

PHYSICAL PROPERTIES AND CONSTITUTION OF MOLTEN SALTS

ELECTRICAL CONDUCTANCE, TRANSPORT, AND CRYOSCOPY

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I. INTRODUCTION

Until recent years, the physical chemist was concerned almost exclusively, so far as liquids are concerned, with aqueous solutions and solutions in organic liquids. The increasing interest in the chemistry of molten salts over the past decade may be attributed, in no small part, to the problems raised by an inadequate knowledge of high-temperature chemistry, a field of considerable importance in modern technology.

The thermodynamics and structure of slags, glasses, and related systems, mainly the concern of metallurgical and ceramics chemists until a comparatively few years ago, have been the subject of a number of recent symposia and reviews (76, 179, 213) and monographs (34, 196), but little has appeared for other systems of molten salts. The present review has been limited to molten inorganic salts in which the units of structure are wholly or predominantly ionic, as distinct from slags and silicates which may be regarded as macromolecules and highly polymerized forms of molten salts. The scope has been further limited to the techniques of electrical conductance, electrical transport, and cryoscopy as these bear directly on the ionic nature and electrical properties of such molten systems (123). The numerous and important contributions towards an under-

standing of the constitution of molten salts by thermochemical and thermodynamic methods (other than cryoscopy), spectroscopy, diffusion, compressibilities, and viscosity are the concern of a sequel to the present review.

II. GENERAL TECHNIQUES OF HIGH-TEMPERATURE EXPERIMENTATION

Two recent monographs (34, 238) provide valuable sources of information concerning the literature on experimental techniques and apparatus used in experimentation upon molten salts. These, supplemented by the latest editions of earlier and better-known reference manuals (1, 100, 101, 220, 249), provide useful information concerning such matters as the design and operation of furnaces, furnace-temperature controllers, and temperature-measuring devices, the properties and selection of refractories and other materials of construction, and the design of ancillary apparatus such as vacuum and controlled-atmosphere systems. For most work, below 1000°C., sufficient information regarding the general principles of design and selection of equipment and materials can be obtained from the manual by Seybolt and Burke (238), while that by Campbell (34) is mainly concerned with temperatures above 1000°C.

In addition to the sources mentioned, a great deal of useful information concerning electric and other furnaces, materials of construction of such furnaces, and temperature measurement and control can be obtained from literature published by the manufacturers of such equipment. Seybolt and Burke (238) give many references to such sources.

Several devices for controlling the temperature of an electrically heated furnace are described in the monographs mentioned. Many designs which have not yet found their way into the preceding reference works have also been published recently (13, 30, 37, 56, 86, 166, 199, 215, 243, 246, 256, 259, 266), including an apparatus (106) for use with condensed phases at 10,000°C.

In addition, reference to the experimental sections of papers mentioned later in this review is recommended for specific details of the equipment and techniques used for the various types of measurement on the particular systems employed.

III. ELECTRICAL CONDUCTANCE

The information which can be gained from measurements of electrical conductance, the relationship between conductance and other properties such as viscosity, and the effect of such variables as temperature are of great value. It is possible to obtain information on such matters as the nature of the ions present, the electrovalency or covalency of the system, the extent of dissociation of an added salt, inter- and intramolecular forces, the energies of activation for conductance by the ions present, the extent of deviation from ideality of the system, the nature of the ionic conductance process, and the structure of the melt (123).

A. EXPERIMENTAL TECHNIQUES

Molten salts, except covalent compounds like the mercuric halides, have high specific conductances. Thus, most molten alkali halides in the region of their melting points have specific conductances (274) falling in the range 1–5 ohm⁻¹

cm.⁻¹, which may be compared with 0.1 *N* aqueous potassium chloride solution and 100 per cent sulfuric acid, which have specific conductances (89, 126) of about 0.01 ohm⁻¹ cm.⁻¹

For measurements of resistance accurate to 0.5 per cent or better, using a good-quality conductance bridge reading to ± 0.1 ohm, it is necessary to use a cell with a cell constant of at least 200 cm.⁻¹ In order to attain such a high cell constant, most workers have had recourse to cells in which the conductance path is through a capillary tube. Descriptions of such cells with constants of 300–500 cm.⁻¹ have been given recently in papers (39, 263) which refer to earlier designs and also discuss the corrections for thermal expansion required and the change in cell constant with use. For cells of the type described, the conventional form of conductance bridge based on the well-known Jones and Josephs design (125) is satisfactory. The monograph by Hague (105) may be referred to for a comprehensive survey of conductance bridges designed before 1943. A number of designs have been published since then (3, 40, 69, 119, 175). In this laboratory, a portable bridge after the design by Fuoss (70, 73) has proved satisfactory.

A different form of cell has been used by other workers (7, 29, 72, 180). This type of cell consists of a crucible, usually of platinum, which acts as one electrode and also as the container for the melt, into which dips a second electrode whose position and depth of immersion are carefully controlled to achieve reproducible cell constants.

The cell constant of such a cell is very low, a typical value for a 50-ml. platinum crucible cell being (72) 0.1122 cm.⁻¹ Cells of this type thus have resistances of about 0.1 ohm when used with molten salts; bridges capable of accurate measurement of resistances of this magnitude must therefore be used. A suitable design of bridge is the Kelvin bridge modified for use with alternating current, such as has been used for measurements on molten alkali chlorides and molten cryolite (72).

The partially filled platinum crucible cell suffers from several faults (72), such as a high dependence of cell constant on temperature, sensitivity of the melt to small amounts of impurities picked up by the open surface, possible thermal discontinuities in the melt, dependence of accuracy on accurate density measurements, difficulty of securing good mixing of multicomponent systems, and loss of material by volatilization.

An improved version of this type of cell has been reported (72), being two hemispherical platinum electrodes rigidly held concentrically to one another, and suspended in a very much larger (400-ml.) platinum crucible acting as container for the melt. It was found that the cell constant did not vary by more than 0.15 per cent with the position of the cell in the crucible provided the cell was completely immersed in the melt and more than "several millimeters" from the walls of the crucible. The resistance of the leads to the cell is an important part of the total resistance measured when using cells of low cell constant. It is therefore necessary to measure accurately the lead resistance of such cells.

The effect of conditioning the electrode surfaces by conditioning with an electrodeposit of platinum black has been studied by various workers (27, 72,

159, 263). Variation of resistance with frequency is about 0.5 per cent over a range of 500–10,000 c/s, the relationship being

$$R_{\text{meas.}} = R_{\text{inf.}} + (K/\omega^{1/2})$$

where $R_{\text{meas.}}$ and $R_{\text{inf.}}$ are the measured resistance at the frequency ω and the polarization-free resistance at infinite frequency, respectively, and K is a constant characteristic of the salt studied. A reported linear relationship (263) between $R_{\text{meas.}}$ and ω^{-2} instead of $\omega^{-1/2}$ is probably a typographical error.

Molten salts have conductances which depend strongly on temperature; the cell must therefore be held in a furnace possessing good characteristics of temperature control.

Another important matter is the material used for the construction of the cell. For much work, Pyrex or Vycor glass or silica will prove satisfactory within the temperature ranges of their usability. Substances which attack silicates may usually be handled in platinum. Yim and Feinleib (276) recently used cells fabricated from compressed boron nitride for measurements on molten alkali fluorides.

B. THEORETICAL PRINCIPLES

The specific conductance, κ , of the system investigated is related to the measured resistance, R , and the geometry of the conductance cell by the relationship:

$$\kappa = G/R$$

Here G is the cell constant, given by the ratio of length to area of cross section of a uniform cell or by an integral of similar form for a nonuniform cell. In practice G is not calculated but is determined experimentally indirectly from the definition of the standard ohm in terms of a mercury resistance by the use of potassium chloride solutions (124). It can readily be shown (157) that the specific conductance is determined by the volume concentration, c_i , of each ionic species in the system, the charge, z_i , on each ion, and the mobility, u_i , of each ion in a uniform electric field of potential gradient 1 volt per cm., i.e.,

$$\kappa = (F/1000) \sum c_i z_i u_i \quad (1)$$

where F is Faraday's constant. For a binary fully dissociated electrolyte, the products $c_i z_i$ are equal for the anionic and cationic species, and equation 1 can be written

$$\begin{aligned} \kappa &= (F/1000) cz \sum u_i \\ &= (F/1000) cz (u_{\text{cation}} + u_{\text{anion}}) \end{aligned} \quad (2)$$

By absorbing the Faraday constant into the velocity term, the equation

$$1000\kappa/cz = (\lambda_{\text{anion}} + \lambda_{\text{cation}}) = \Lambda \quad (3)$$

may be derived, where λ_{anion} , λ_{cation} , and Λ are the ionic conductances of the anion and cation, and the equivalent conductance of the solution, respectively.

The concentration term c is expressed in moles of solute per liter of solution; thus $cz/1000$ is in equivalents per milliliter.

In the case of a fully dissociated pure molten salt, $1000/cz$ can be replaced (25) by M_e/ρ , the equivalent weight of the salt divided by the density.

For binary mixtures of molten salts Bloom and Heyman (25) replace M_e , the equivalent weight of the pure salt, in the equation

$$\Lambda = \kappa M_e \rho^{-1} \quad (4)$$

by M_m , the mean equivalent weight of the mixture given by

$$M_m = M_{e(1)}f_{(1)} + M_{e(2)}f_{(2)} \quad (5)$$

the terms f_1 and f_2 being the equivalent fractions (number of equivalents of given component/total number of equivalents present = $c_i z_i / \sum c_i z_i$) of the components of the mixture. The complexity of equation 5 in its expanded form masks the fact that it is actually

$$M_m = (\text{total weight of system})/(\text{total number of equivalents present})$$

It should be borne in mind when use is made of equations such as equations 2-4 that they involve the assumption of complete ionization and complete ideality. An example will be given below to show how an approach to the problem of finding degrees of dissociation from conductance measurement has been made.

The temperature dependence of the electrical conductance of molten salts has been found experimentally (25) and theoretically (29) to fit equations of the basic Arrhenius type

$$\kappa = A_\kappa \exp(-\Delta E_\kappa/RT) \quad (6)$$

or

$$\Lambda = A_\Lambda \exp(-\Delta E_\Lambda/RT) \quad (7)$$

Since the conductance process takes place at constant pressure and volume, some workers (263) use the heat of activation, ΔH^\ddagger , instead of the energy of activation, ΔE , to which it is equal under these conditions.

Bloom and Heymann (25) treat the liquid salt as a very disordered solid, making use of theories of the relationship between ionic conductance in solid salts and the presence of imperfections in the crystal lattice (198).

The high-temperature conductance of a solid salt is proportional to the volume concentration of such defects and to their mobility. Both factors vary exponentially with temperature, resulting in an expression

$$\kappa = A \exp[-(W/2 + U)/kT] \quad (8)$$

where W is the energy necessary to produce the lattice defect and U is the height of the energy barrier involved in its migration. Equation 8 applies strictly only to the case where migration of a single ion alone is the cause of the conductance of the solid salt (198).

