calculations of the entropy of fusion of NaCl and KCl (2.84 and 2.40 cal deg^{-1} g-ion^{-1}) were close to the experimental values.

The progress in the statistical theory of the liquid state associated with the use of the methods of Kirkwood, Bogolyubov, and Green[403-408], based on the calculation of molecular distribution functions permits these methods to be applied to molten salts. Calculation of the correlation functions with allowance for both coulombic forces and short-acting repulsive forces:

$$U(r) = \epsilon^2/r + U_0(r), \quad (67)$$

still meets with insuperable mathematical difficulties. Bogolyubov[405] proposed, as a first approximation, the use of smoothing coulombic potentials

$$U(r) = \epsilon^2 [1 - \exp(-\alpha r)]/r. \quad (68)$$

This idea was employed in several works[409-411], which related, however, to aqueous solutions of electrolytes. Works on the theory of ionic liquids[412-419] were all based on a model in which the ions were represented by rigid charged spheres. The question as to how far this model is suitable for describing the properties of molten salts is still not solved. Undoubtedly some successes have been achieved in this direction. In particular, mention can be made of works[417,418] in which a formula was derived for the surface tension of melts:

$$\sigma = \frac{kT}{4\pi a^2} \left[\frac{12y}{1-y} + \frac{18y^2}{(1-y)^2} \right], \quad (69)$$

TABLE 19. Verification of the Reiss–Mayer equation, Eqn. (69).

Salt	t, °C	σ, dyn cm^{-1}	
		expt.	calc.
NaCl	1000	98	111
KCl	900	90	96
RbCl	828	89	81
CsCl	830	78	79
$BaCl_2$	1000	157	152

where $y = \pi a^3 \rho/\sigma$, a is the mean diameter of the ions, and ρ the density. This formula agrees well with experiment (Table 19). Satisfactory results were also obtained by Rice[419] in calculating the diffusion coefficients, viscosity, and thermal conductivity of melts.

All the theories considered relate only to molten alkali metal halides. With other molten salts the matter is more complicated. As already noted, in many instances the formation of autocomplexes of the type $BeCl^+$, $BeCl_3^-$, etc.[316] on melting is assumed. However, it is possible that in addition to autocomplexes the melt retains fragments of the crystal lattice in several instances, for example, $ZnBr_2$.[240] Finally, in melts of the mercury halide type the equilibrium

$$HgX_2 \rightleftarrows HgX^+ + HgX_3^-$$

is probably established, with a strong displacement towards the side of formation of neutral molecules[421]. Naturally the construction of a theory for such complicated ionic-molecular systems is encountering great difficulties.

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