Bloom and Heymann (25) suggest that the degree of disorder of the salt in the molten state is so high that the fraction of mobile ions is very great. If no consti-

tutional changes occur in the liquid with change of temperature, then within certain limits this fraction of mobile ions may be assumed constant. The equation

$$\kappa = A_{\text{cation}} \exp(-\Delta E_{\text{cation}}/RT) + A_{\text{anion}} \exp(-\Delta E_{\text{anion}}/RT) \quad (9)$$

may be expected for a purely ionic binary melt, since the contribution of each ionic species to the specific conductance will, under these conditions, be proportional to an exponential term containing only the U -term of equation 8.

If ΔE_{anion} and ΔE_{cation} are nearly equal, equation 9 may be replaced by the simpler equation 6. If ΔE_{anion} and ΔE_{cation} are very different, the conductance may again be expressed by equation 6, since the ion with the lower activation energy may be the predominantly conducting species.

Martin (187) has shown that by taking logarithms of equation 4 and differentiating with respect to reciprocal temperature,

$$d \ln \Lambda/d(1/T) = d \ln \kappa/d(1/T) - d \ln \rho/d(1/T)$$

and substituting the definitions of coefficient of thermal expansion

$$\alpha = -(1/\rho)(d\rho/dT)$$

and energy of activation

$$\Delta E_{\Lambda} = -R d \ln \Lambda/d(1/T)$$

$$\Delta E_{\kappa} = -R d \ln \kappa/d(1/T)$$

the relationship between ΔE_{κ} and ΔE_{Λ} is

$$\Delta E_{\Lambda} = \Delta E_{\kappa} + RT^2\alpha \quad (10)$$

From equation 10 it can be seen that the two forms of the activation energy can be equated only for systems having very small temperature coefficients of expansion, such as the molten silicates, or for systems studied at relatively low temperatures, a value of 400°K. being suggested (187) as the maximum temperature for which this might be feasible.

By application of the absolute reaction rate theory to the problem of ionic motion under the influence of an applied electric field, it has been shown (29) that the expanded form of equation 7 for a single ion is

$$\Lambda = \frac{2}{3}(FzXd^2/RT)(kT/h) \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT) \quad (11)$$

where F = Faraday's constant, z is the number of charges on the ion, X is the "effective" potential gradient on the ion in an applied field of 1 volt cm.⁻¹, d is half the distance between the initial and final positions of the ion along the coordinate of motion, R is the gas constant, k is Boltzmann's constant, h is Planck's constant, T is temperature in °K., and ΔS^{\ddagger} and ΔH^{\ddagger} are the entropy and enthalpy of activation for the process, respectively.

Making the assumption (92, 117) that the effective potential gradient in a

medium of dielectric constant D is $(D + 2)/3$ times the applied potential gradient, and collecting the constants, equation 11 can be simplified (263) to

$$\Lambda = \text{const.} \times (D + 2)z\bar{d}^2 \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT) \quad (12)$$

where the constant has the value 5.18×10^{18} .

Bockris (29) used a value of $D = 5$ for the liquid silicates, while in a recent paper by Van Artsdalen and Yaffe (263) making use of this treatment the value $D = 3$ was assumed for the molten alkali halides. Fortunately, the value of ΔS^\ddagger is largely insensitive to errors in D ; it has been pointed out (263) that even changing D from 3 to 15 makes an error in ΔS^\ddagger of only about 2 e.u./equiv. in about 6 or 7 e.u./equiv.

Oldekop (202) has applied the Debye-Hückel theory to salt melts, to which a Born and Green (99) statistical model was assumed to apply. Although it is claimed that the calculations agree very well with experiment, the diagrams given in the original paper show that both the absolute magnitudes and the temperature coefficients of the properties, conductance, and viscosity as calculated differ by up to 100 per cent from the experimental results.

Sundheim (251) has recently suggested that the conductance of a solution of two salts is an extensive property which may be formally represented in terms of the "partial equivalent conductances" of the components. From the equations given earlier, it can readily be shown that following this suggestion the equations

$$\kappa = (c_1/1000)\tilde{\Lambda}_1 + (c_2/1000)\tilde{\Lambda}_2$$

$$\mu = x_1\tilde{\mu}_1 + x_2\tilde{\mu}_2$$

$$\Lambda = f_1\tilde{\Lambda}_1 + f_2\tilde{\Lambda}_2$$

apply to express the specific, molar, and equivalent conductances (κ , μ , and Λ , respectively) of a binary mixture of two salts, where c , x , and f are concentrations in moles l^{-1} , mole-fractions, and equivalent fractions ($c_i z_i / \sum c_i z_i$; as used in equation 5), respectively. $\tilde{\Lambda}$ and $\tilde{\mu}$ are partial equivalent and partial molar conductances, given by terms of the form

$$\tilde{\Lambda}_1 = (\partial\Lambda/\partial c_1 z_1)_{T, c_2 z_2}$$

$$\tilde{\mu}_1 = (\partial\mu/\partial c_1)_{T, c_2}$$

It should be noted that the equations given by Sundheim (251) apply only to uni-univalent electrolytes, although no such limitations are imposed in the original paper. The restrictions arise from the use of equivalent conductance terms in the equations where molar conductance terms should be used, these quantities only being equal in the case of 1:1 electrolytes. A graphical construction similar to that used for partial molar volumes (168) may be used to calculate the values of $\tilde{\Lambda}$ and $\tilde{\mu}$. These partial molar and equivalent conductances are the quantities most meaningfully compared from one solution to another, since the change in conductance of the first constituent salt on addition of the second is taken into account. It may be seen from the derivation of the equations that the

partial equivalent conductance is a direct measure of the mobility of the one salt in the other, not only at vanishingly small concentrations as stated by Sundheim, but at all concentrations. Heats of activation for conductance may be calculated from the partial equivalent conductance data.

C. RESULTS

1. *Pure salts*

Since the first qualitative measurements of the electrical conductance of molten salts by Faraday (75) in 1833, there have been a great many studies made. Fortunately, there are several sources from which references to the earlier work may be obtained. Lorenz (170) has reviewed the literature prior to 1905. In his compendium on inorganic chemistry, Mellor (189) included such conductance data as was available on each compound described. An early investigation into the electrical conductance of salts (260) showed that in solid and liquid silver and thallium halides Faraday's laws were obeyed, and that the specific conductance dropped considerably on solidification of the melt. Lorenz and Kalmus (173) studied the conductances and viscosities of several salts. Later, densities were also measured (172). A great deal of work was performed by Goodwin and Mailey (95, 96, 97), particularly on metal nitrates, by Jaeger and Kapma (121) on nitrates and halides, and by Arndt and his coworkers (4, 5, 6, 7) on the conductances (and often the densities and viscosities, too) of a wide range of metal halides and nitrates, also several phosphates, borates, and similar salts, in the period 1900-1925.

The conductance measurements made by Biltz and Klemm on metal chlorides are included in their review of data (23) up to 1926. Drossbach (62) extended the data up to 1938 (though without giving references). His tables were reproduced (together with some additional data on densities of molten salts) by Kortum and Bockris (157). Little work of any significance was then reported until the period 1935-45, when various Russian (11, 14, 15, 16, 17, 19, 120, 128, 150, 151) and Japanese (240, 241, 242, 275) workers published the results of their experiments and, in some cases, attempted to provide a theoretical interpretation.

References to much of the work performed between 1935 and 1955 may be found in papers by Van Artsdalen and Yaffe (263, 274). Table 1 presents a useful compilation of conductance data of molten chlorides in Periodic Table form after Biltz and Klemm (23). Included also are data on cationic radius, molar volumes at the melting point, and the melting point. Where possible, the data given are the most recent values.

Inspection of table 1 shows that greater conductances are found in the chlorides of Groups I and II, which are known to be highly ionic, whereas in Groups V and VI zero conductance is found. For low conductances a molten salt may occur as simple covalent molecules. In a broad sense, therefore, the magnitude of the conductance of a molten salt is a guide to its degree of electrovalency. In the original compilation the "stepladder" shaped line across the table was to separate ionic from covalent compounds. The classification is now known to be not rigorous.

TABLE 1

Equivalent conductances (Λ), cation radii (r_c), molar volumes at the freezing point (V_f), and the freezing points (T_f) of some chlorides in the order of the Periodic Table of the elements

(After Biltz and Klemm (23) and Drossbach (62))

	LiCl	BcCl ₂	BCl ₃	CCl ₄		
Λ	183	0.088	0	0		
r_c (A.).....	0.68	0.35	0.23	0.16		
V_f	28.3	52.7	72	92		
T_f (°C.).....	610	440	-107	-22.9		
	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₅	
Λ	150	35	15.1	0	0	
r_c (A.).....	0.97	0.66	0.51	0.42	0.35	
V_f	37.7	56.6	101	102		
T_f (°C.).....	808	714	192	-68	160	
	KCl	CaCl ₂	ScCl ₃	TiCl ₄	VCl ₅	
Λ	120	64	15	0	0	
r_c (A.).....	1.33	0.99	0.81	0.68	0.59	
V_f	48.8	60	91	105		
T_f (°C.).....	772	782	939	-23		
	CuCl	ZnCl ₂	GaCl ₃	GeCl ₄		
Λ	94	0.02	—	0		
r_c (A.).....	0.96	0.74	—	0.53		
V_f	26.9	53.8	77	106		
T_f (°C.).....	430	275	124	-49.5		
	RbCl	SrCl ₂	YCl ₃	ZrCl ₄	NbCl ₅	MoCl ₆
Λ	94	69	9.5	0.85	2×10^{-7}	1.8×10^{-6}
r_c (A.).....	1.47	1.12	0.92	0.79	0.69	0.62
V_f	53.7	58.7	77.5	—		
T_f (°C.).....	717	875	700	437	194	194
	AgCl	CdCl ₂	InCl ₃	SnCl ₄		
Λ	118	58.5	14.7	0		
r_c (A.).....	1.26	0.97	0.81	0.71		
V_f	29.6	54.8	103	110		
T_f (°C.).....	455	568	586	33.3		
	CsCl	BaCl ₂	LaCl ₃	HfCl ₄	TaCl ₅	WCl ₆
Λ	86	77	29.0	—	3×10^{-7}	2×10^{-6}
r_c (A.).....	1.67	1.34	1.14	0.79	0.69	0.62
V_f	59.9	66.3	77.8	—	—	—
T_f (°C.).....	645	962	870	432	211	275
	AuCl	HgCl ₂	TlCl ₃	PbCl ₄		
Λ	—	3×10^{-2}	3×10^{-3}	2×10^{-5}		
r_c (A.).....	1.37	1.10	0.95	0.84		
V_f	—	53.1	—	108		
T_f (°C.).....	170 (d.)	277	25	-15		

Drossbach (62) distinguished the following rules: (*i*) molten covalent compounds have higher molar volumes than ionic compounds, (*ii*) there is a gradual transition of covalent melts through incompletely dissociated intermediates to ionic melts, (*iii*) with covalent melts, the coefficient of expansion is greater than for ionic melts, (*iv*) within Group I there occurs a rise in the molar volume and a decrease in the equivalent conductance, (*v*) with covalent melts the molar volume generally increases with molecular weight. To these rules, Bloom and Heymann (25) from more recent work were able to add another from a consideration of the activation energies of conductance: (*vi*) for compounds of similar valence structure the activation energies for ionic migration tend to be relatively less when the compound is more covalent. These rules may be interpreted, according to Kortum and Bockris (157), in the following way. In the case of molten salts the strength of the bond between the atoms or ions is decisive in determining the conductance of the substance in the liquid state. If a highly polar component of bonding occurs, then there is extensive dissociation and high conductance. The coördination number of an atom is closely associated with its state of bonding. If the atom is fully coördinated in the solid state a molecular lattice will exist and consequently little formation of ions occurs. Thus the data summarized in table 2 clearly show that Λ for the lower chlorides is normally greater than for the higher coördinated chlorides. The alkali and alkaline earth halides and halides of selenium, vanadium, and lanthanum are in the highly conducting group. Boron and aluminum (elements of small radius) and carbon, silicon, titanium, and phosphorus (elements having four or more valences and powerful properties of coördination) form chlorides which are very poor conductors.

After 1945 came the period, extending to the present day, when the importance of a knowledge of conductances of molten salts to practical and theoretical chemistry came to be recognized more and more.

Heymann and Bloom (114) started the period with a brief report showing, in contradiction to earlier beliefs, that the activation energies for conductance and viscosity in molten salts were, in general, not equal. The activation energy for viscosity was, in fact, sometimes as much as three times that for conductance. In later papers (25, 27) the original work was considerably extended. These workers discussed the application of the Arrhenius equation

$$\kappa = A_{\kappa} \exp(-\Delta E_{\kappa}/RT) \quad (6)$$

to the conductance of molten salts and also the application of equations of the form of equation 9. Linearity of plots of $\log \kappa$ against $1/T$ was reported by Bloom and Heymann (25) for the alkali and alkaline earth halides, silver chloride, thallos chloride, cadmium chloride, and lead bromide. Similar plots for silver bromide, lanthanum chloride, lead chloride, and zinc chloride were not linear. Lead and zinc chlorides are known to be more covalent than the alkali chlorides; it was suggested (25) that the nonlinearity of the plot may indicate the occurrence of constitutional changes within the melt on variation of temperature. Other salts, such as lithium chloride, potassium bromide, cadmium iodide, sodium nitrate, and potassium nitrate, were later reported (27) to give approximately linear plots of $\log \kappa$ against $1/T$ when in binary admixture.

TABLE 2
Equivalent conductances of some mono-, di-, and trichlorides (62)

Salt	Equivalent Conductance	Melting Point	Salt	Equivalent Conductance	Melting Point
		°C.			°C.
HgCl.....	40	302	SnCl ₂	21.9	246
HgCl ₂	25 × 10 ⁻⁴	276	SnCl ₄	0	80
InCl.....	130	225	PbCl ₂	53	501
InCl ₃	29	235	PbCl ₄	2 × 10 ⁻⁵	-15
InCl ₃	17	586	TlCl.....	46.5	430
			TlCl ₃	25 × 10 ⁻⁴	25

TABLE 3
Conductance parameters of some pure metal halides (25)

Salt	Λ	ΔE_{κ}	ΔE_{Λ}	A_{κ}
	<i>ohm⁻¹ cm.² equiv.⁻¹</i>	<i>kcal. mole⁻¹</i>	<i>kcal. equiv.⁻¹</i>	<i>ohm⁻¹ cm.⁻¹</i>
LiCl.....	183	1.15	1.72	11.5
NaCl.....	150	1.54	2.70	7.3
KCl.....	120	2.30	3.28	6.5
RbCl.....	94	2.83	3.66	6.5
CsCl.....	86	3.33	3.75	6.6
LiBr.....	177	1.75		13.8
NaBr.....	148	1.84	2.58	7.4
KBr.....	109	2.55	3.42	5.8
NaI.....	150	1.25	2.00	4.8
KI.....	104	2.75	3.70	5.5
AgCl.....	118	0.99	1.20	7.4
AgBr.....	99	0.70-1.00	0.99	
AgI.....	105	0.80	0.90	4.0
CuCl.....	94	0.85	1.06	6.2
MgCl ₂	35	3.56	3.97	6.4
CaCl ₂	64	4.10	4.72	13.8
SrCl ₂	69	4.00	4.65	11.0
BaCl ₂	77	4.15	4.35	10.5
CdCl ₂	58.5	2.30	2.13	7.3
CdBr ₂	41.2	2.75		5.4
PbCl ₂	53.0	3.30-4.50	4.20	
PbBr ₂	27.0	4.35	4.32	16.0

A summary of some of the data on conductances and on energies of activation for conductance given by Bloom and Heymann (25) is given in table 3.

The electrical conductances of lithium chloride, sodium chloride, potassium chloride, and cryolite (Na₃AlF₆) were found later (72) to fit linear plots of log κ against $1/T$ for the temperature ranges from their respective melting points up to over 1000°C. The values of activation energy calculated from these plots agreed well with previous values.

Accurate measurements on the electrical conductances and other properties of pure and mixed alkali halides have recently been published (263, 274). Reference has been made, above, to the application of the absolute reaction rate theory to these results. It was found that for each of the pure salts studied, log Λ

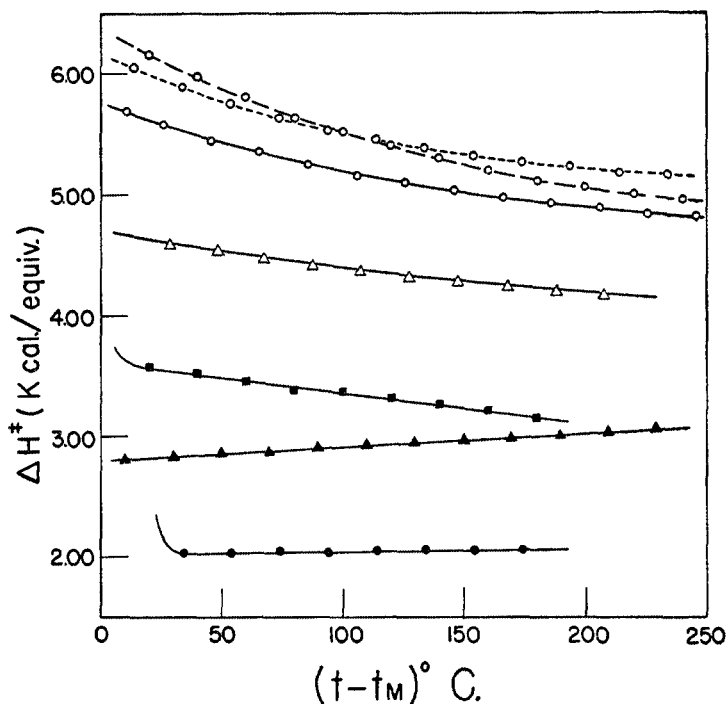


Fig. 1. Heat of activation for conductance of molten alkali halides as a function of temperature (274). ●, Li; ▲, Na; ■, K; △, Rb; ○, Cs; —, Cl; ---, Br; - - -, I.

against $1/T$ was nonlinear, and the heats of activation computed were not constant, except for lithium chloride. Figure 1, from the work of Yaffe and Van Artsdalen (274), shows the temperature dependence of this parameter. In general, the heat of activation decreases with decreasing size of the cation for a given anion and with decreasing size of anion for a given cation. These authors suggest that the heat of activation depends on at least two opposing factors, one being the expansion of the melt with temperature with consequent decrease in total coulombic forces and ΔH^\ddagger , the second being the decrease in the average number of nearest neighbors with temperature (due mainly to an increase in the number of holes, according to the "hole theory" of liquids) with a resultant increase in the attractive force per nearest neighbor and thence ΔH^\ddagger . The constancy of ΔH^\ddagger with temperature for lithium chloride is ascribed to the essentially chloride-chloride ion contact, the lithium ion being small enough to move freely at all temperatures. The equation

$$\log \Lambda = A + B(1000/T) + C \log (1000/T)$$

has been found (263) to apply very closely to the equivalent conductances of such salts as lithium chloride, sodium chloride, potassium chloride, and potassium iodide, which give linear plots of ΔH^\ddagger against $1/T$. The entropies of activation were found (274) to be practically independent of temperature and of about the same magnitude for all the salts.

TABLE 4

Equivalent conductances of molten alkali halides at corresponding temperatures

$$T_{\theta} = 1.05 T_m (\text{°K.})$$

(From reference 276, based largely on data from reference 274)

Molten Salt	Equivalent Conductance	Molten Salt	Equivalent Conductance	Molten Salt	Equivalent Conductance
LiF.....	128	NaF.....	113	KF.....	124
LiCl.....	170	NaCl.....	143	KCl.....	114
LiBr.....	170	NaBr.....	136	KBr.....	99
LiI.....	163	NaI.....	132	KI.....	94

A recent investigation (276) has added conductance data on the alkali fluorides to that previously available on the other alkali halides. Table 4 compares the equivalent conductances of the various lithium, sodium, and potassium halides at "corresponding temperatures", T_{θ} , defined (25, 274) as equal fractions above the melting point, T_m ,

$$T_{\theta} = \theta T_m$$

where in this case $\theta = 1.05$. In view of the considerable experimental difficulties involved in the measurement of the conductances of molten fluorides, such as porosity of the boron nitride containers and electrical leakage through the containers and their graphite supports, the values for the fluoride salt are probably best regarded as good "order-of-magnitude" values rather than as precise quantities.

A careful study of the temperature dependence of the conductance of molten potassium and sodium nitrates, with particular reference to the extent of electrode polarization, has recently been made (159). The results for potassium nitrate agree quite well with those of previous workers; those for sodium nitrate do not agree with either of the conflicting sets of earlier results.

Sakai (232) has measured the temperature dependence of the electrical conductance of silver chloride, cuprous chloride, cadmium chloride, lead chloride, tin(II) chloride, lithium nitrate, sodium nitrate, and potassium nitrate. An equation of the form

$$\kappa = \text{const.} \times T^{(a-1/2)} \exp(-\Delta E/RT)$$

was proposed to account for the temperature dependence of the energy of activation, where a is a positive number related to the mean free path, l , by the expression

$$l = \text{constant} \times T^a$$

Yaffe and Van Artsdalen (274) have pointed out that this is of the same form as equation 12, but that an analysis of data shows a to be temperature-dependent and to vary too widely for one to be able to ascribe any physical significance to its magnitude.

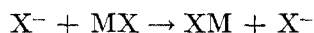
The theory of conductance as a rate process has been dealt with by Polissar (217) on the basis of the "cage" model of liquids. The ionic migration is con-

sidered as "the cumulative effect of a feeble, sporadic, but directed perturbation of the violent but random Brownian movement." This type of ionic motion, intermittent jumps to and fro but slightly more often in the direction of the electric field than against it, may be compared with the continuous, smooth, "drifting" motion taken as the model for the hydrodynamic theory. The Polissar model has been considered also by Hermans (113). Although Polissar considered this type of motion to occur also in diffusive processes, Noyes (200) has recently claimed that in molecular diffusion the data currently available suggest that the process involves almost continuous motion, very small but very frequent displacements, rather than "jumps" of the order of a molecular diameter as required by Polissar's treatment.

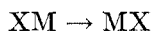
Erdey-Grúz (74) had discussed the relationship between the viscosity and electrical conductance of molten salts. For those cases where Walden's law

$$\Lambda_{\text{solution 1}} \eta_{\text{solution 1}} = \Lambda_{\text{solution 2}} \eta_{\text{solution 2}}$$

is not obeyed, he suggested that a Grotthus charge-transfer mechanism may be present:



followed by rotation:



Although this conductance mechanism has been used recently to explain the conductance of the proton in water (38), hydrogen peroxide-water mixtures (239), and sulfuric acid (90, 91), the HF_2^- ion in anhydrous hydrofluoric acid (134), and the HCl_2^- ion in nitrobenzene solutions of hydrogen chloride (112), the evidence in these cases is much more substantial than the mere noncompliance of data with an equation known to be at best only a nonrigorous relationship derived by the aid of severe assumptions. These remarks hold also for modifications of Walden's law such as (130):

$$\Lambda^v \eta = \text{constant}$$

Using the assumptions (*i*) that the molecular conductance of a salt is an extensive property of the equivalent conductances of the constituent ions, (*ii*) that the equivalent conductance of a uni-univalent metal chloride is given by the semiempirical relation

$$\Lambda = k(1/r_+^2 + 1/r_-^2)$$

and (*iii*) that in different molten salts in corresponding states the chloride ion has the same mobility, Markov and Delimarskii (185) calculated degrees of ionization, α , for the processes



where MX_2 is a chloride of beryllium, magnesium, calcium, strontium, or barium. These calculations showed that in calcium chloride, strontium chloride, and barium chloride reaction II proceeded to completion while reaction III went only to the extent of 25, 43, and 70 per cent, respectively, while in magnesium chloride and beryllium chloride reaction II went 97 and 0.28 per cent to completion, respectively, while reaction III did not take place at all. However, while the assumption about the effect of ion size on conductance has some experimental support, there is considerable doubt about the validity of the third assumption concerning the constancy of the ionic mobility of a given ion in different molten salts.

The treatment which was used involves the assumption that if $\alpha_{\text{II}} > 1$ (α = degree of dissociation) in the first step of the calculation, then α_{II} determines the rest of the conductance, while if $\alpha_{\text{II}} < 1$ in the first step then $\alpha_{\text{III}} = 0$. There is no real justification for this. It is readily shown that the equivalent conductance is given by

$$\Lambda = \alpha_{\text{II}}[(1 - \alpha_{\text{II}})\lambda_{\text{MCl}^+} + (1 + \alpha_{\text{III}})\lambda_{\text{Cl}^-} + \alpha_{\text{III}}\lambda_{\text{M}^{2+}}$$

and that the assumed independence of α_{II} and α_{III} which is necessary to solve for α values in the manner of Markov and Delimarskiĭ is not valid, since the system is in a state of dynamic equilibrium. For example, for strontium chloride it follows that α_{II} lies in the range 1.0–0.5, and the equivalent conductance of the salt can be accounted for if α_{III} has an appropriate value in the range 0.43–0.00. It should be pointed out that these comments on the Markov–Delimarskiĭ computation method do not imply any support for either the method of calculating the ionic conductance data used or the assumption concerning the constancy of ionic mobility in different melts which has to be used but serve only to illustrate the inherent difficulties in this approach and the assumptions made.

Investigations on the relationship between melting and crystal structure have been reported recently by Ubbelohde and his coworkers. Among the salts studied were alkali hydrogen sulfates (225), nitrates (47), thiocyanates (216), and cryolite (164).

Measurements of the electrical conductance of the solid and molten salts, thermal analysis, change of volume on melting, and heats and entropies of fusion were carried out, and were correlated to provide information on the structures of the crystals and the melts, and the natures of the species present.

The problem of complex ions in binary fused salts has been recently considered by Antipin (2). The character of the change in conductance is discussed in the light of the Periodic Law, and complex formation is pictured as due to partial screening of the cation by the anions in the melt. An interpretation of the conductance and cryoscopic properties of sodium fluoride as due to the formation of the complex Na_2F^+ , rather than the formation of simple ions on fusion, is developed in this reference.¹

¹ *Note added in proof:* More recently Comescaisse (P. Comescaisse: J. chim. phys. 54, 795 (1957)), from a consideration of the shielding of the cation by one or more anions and the change in volume on fusion, has proposed an empirical relation based on the simple Newtonian force of attraction between anions and cations for the specific conductance of molten

Attention is directed to several papers that have appeared in Russian (152, 153, 184, 186, 265) and Japanese (201) journals too recently for consideration in the present work.

2. *Mixtures of molten salts*

Solutions of molten salts differ from conventional aqueous solutions in that the solute, even in the dilute concentration range, is subject to strong interionic effects because of the closeness of approach of charged ions to one another. They may be regarded as very concentrated electrolytes and, as such, are of considerable theoretical interest. Accordingly, studies of salt mixtures will contribute to a more complete understanding of complex-ion or ion-pair formation and to the theoretical treatment of concentrated electrolytes.

The phase diagrams for two-component systems give a complete description of the temperature-composition variations of the solid-liquid equilibria in such systems; many investigations have been made of different types of systems (simple eutectic, congruent and incongruent melting compounds, solid solutions, etc.) with the aim of finding out to what extent the structural conditions pertaining to the solid persist in the liquid.

Bloom and Heymann (25) studied the mixtures $\text{PbCl}_2\text{-KCl}$, $\text{CdCl}_2\text{-KCl}$, $\text{CdCl}_2\text{-NaCl}$, $\text{CdCl}_2\text{-CdBr}_2$, and $\text{CdCl}_2\text{-PbCl}_2$. The system $\text{CdCl}_2\text{-CdBr}_2$ shows no evidence in its phase diagram of complex-ion formation; the plot of conductivity against mole-fraction composition shows slight negative deviations from additivity. This type of behavior was found for the other noncomplexing systems studied. Only one system ($\text{CdCl}_2\text{-PbCl}_2$) was found to exhibit positive deviations from additivity. Systems in which complex ions exist, according to their phase diagrams, show strong negative deviations from additivity. The conductance isotherms of the systems $\text{PbCl}_2\text{-KCl}$ and $\text{CdCl}_2\text{-KCl}$ possess minima at all temperatures; the phase diagrams show the existence of congruently melting compounds. Additional minima in the conductance isotherms occur at low temperatures near compositions at which the phase diagrams show the presence of incongruently melting compounds; these minima vanish at higher temperatures. Bloom and Heymann (25) observe that the presence of a negative deviation in the conductance isotherms is compatible with the assumption of the presence of a certain amount of complex ion in the melt, and that the decrease in the extent of deviation with rise of temperature suggests that the complex dissociates into simple ions on heating. These workers found that on the addition of potassium chloride to cadmium chloride, the equivalent conductance decreases even though the conductance of pure potassium chloride is greater than that of cadmium chloride. The conductance isotherms and phase diagram are shown in figure 2. The system has one congruently melting compound ($\text{CdCl}_2\cdot\text{KCl}$) and one incongruently melting compound ($\text{CdCl}_2\cdot 4\text{KCl}$). The explanation offered is that since for mixtures containing up to 40 mole per cent potassium chloride the negative deviation is proportional to the mole-fraction of potassium

salts. Deviations from this principle are suggested as a measure of complex formation in the molten salts.

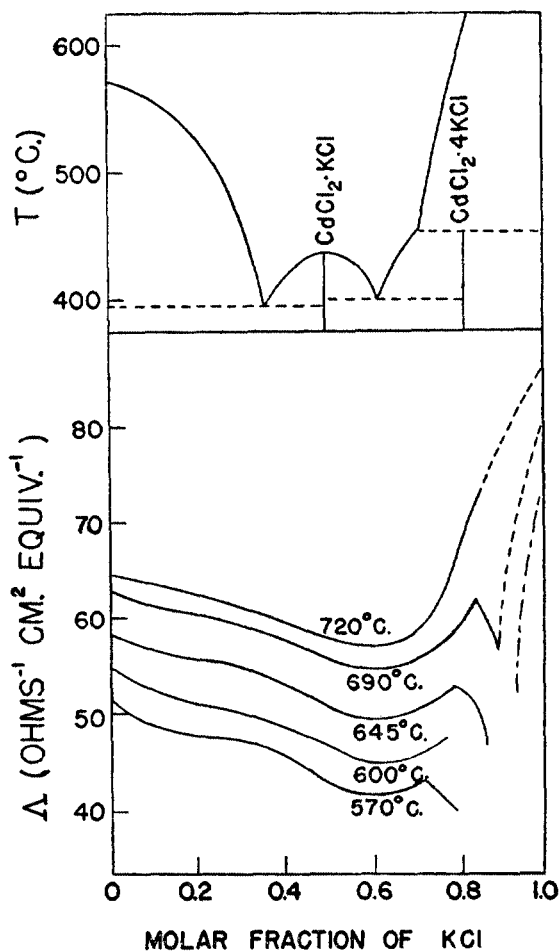


Fig. 2. Phase diagram and conductance isotherms of the cadmium chloride-potassium chloride system (25).

chloride, addition of this compound probably leads to the formation of a complex ion. The phase diagram suggests $(\text{CdCl}_3)^-$ ions. If this were the only complex in the melt, the maximum negative deviation should be near $x_2 = 0.5$, but it occurs at $x_2 > 0.5$, so another complex containing more chloride ions is probably present. The incongruently melting compound $\text{CdCl}_2 \cdot 4\text{KCl}$ suggests $(\text{CdCl}_6)^{4-}$ ions. This is shown by a deep minimum at $x_2 = 0.85$ at temperatures of 690°C . and below. The minimum disappears at higher temperatures. Accordingly the complex probably dissociates into simple ions on heating. These results favor the conclusion that even if an intermediate phase of a binary salt system has an incongruent melting point, the complex ion corresponding to that compound may persist in the molten state in a limited range of temperature. The energy of activation in the high-temperature range has a maximum near the composition corresponding to the compound $\text{CdCl}_2 \cdot 4\text{KCl}$. It may be that the energy of activa-

tion includes part of the heat of dissociation of the $(\text{CdCl}_6)^{4-}$ complex ion into Cd^{2+} and Cl^- ions.

The conductances of binary mixtures of lead chloride, cadmium chloride, and cuprous chloride with potassium chloride were also measured over a wide range of temperature by Sakai (233), who later (234) interpreted the results on the basis of the existence of complex ions such as had been suggested earlier (25).

The conductances of the systems KCl-NaCl , KCl-LiCl , and KCl-KI have been investigated by Van Artsdalen and Yaffe (263) over the whole composition range from temperatures a few degrees above the melting point to over 900°C . Isotherms at 800°C . for the three systems are shown in figure 3. The phase diagrams show that KCl-LiCl forms a simple eutectic with no solid solution, KCl-NaCl forms mixed crystals as well as a eutectic, and KCl-KI forms rather simple solid solutions with a minimum melting point. These systems were found to be reasonably ideal in their equivalent volume relationships, i.e., showing only small deviations from additivity. Inspection of the results (figure 3, 800°C .) shows that with respect to conductance, the systems are far from additive, negative deviations being found in each. The pronounced minimum in the equivalent conductance was explained qualitatively (263) in terms of the following model. Assuming that the long-range order of the solid state is destroyed, but that short-range order persists after fusion, the molten solution will consist of a semi-lattice of chloride ions with the smaller cations occupying positions

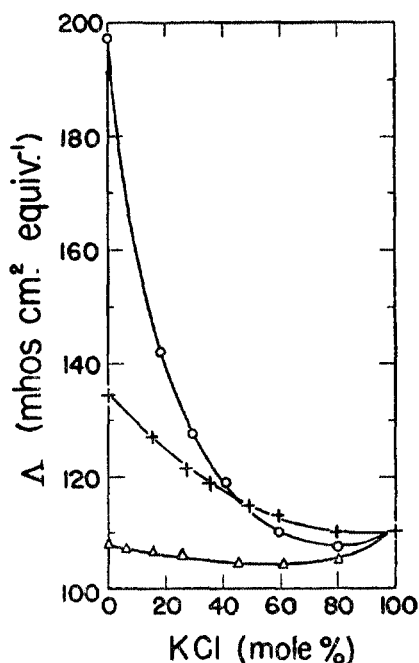


FIG. 3. Equivalent conductances at 800°C . as a function of composition for some binary alkali chloride mixtures (263): \circ , KCl-LiCl ; $+$, KCl-NaCl ; \triangle KCl-KI .

much as in the crystal. The size of the chloride-ion lattice will determine the molar volume, this quantity getting smaller as pure lithium chloride is approached. This is because lithium ions have a larger charge density and thus provide a better "glue" for the chloride ion semi-lattice. It is also assumed that the conductance of the melt is essentially cationic in nature. On the addition of lithium chloride to pure potassium chloride, the lattice shrinks in the melt, so migration of potassium ions will become more difficult. Since most of the conductance will still be due to potassium ions, the equivalent conductance should thus decrease. As the percentage of lithium ions increases, the equivalent conductance should thus decrease. As the percentage of lithium ions increases further, the equivalent conductance should increase to the value of pure lithium chloride. This explanation suggests the possibility of positive deviations near pure lithium chloride upon addition of potassium ions owing to expansion of the lattice, though the data seem to deny this. It may be that expansion of the chloride-ion lattice has no effect on the mobility of lithium ions, since the potentials restricting it are much less than that of potassium ions. It was pointed out (263) that caution should be applied in ascribing minima in equivalent conductance isotherms to the formation of complexes or compounds within the melt, unless other confirming evidence is available, in view of these results. These workers extended their theoretical study of the conductance of molten salts from pure salts to mixtures, using equation 12 to compute the entropies and heats of activation. The entropy of activation was found to be nearly the same for all compositions of the binary systems studied as for the pure salts. The heat of activation for the mixtures, however, increased toward a maximum at the composition where a minimum was observed in the equivalent conductance isotherm. If two cations are conducting in these melts there should be two heats of activation, one for each cation. Accordingly there would be two rate processes, each with its own characteristic composition-dependent heat of activation, both having the same order of magnitude, i.e.:

$$\Lambda = A_1 \exp(-\Delta H_1^\ddagger/RT) + A_2 \exp(-\Delta H_2^\ddagger/RT)$$

Others have suggested (245) that for systems having the smallest ion in common, such as AgCl-AgBr or AgCl-AgNO₃, the basic conductance equation

$$\Lambda = A \exp(-\Delta E/RT)$$

should hold if

$$\Delta E_{\text{mix}} = x_1 \Delta E_1 + x_2 \Delta E_2$$

i.e., if the energy of activation of each constituent is multiplied by the appropriate mole-fraction. The application of this relation, treating the energy of activation for conductance as an additive property, has been considered for the AgCl-AgNO₃ system (245). The energy of activation for pure silver chloride (1.3 kcal.) is temperature-independent, whereas for pure silver nitrate it decreases from 3.25 kcal. to 2.7 kcal. as the temperature is increased from 220° to 320°C. and is constant above this temperature. For the AgCl-AgNO₃ mixtures, the energy of

activation decreases considerably as the composition increases in silver chloride, even above 320°C. where presumably the heats of activation for the pure components are essentially constant. It is apparent in this system that the energy of activation for conductance in a mixture is not simply an additive property of the energies of activation for the pure components, but is a more complex problem. Harrap and Heymann (107) studied the AgCl–AgBr system and have suggested that the total equivalent conductances of all the components in the mixture should be additive, since this takes the contributions of all ions into account. This is basically the significance of equations 4 and 5.

A number of other binary systems of ionic salts have been studied. These include AgNO₃–NaNO₃ (32), AgNO₃–KNO₃ and AgNO₃–LiNO₃ (39), KCl–MgCl₂ (129), and Cd(NO₃)₂, Cd(NO₃)₂–RbNO₃, and Cd(NO₃)₂–AgNO₃ (218), to name only a few. Additional examples will be found in the references cited in this review and in the papers referred to in those references.

More complicated mixtures have also been investigated; for example, the MgCl₂–CaCl₂–KCl–NaCl system (275). Systems such as AlCl₃–NaCl, where one salt is a covalent compound, have also been studied extensively. Apart from those systems mentioned above, the systems BeCl₂–NaCl (48), ZnCl₂–KCl (63), aluminum chloride with a wide range of second components (192, 193, 197, 240), aluminum fluoride–alkali fluoride systems of the cryolite type (71, 72, 276), and mercuric halides with a wide range of added salts (122) were studied.

To summarize the results very briefly, it would appear that whereas addition of, say, potassium chloride to an ionic salt melt causes little change in the equivalent conductance other than a slight departure from the additivity which might be expected, a similar addition to a salt which is not completely or predominantly ionic causes a larger change which is usually ascribed by the investigator to the formation of complex species. It is not improbable that for convenience some formal distinction may have to be made between high-melting "ionic" salts and low-melting "covalent" salts when future discussion of their electrochemistry is made, just as in this review a distinction has been drawn between these systems and "molten oxide" systems of the silicate type.

IV. ELECTRICAL TRANSPORT

From measurements of electrical conductance and transport numbers of ions in aqueous solutions of electrolytes, and solutions of electrolytes in other solvents which act as inert "supporting media," it is possible to measure the velocities of the separate ions, and thence to obtain information on the natures and sizes of the ions, the nature and extent of their solvation, and the mechanism by which they move in the fluid.

In molten salts, direct measurement of transport numbers is not as readily applied as in aqueous systems, since in molten salts the solvent too is ionized. In pure molten salts the interpretation of the measurements is complicated further, since the conventional frame of reference, the solvent, is no longer available. Even in the case of mixtures, there are theoretical difficulties to be solved. The problem is attractive both theoretically and experimentally, and recently has been receiving attention by several groups of investigators.

A. EXPERIMENTAL TECHNIQUES

The fundamental principles of the design of transport number apparatus were derived by Hittorf in 1853 in a now classical series of experiments. Kortum and Bockris (157) give a good account of these principles and the calculations by which transport numbers are obtained from the quantities measured.

The first experiments on transport numbers in molten salts were performed by Lorenz and Fausti (171) in 1904, using a form of the basic Hittorf three-compartment cell, the anode and cathode compartments being separated by U-shaped tubes. This type of cell was used also by later workers (9, 10, 11, 115, 127, 236, 237). In at least one case, it was found (237) that severe interference was caused by convection set up in the connecting tubes by the passage of the electric current.

In a second design of apparatus, the anode and cathode compartments are separated by means of a porous diaphragm. Such cells were used first by Lorenz and Ruckstuhl (174). A three-compartment cell with sintered-glass diaphragms separating the end compartments from the center one was used by Wirths (270), with radioactive tracers added to the molten salts to provide the transference data from which the transport numbers were calculated.

These methods are suitable for mixtures of two molten salts, but not for pure molten salts. As will be discussed in detail below, pure molten salts cannot be studied by the conventional methods since no concentration changes can be observed in such a system.

Karpachev and Palt'guev (127) used an H-shaped cell, the connecting tube of which was packed with asbestos, both with and without the use of radioactive tracer solute, and also a three-compartment cell in which the center compartment was large enough to "buffer" any nonelectrolytic transfer from one electrode chamber to the other. The cells used in these experiments were cooled and broken apart so that radioactivity measurements could be made on the contents of the electrode chambers. The results were not influenced, it was claimed, by the design of the cell. A modification of the diaphragm type of cell was used by Duke and Laity (65, 66) in what was claimed to be the first practical method for the measurement of transport numbers of pure salts. The diaphragm used was found not to affect the results provided it was of sufficiently fine porosity. Volume changes between the compartments which occurred as a result of electrolysis were measured by using the current-induced transfers to compensate for the addition of a known quantity of salt to one side of the cell, an air bubble in a capillary tube connecting the two chambers being used as a means of detecting when the correct amount of transfer had been made.

Possible interference due to gravitational flow through the diaphragm was eliminated in an apparatus by Bloom and Doull (24) which consisted of a perfectly horizontal capillary tube fitted with a porous diaphragm at its mid-point. The movement of the boundary between the anolyte and the molten-metal electrode was used to measure the changes in volume of the electrode compartments. In a recent evaluation (169) of the moving indicator bubble (Duke and Laity) and electrode displacement (Bloom and Doull) techniques it was found

that in the moving bubble method a hydrostatic head of melt had to be built up before the bubble would move. In the case of salts such as molten silver chloride, as a result of bubble "stickiness" in the capillary indicator tube the hydrostatic head was large. For salts such as lead chloride the "stickiness" was much less severe, and the hydrostatic head was relatively small. It was noted that the technique used in the indicator bubble method largely compensated for the hydrostatic head needed to initiate movement, giving accordingly more reliable transport numbers. The electrode displacement method gives results which may be in serious error owing to "stickiness" of the molten-metal electrodes at the open ends of the capillary, possibly because of oxide formation or surface tension effects. The latter method has recently been modified so that the molten pools of metal do not move, while the less "sticky" molten salt acts as its own indicator boundary (26).

Arnikar (8) has measured the ionic mobilities of the alkali metal and halide ions in molten sodium nitrate directly by an electrophoresis experiment on asbestos paper, using radioactive tracer ions to follow the movement of the ions.

Several papers (35, 36, 143, 149, 195) concerned with the separation of isotopes by the passage of an electric current through mixtures of molten salts containing radioactive tracers have appeared. Independent ionic mobilities cannot be found, but the mobilities of ions relative to an arbitrarily chosen ion can be measured. The apparatus used consists, essentially, of a vertical moving-boundary cell mounted inside a suitable furnace.

Radioactive moving-boundary experiments have been carried out on pure salts also (33, 148, 176, 177, 178). In these experiments only the relative mobilities of the radioactive and nonradioactive species can be found, so that transport numbers themselves are not obtained. The limitations of the Hittorf type of transport number measurement have recently been discussed by Forland and Krogh-Moe (85). They accept the proposition of Sundheim (250) that such a volume-transfer experiment on pure molten salts yields quantities which are mass ratios and not transport numbers, and point out that measurements of, say, the relative amounts of sodium and potassium in both electrode compartments after electrolysis of a mixture of fused sodium chloride and potassium chloride can only give the ratio of the transport numbers of the two cations. The case of hydroxides in water is shown to be analogous to that of mixed salts, and thus the complexity of behavior of even such an apparently simple system as an aqueous sodium hydroxide solution was demonstrated.

B. THEORETICAL PRINCIPLES

A number of workers, one of the first being Schwarz (236), have pointed out that in pure molten salts there can be no concentration changes; so there can be no measurement of transport numbers in these systems. In fact, the results of Hittorf-type measurements make the transport number of that ion to which the electrodes are reversible apparently equal to unity. This problem will be dealt with later, but it is apparent that a conceptual difficulty arises in the definition of a transport number in a pure molten salt. The problem is less in mixtures

of molten salts, though many workers have glossed over the fact that there are still severe problems involved in defining these quantities.

As an introduction to the treatment, the situation of an electrolyte in an inert solvent may be considered. An ionic transport number t_i may be defined (157) as the fraction of the total current passing through the system which is carried by the given ion, i.e.,

$$t_i = I_i / \sum I_i \quad (13)$$

where I_i is the electric current carried by the given ionic species.

From the definition of t_i it can be seen that

$$\sum t_i = 1$$

It can readily be shown by the application of Ohm's law, current = (potential difference)/resistance, or current = (potential difference)(conductance), and equation 1,

$$\kappa = (F/1000) \sum c_i z_i u_i \quad (1)$$

relating the specific conductance (conductance of unit cube of the material) to the ionic concentrations, charges, and velocities under a potential difference of 1 volt per cm., to equation 13 that

$$t_i = c_i z_i u_i / \sum c_i z_i u_i \quad (14)$$

or

$$t_i = c_i z_i \lambda_i / \sum c_i z_i \lambda_i \quad (15)$$

In the simplest case, a single, fully dissociated, uni-univalent electrolyte as solute, it can be seen from equations 14 and 15 that

$$t_+ = u_+ / (u_+ + u_-) = \lambda_+ / (\lambda_+ + \lambda_-) \quad (16a)$$

$$t_- = u_- / (u_+ + u_-) = \lambda_- / (\lambda_+ + \lambda_-) \quad (16b)$$

For more complicated cases, t_i must be derived from equation 14.

In the derivation of equation 14 it was stated that the mobility, u_i , of the ion is the ionic velocity under a unit potential gradient. This is an oversimplification, since the frame of reference to which the velocities are referred has not been defined. In an inert solvent, the solvent particles remain at rest insofar as the current flow is concerned (though they move, of course, by thermal diffusion), and in such systems the solvent itself provides the frame of reference. This is the case in aqueous solutions. When the "other part" of the system through which the ion is moving is composed of the other ion of the salt, then the customary frame of reference has been lost. The case where there is more than one type of cation or anion present has been dealt with in one approach (236) by assuming that the species present in largest concentration does not move at all, and then defining the other mobilities relative to this species. In another approach (162) applicable to pure salts as well as to mixtures the mobility of the ion is defined as the velocity of the ion, under unit potential gradient, with respect to ions of the same kind not possessing sufficient energy to move at that

particular instant, multiplied by the fraction of ions jumping. This definition is derived from a model of the system based on the hole theory of liquid structure. It has the advantage over the preceding definition that no one ionic species is arbitrarily set "immobile."

Aziz and Wetmore (9), wishing to avoid ambiguity about the frame of reference, defined a quantity θ_i as the transport fraction which was the number of equivalents of the given ion transported per faraday of charge passed through the melt.

Consider a system such as a mixture of silver nitrate and sodium nitrate. The quantities θ_1 , θ_2 , and θ_3 may be defined as the number of equivalents of silver ion, sodium ion, and nitrate ion, respectively, transported per faraday. Originally the mole-fractions are x_1^0 , x_2^0 of silver nitrate and sodium nitrate. After electrolysis the anolyte is taken as the indefinite volume about the anode which meets the condition that it includes all variations from the initial composition. The indefinite volume of the anolyte consists of n_1 , n_2 equivalents of silver nitrate and sodium nitrate. For n faradays passed through the cell $n(1 - \theta_1)$ is the number of equivalents of silver nitrate transferred from catholyte to anolyte so that

$$\begin{aligned} \text{Similarly} \quad n_1 - n(1 - \theta_1) &\equiv n_1^0 \\ n_2 + n\theta_2 &\equiv n_2^0 \end{aligned}$$

now

$$n_2^0 = n_1^0 x_2^0 / x_1^0$$

and

$$\theta_1 + \theta_2 + \theta_3 = 1$$

Therefore

$$\phi = (n_1 + n_2)(x_1 - x_1^0)/n = 1 - \theta_1 - x_1^0 \theta_3 \quad (17)$$

Upon analysis of the indefinite volume of anolyte for constant composition along the horizontal portion of the cell n_1 , n_2 are known. From x_1^0 , x_2^0 and putting θ_3 equal to unity, the upper limit of θ_1 , θ_1^{\max} , may be found. The lower limit, θ_1^{\min} , may be found by successive approximation, setting θ_3 initially at unity.

The Duke and Laity (65, 66) indicator bubble technique consists, essentially, in passing an electric current until the bubble movement so caused is equal in magnitude and opposite in direction to that caused by the addition of a known amount of pure salt to one of the electrode compartments. These investigators used lead chloride in their experiments.

In such a case, if it takes n faradays to move the bubble back to its original position after W g. of lead chloride, density d_{salt} and equivalent weight $M_{e(\text{salt})}$, have been added, it can readily be shown that

$$nt_-(M_{e(\text{salt})}/d_{\text{salt}}) = nM_{e(\text{metal})}/d_{\text{metal}} + W/2d_{\text{salt}} \quad (18)$$

where $M_{e(\text{metal})}$ and $d_{(\text{metal})}$ are, respectively, the equivalent weight and density of the metal to the ions of which the electrodes are reversible. Hence

$$t_- = (W/2nM_{e(\text{salt})}) + (M_{e(\text{metal})}/M_{e(\text{salt})})(d_{\text{salt}}/d_{\text{metal}}) \quad (19)$$

In the Bloom and Doull (24) electrode displacement method the total quantity of salt transformed is proportional to the quantity of electricity, provided no diffusive processes occur, and therefore in this experiment

$$t_- = (2d_{\text{salt}}/M_{\text{salt}})(v/n) = 2W/nM_{\text{salt}} \quad (20)$$

where an increase in volume v occurs in the anode compartment owing to the passage of n faradays of current, or the transfer of W g. of salt.

Consider the passage of 1 faraday of electricity through a transport cell containing the salt silver chloride. At the anode, one equivalent of silver ion will pass into the molten salt. At the cathode one equivalent of silver ion will be deposited. If the chloride ions do not contribute to the transport process, then the mass changes in the two compartments correspond to the decrease of one equivalent of silver in the anode compartment and an equal increase in the cathode compartment. If the chloride ions do contribute in the transport process and carry a fraction t_- of the total current, then an equivalent fraction t_- of silver ion must remain in the anode compartment to preserve electroneutrality. This consideration leads to the following mass changes in the anode compartment for each faraday of current passed:

$$W/n = t_- M_{e(\text{salt})} - M_{e(\text{metal})} \quad (21)$$

If the transport processes are assumed to be of such a nature that the net transfer of mass is zero

$$t_- = M_{e(\text{metal})}/M_{e(\text{salt})}$$

Thus

$$t_- = M_+/(M_+ + M_-)$$

in the case of uni-univalent salts, which is the equation derived by Sundheim (below) from considerations of momenta. This present derivation is severely limited in its application because of the requirement of zero net mass transfer. A similar treatment of the Duke and Laity equation (equation 19) shows that under conditions of zero net mass transfer in a 1:1 electrolyte:

$$t_- = [M_+/(M_+ + M_-)](d_{\text{salt}}/d_{\text{metal}})$$

A theoretical treatment of the problem of transport numbers in molten salts presented by Sundheim (250) is claimed to have invalidated all transport measurements in pure molten salts. The approach is based on the conservation of momentum, and it is concluded that transference numbers in melts have little significance, since this theoretical analysis shows that the "transport number" measured is given by:

$$t_+ = M_-/(M_+ + M_-) \quad \text{or} \quad t_- = M_+/(M_+ + M_-)$$

where M_+ and M_- refer to the masses of cation and anion in the salt, respectively. Thus the transport number in a molten salt is solely a function of the masses of the constituent ions, and not in any way dependent on the charge of the species. The validity of this treatment is hard to disprove. If Sundheim's initial assumptions are accepted, the purely mathematical analysis appears to be sound, but objections have been raised both to Sundheim's mathematical approach and to his theoretical treatment. Beshers (21) has pointed out that the conservation of momentum equation derived by Sundheim is never used; the final equations are derived immediately from the definition of center of mass, and the result just gives the velocities of the components of a two-component system relative to the center of mass of the system. It is for this reason that insertion of the conditions for zero mass transfer into equation 21 leads to Sundheim's transport equation; there can never be any mass transfer relative to the center of mass of a pure molten salt. The validity of the assumptions concerning the treatment of a molten salt as a neutral body in a homogeneous electric field and therefore subject to no net force, and the applicability of the law of conservation of momentum to an ion moving from one equilibrium position to another over a distance which is of the order of magnitude of a molecular diameter have also been questioned (28). An extension of Sundheim's treatment to binary salt mixtures having an ion in common has also been made (252). Relationships between the terms derived by this treatment and the quantities known as transport numbers and diffusion coefficients are given. Because of the mathematical nature of the original paper, it is not possible to discuss it in detail here.

C. RESULTS

1. *Mixtures of molten salts*

A comparison of cell designs, analysis of results, temperature range, and transport numbers for the mixtures of molten salts studied by various workers is given in table 5.

The work of Lorenz (171, 174) is more of historical interest than quantitative significance, since the values obtained for the transport number varied with the design of the porous clay diaphragms used to separate the compartments. There was little control of convectional or gravitational interferences. Each of the later workers whose measurements are reported in the table claimed to have obtained reproducibility of results. Schwarz (237) had considerable experimental difficulties arising from convective flow of the electrolyte. He was able to demonstrate that the chloride ion possessed a higher mobility than the iodide ion, but was not able to obtain any information about the mobility of the stannous ion.

From the manner in which transport numbers were defined by Aziz and Wetmore (9), and by Hill and Wetmore (115), as in equation 17, it may be seen that they can be related to experimentally determinable quantities but cannot be determined from Hittorf-type measurements alone for the separate ions from changes in concentration; a procedure was given for assessing the maximum and minimum limits of the values. Hill and Wetmore (115) found it necessary to

TABLE 5
Transport numbers in mixtures of molten salts

System	Cell Design	Measurement	Temperature	Composition	Transport Numbers	Reference
KCl-PbCl ₂	Unglazed clay crucibles; carbon electrodes	Weight composition	800	1:1	$t_{K^+} = 0.19-0.36$ $t_{Pb^{2+}} < 0$	(171)
KCl-PbCl ₂	Unglazed clay crucibles; carbon electrodes	Weight composition	800	96% PbCl ₂ 48% PbCl ₂	$t_{Pb^{2+}} = 0.72$ $t_{Pb^{2+}} = 1.60$	(174)
KCl-PbCl ₂	Three-component; fritted-glass discs between carbon electrodes; chlorine at anode	Thorium B migration	450-550	2:1 1:1 1:2	$t_{Pb^{2+}} < 0$	(270)
KCl-MgCl ₂	Three-component with various salt bridges	Weight composition	550	1:1 2:1	$t_{K^+} = 0.49$ $t_{Mg^{2+}} = 0.14$ $t_{K^+} = 0.72$ $t_{Mg^{2+}} = 0.0$	(10)
NaNO ₂ -AgNO ₃	H-cell; folded-tube bridge with analysis bulbs; silver electrodes	Composition	330	5-25 mole per cent AgNO ₃	$t_{Ag^+} = 0.194-0.8$	(9)
NaNO ₂ -AgNO ₃	(a) Hittorf cell and (b) H-cell with porous glass diaphragm	(a) Composition (b) Volume changes	305	0-100%	$t_{NO_2^-} = 0.3$ t_{Ag^+}, t_{Na^+} proportional to composition	(67)
AgCl-AgNO ₃	H-cell; folded-tube bridge with analysis bulbs; silver electrodes	Composition	270	11.8-23.2 mole per cent AgCl	$t_{Ag_2Cl^+} = 0.057-0.115$	(115)
SnCl ₂ -SnI ₂	Double U-tube; 5.5 mm. without diaphragm; tin electrodes	Composition	250	4:1	Cl ⁻ anode enrichment	(237)
CaO-Na ₂ O-SiO ₂	Two crucibles with bridge or 1.5-mm. hole between them	Na ²⁴ , Ca ⁴⁵ migration	1150	1:1:4	$t_{Na^+} = 0.70$ $t_{Ca^{2+}} = 0.35$	(182)
CaO-P ₂ O ₅	Two crucibles with bridge or hole between them	Radioactive tracer	1000		$t_{Ca^{2+}} = 1.05$	(183)

postulate the existence of the Ag_2Cl^+ ion in silver chloride-silver nitrate mixtures to avoid a negative transport number for chloride ion, which migrates towards the cathode. They suggested that the silver ion might conduct by repeated rotation of the complex Ag_2Cl^+ ion and transfer of a silver ion to an adjacent silver chloride ion-pair on the cathode side, a Grotthus chain mechanism (157), in fact, to account for the high mobility observed for the silver ion.

Duke, Laity, and Owens (67) have recently shown that if Hittorf-cell data of the type obtained by Aziz and Wetmore (9) are combined with volume-change data (66) then sufficient is known for calculation of the transport numbers of all

the ions in a binary system such as $\text{AgNO}_3\text{-NaNO}_3$. The value of $t_{\text{NO}_3^-}$ is constant at about 0.3 at 305°C ., within experimental error, over the complete range of composition. The transport numbers of silver ion and sodium ion appear to be directly proportional to the mole-fraction of the salt; they are zero in the pure other salt and about 0.7 in the pure salt. Taken with data on the conductance of the system (32) these results show that the mobilities of the ions are constant, leading to the suggestion that there is no systematic change in the character of either salt when diluted with the other. This is regarded (60) as nonthermodynamic evidence for the complete ionization of these fused nitrates in mutual mixtures and the pure salts. In mixtures of lead chloride with potassium chloride, Wirths (270) found some migration of lead towards the cathode, suggesting the presence of complex ions. Transport measurements (10) on various mixtures of potassium and magnesium chlorides in a Hittorf-type cell at $550\text{-}700^\circ\text{C}$. gave values of t_{K^+} which varied from 0.49 at the composition $\text{KCl}\cdot\text{MgCl}_2$ to 0.79 at the composition $(2.5\text{KCl})\cdot\text{MgCl}_2$. In these mixtures $t_{\text{Mg}^{2+}}$ was 0.14 and 0.00, respectively. The results obtained, however, were of poor reproducibility. In the NaCl-AlCl_3 system, similar measurements showed that in the region of composition 1:1 the current is all carried by the sodium ions (12).

The $\text{PbCl}_2\text{-KCl}$ system has been studied by radioactive tracer techniques (64). The transport number of the chloride ion decreased fairly steadily as the composition of the mixture changed from pure lead chloride to pure potassium chloride; that of the lead ion was fairly steady for a while and then dropped rapidly to zero; and that of the potassium ion rose, steadily at first and then more sharply as the proportion of potassium chloride increased. These changes were related to the ionic mobilities; the mobilities of the chloride and lead ions decrease a little as potassium chloride is added to lead chloride, while the mobility of the potassium ion increases markedly. No evidence could be found for the formation of complex ions from the mobility data.

Measurements of transport numbers by radioactive tracer methods in the molten systems $\text{CaO-P}_2\text{O}_5$ and $\text{CaO}\cdot\text{Na}_2\text{O}\cdot 4\text{SiO}_2$ have shown that in the former case (183) the calcium ion has a transport number of 1.05, and in the latter case (182) the transport numbers of the sodium ions and calcium ions are 0.7 and 0.35, respectively. In both of these systems, therefore, the anions would appear to take no part in the conductance process.

Monse has shown (195) that in the system 65.9 mole per cent silver nitrate + 34.1 mole per cent silver chloride, the relative mobilities at 250°C . are

$$\begin{aligned} \text{NO}_3^- \text{ relative to } \text{Ag}^+, & 3.42 (10^4 \text{ cm.}^2 \text{ sec.}^{-1} \text{ volt}^{-1}) \\ \text{Ag}^+ \text{ relative to } \text{Cl}^-, & 3.68 \\ \text{NO}_3^- \text{ relative to } \text{Cl}^-, & -0.26 \end{aligned}$$

The "transport number" defined by Schwarz (236) may be written (see above),

$$t_{(\text{Ag}^+ \text{ relative to } \text{Cl}^-)} = Fc_{\text{Ag}} + u_{(\text{Ag}^+ \text{ relative to } \text{Cl}^-)}/k$$

and yields a value of 0.36 for $t_{(\text{Ag}^+ \text{ relative to } \text{Cl}^-)}$ from these data compared with a value of 0.05 calculated from the data given by Schwarz.

The recent "paper electromigration" experiments by Arnikař (8) on solutions of alkali metal chlorides and bromides in molten sodium nitrate gave the following ionic mobilities, expressed in $10^4 \text{ cm.}^2 \text{ sec.}^{-1} \text{ volt}^{-1}$ at $350 \pm 5^\circ\text{C.}$:

Li ⁺	3.75	Cl ⁻	1.95
Na ⁺	4.16	Br ⁻	1.43
K ⁺	3.74		
Rb ⁺	3.58		
Cs ⁺	3.38		

Separation or enrichment of isotopes by the application of electrolysis techniques to molten salts has been shown theoretically by Klemm (135, 136, 137, 140, 141, 142, 149) and experimentally by Klemm and other workers to be feasible. Measurements carried out recently on the PbCl₂-LiCl system, using radioactive isotopes of lithium (149), have shown that the mobility of the lithium ion relative to the chloride ion is about twice that of the lead ion, and that the relative mobility of the lithium isotope of mass 6 is about 2 per cent greater than that of the isotope of mass 7.

Among the isotopes enriched by electrolysis in mixtures of molten salts have been Li⁶/Li⁷ and K⁴¹/K³⁹ in LiCl-KCl (143), Tl²⁰⁵/Tl²⁰³ in TlCl-ZnCl₂ (146), Na²²/Na²⁴ in NaNO₃-KNO₃ (36), and many others (35, 149, 195).

2. Pure molten salts

Table 6 summarizes the results obtained from measurements of transport number on pure molten salts.

Duke and Laity (65, 66) and Bloom and Doull (24) have both studied pure lead chloride; the former gave a value of $t_{\text{Cl}^-} = 0.67$ to 0.75 , and the latter gave $t_{\text{Cl}^-} = 0.39$. In the light of the recent assessment (169) of the two methods, which theoretically should give the same value for t_{Cl^-} , it appears that the value for t_{Cl^-} in lead chloride is much closer to 0.75 than to 0.39 . The latter value can be explained as the result of a flow of electrolyte through the cell membrane under the influence of hydrostatic forces set up by "stickiness" at the lead/air interface in the silica capillary tube. Some less exact experiments by Karpachev and Pal'guev (127) had earlier given a value of $t_{\text{Cl}^-} = 0.8$ in lead chloride, while some experiments carried out in 1955 on lead chloride (49) and bromide, but apparently overlooked, had given $t_{\text{Cl}^-} = 0.83$. Richards (221) has recently repeated Bloom and Doull's measurements, using radioactive tracers, and reports a value of 0.7 for t_{Cl^-} in lead chloride.

The only other direct measurements of transport number so far reported as having been made on pure molten salts are on cadmium chloride (24) and silver nitrate (26). A value of $t_{\text{Cl}^-} = 0.34$ was obtained for cadmium chloride, the same value as for lead chloride, by the original electrode displacement technique. A modified electrode displacement technique was used for silver nitrate to overcome the "stickiness" of the molten-metal electrodes, and also because the electrodes were solid at the temperature of the melt.

In silver nitrate, $t_{\text{NO}_3^-}$ was only 0.25 . From the binary mixture measurements

TABLE 6
Transport numbers in pure molten salts

Salt	Cell Design	Measurement	Temperature	t_{Cl^-}	Reference
			°C.		
PbCl ₂	Three-compartment cell (a) Connecting tubes (b) Asbestos diaphragms	(a) Lead migration (b) Weight changes	520-680	0.8	(127)
PbCl ₂	H-cell with fritted discs; air bubble moved	Volume changes	565	0.67-0.75	(65)
PbCl ₂	Horizontal cell with fritted disc; lead electrodes moved	Volume changes	528	0.393	(24)
PbCl ₂	Two-compartment cell, separated by powdered corundum		550-580	0.83	(49)
PbCl ₂	Horizontal cell with fritted disc; lead electrodes moved			0.7	(221)
PbBr ₂	Two-compartment cell, separated by powdered corundum		430	(t_{Br^-}) 0.92	(49)
CdCl ₂	Horizontal cell with fritted disc; lead electrodes moved	Volume changes	602-608	0.34	(24)
AgNO ₃	Horizontal cell with fritted disc; silver nitrate melt moved; solid silver electrodes	Volume changes	232	($t_{NO_3^-}$) 0.251	(26)

on the NaNO₃-AgNO₃ system made recently (67) a fairly constant value of $t_{NO_3^-}$ was obtained over the whole range of composition. The value of $t_{NO_3^-}$ was a little less than 0.3, in fair agreement with the value quoted above.

Sundheim's theoretical treatment (250) of transport in pure molten salts, which would explain the quantities measured as being functions of the ionic masses, has already been referred to above. Laity (162) has discussed the conceptual difficulties involved in defining transport numbers in pure molten salts, and has arrived at the conclusion that the problem is experimental rather than conceptual, that satisfactory definitions *can* be arrived at, but that a technique suitable for measuring the quantities defined has not yet been devised.

Measurements of relative mobility have been carried out on pure molten salts as well as on mixtures (see above). The fact that isotopes can be separated, even partially, by electrolysis makes it apparent that different isotopes have different mobilities (and hence different transport numbers).

Isotopes which have been enriched by the electrolysis of pure salts include Ag¹⁰⁷/Ag¹⁰⁸ in silver chloride (78), Br⁷⁹/Br⁸⁰ in lead bromide (33), Li⁶/Li⁷ in lithium chloride (139), Li⁶/Li⁷ in lithium nitrate (177), and other similar systems (138, 144, 145, 147, 148, 176, 178).

Since this work is not yet capable of yielding more than relative values, this brief mention of the literature, without discussion, will suffice for the present purpose.

V. CRYOSCOPY

Freezing-point measurements yield information about the natures and activities of the molecular and ionic species and the modes and degrees of dissociation occurring in a solute-solvent system (123). Data such as heats and entropies of fusion can also be derived for use in elucidating the structures of the melts.

Freezing-point measurements on molten salts can be divided into two overlapping groups. In phase-rule studies the range of composition studied is usually from 0 to 100 per cent of added constituent, the temperature often being measured with an accuracy of only plus or minus several degrees. Analyses of the solid phases which separate out on freezing the liquid are also often made. For cryoscopy (or, more correctly cryometry) the concentration range studied is usually low, usually up to about 0.1 mole-fraction, and the freezing points are measured with an accuracy of usually $\pm 0.1^\circ\text{C}$. or better. In this review only investigations sufficiently precise for the determination of physicochemical data will be considered; reference may be made elsewhere (235) for reviews of phase-rule investigations.

Several reviews are available (41, 42, 52, 53, 123, 204, 209, 210, 261) which deal with the various general aspects of cryoscopy in molten salts.

A. EXPERIMENTAL TECHNIQUES

The well-known techniques used in measuring the melting points of organic compounds are not often used in studies of inorganic salts because of the different, usually more difficult, manipulative problems involved and the greater accuracy which is desired. In a recent investigation on the cryoscopic behavior of solutions in mercuric bromide (122) use was made, however, of melting-point capillary tubes attached to a mercury-in-glass thermometer. Most modern accurate investigations have been performed by measurement of the temperature at which solid forms when the molten salt is cooled, i.e., the freezing point.

Particular care must be paid in molten-salt cryoscopy to ensure that agitation is sufficiently vigorous for true thermal equilibrium between solid and liquid. In the case of many inorganic salts, atmospheric gases or moisture have undesirable effects; recourse must then be made to completely sealed or controlled-atmosphere apparatus for accurate measurements.

A discussion of several types of apparatus used in cryometric studies has been given recently in a paper (244) presenting an improved form of a controlled-atmosphere cryoscope for use with inorganic salts up to moderately high temperatures. About 50 per cent of the more common pure inorganic salts melt below 500°C . (98) and may therefore be handled in Pyrex glass; only about 30 per cent melt above 900°C . and cannot be handled in Vycor glass.

Temperature measurement is usually by means of thermocouples (224), though for many purposes thermistors or platinum resistance thermometers have been suggested (31, 188, 246).

Only three recent papers (122, 155, 194) appear to have suggested the use of a liquid-in-glass thermometer.

For a detailed discussion of the ranges and conditions for which the various types of thermometer may be used, reference may be made to standard works on the subject such as those mentioned earlier in this review.

Apparatus suitable for automatically recording the cooling curve has been described by several workers (31, 43, 61, 165, 214, 244a, 258, 267, 268, 269, 278), but only a few of these devices have actually been used for molten-salt cryometry. Many suffer from the disadvantage that the actual temperature of some hundreds of degrees is recorded while the cooling curve itself only covers a range of perhaps 10°. Some use a circuit containing two galvanometers, the second being operated from the first by means of a photocell and light beam. Recently a "recording Beckmann thermometer" was described (244b) which can be used with a thermocouple to measure and record on a 10-in. wide chart temperature changes of from 200° to 5°C., in six ranges, with a platinum/platinum-rhodium couple, or down to 1.3°C. with other couples. It possesses the advantage that it is possible to construct it entirely from commercially available units.

Extrapolation of the cooling curve back to the point of onset of supercooling gives a value for the freezing point which is sufficiently accurate for most work (131). No investigations on molten salts reported to date have been sufficiently precise thermometrically to require corrections such as are applied in precision hydrocarbon-solvent cryometry (181).

B. THEORETICAL PRINCIPLES

The basic equation relating the activity of a solvent, a_1 , to the freezing point of its solution, T , is

$$d \ln a_1/dT = \Delta H_f/RT^2 \quad (22)$$

where ΔH_f is the heat of fusion of the solid solvent and R is the gas constant.

From this equation may be derived the classical equations:

$$\Delta T_f = (RT^2/\Delta H_f)x_2 \quad (23)$$

or

$$\Delta T_f = (RT^2 M_1/1000 \Delta H_f)m_2 = (k_f)m_2 \quad (24)$$

relating the lowering of the freezing point, ΔT_f , of the solvent to the mole-fraction, x_2 , or molal concentration, m_2 , of an ideal, inert, unionized solute in the solution. The terms in brackets in these equations are constants characteristic of the solvent, the term k_f being known as the "molal freezing-point depression" or "cryoscopic constant."

When the solute ionizes or dissociates, to give a total of ν particles per added molecule, each particle acts independently of the others and the equation corresponding to equation 24 is

$$\Delta T_f = \nu k_f m_2 \quad (25)$$

In the derivation of these equations, higher terms than the first in a power series expansion were neglected. These equations are therefore only limiting expressions, but they may often be used for work of moderate accuracy up to fairly

high concentrations. Thus there is usually an error of only about 1 per cent at 0.2 mole-fraction from this approximation.

One assumption made in the derivation of these equations is that the solid which separates is pure solvent. If this is not so, the actual concentration of the solution will change with the amount of solid solution crystallized out at any given time. The relationship

$$\Delta T_f = (k_f)(1 - \rho)m_2 \quad (26)$$

where ρ is the distribution coefficient of the solute between the solid and the liquid phases, may be used for such systems.

So far, only undissociated solvents have been considered. When the solvent is partially dissociated, added ions or molecules common with those produced by the solvent will repress the dissociation. This effect has been studied extensively for nonaqueous systems such as solutions in sulfuric acid (88), which undergoes a dissociation



which is repressed by the addition of metal hydrogen sulfates, e.g.:



Addition of small amounts of a "common species" to such a solvent will, initially, cause no change of the freezing point. As more solute is added, the dissociation of the solvent is repressed until finally all added species are effective in lowering the freezing point. The freezing-point depression in dilute solution is given by

$$\Delta T_f = nk_fm_2 \quad (27)$$

where n is the number of "foreign" particles, i.e., ν minus the number of "common" particles produced per molecule of solute; the depression in the concentrated solutions is given by equation 25, insofar as this applies to concentrated solutions. As the degree of dissociation of the solvent increases, the range of concentration over which n , and not ν , should be used also increases. In the case of completely dissociated solvents, addition of even very high concentrations of a common ion cannot affect the freezing point.

In some of the earlier papers on cryoscopy in molten salts (229–231) it was suggested that the smaller than expected freezing-point depression produced by a solute having an ion in common with the solvent was due to nondissociation of the solute caused by the mass action effect of the large excess of solvent species on the dissociation of the solvent; this is not now believed. Rather, it is believed that dissociation takes place but that the activity of the solvent is unaffected by the common species.

The theoretical treatment for the common-species effect has been derived rigorously by various workers for several different types of system. The earliest treatment was given by Stortenbeker, after discussion with H. A. Lorentz (247). The Stortenbeker theory has been presented again by Darmois (41, 42), while other authors (168, 264) have given simpler versions of the same treatment.

Other forms of treatment designed to cover the conditions pertaining to various different types of dissociated solvent-solute systems have been published (68, 87, 271-273).

Hoenen, in 1913, developed a rigorous thermodynamic treatment for the effects of various types of added species on pure salts and on various phase-point mixtures of salts (116). It is usually this treatment which is used by molten-salt cryoscopists, even though the other methods lead to exactly the same results.

Other workers (77, 83, 104, 158, 161) have used methods based on the application of the principle of mass action. The treatment developed by Haase (104) is used in France (51, 53, 58, 60, 204).

It must be stressed that the conclusions reached by all these different workers are the same: that in very dilute solutions addition of a species as solute which is already present as a result of the dissociation of the solvent should cause no change of freezing point, and that in ideally behaving molten salts or other fully dissociated solvents this behavior should be observed over the entire concentration range.

The thermodynamic aspect of the effects of "common" and "foreign" ions has been given a "structural" interpretation. Temkin (257), who investigated these effects in molten slags, interpreted them on the basis of a model for the liquid structure in which ions of like sign are randomly distributed but ions of opposite sign are ordered. He showed, essentially, that the basic freezing-point equation (equation 22) is obeyed if the activity of the solvent, a_1 , is given by an expression of the type

$$a_1 = (a_{\text{cation}})(a_{\text{anion}}) = (N_{\text{cation}})(N_{\text{anion}}) \quad (28)$$

where a_{cation} , a_{anion} , are the activities of the cationic and anionic species produced by the self-dissociation of the solvent, and N_{cation} , N_{anion} are the corresponding "ionic fractions":

$$N_{\text{cation}} = (n_{\text{cation from solvent}})/(n_{\text{all cations in mixture}}) \quad (29)$$

As in cases where mole-fractions are equated to activities, the assumption of ideality is made in equating ionic fractions to activities.

Temkin's equations and similar equations proposed by other workers have been discussed in detail elsewhere (79, 80, 222).

Herasymenko and Speight (111) used equation 28 for the activity of the solvent in slags, but instead of equation 29 used

$$a_{\text{cation}} = n_{\text{cation}}/(n_{\text{cation}} + n_{\text{anion}})$$

which implies that there is no restriction on the positioning of cations relative to anions in such melts. Another equation suggested (80) for the activity of an ion used terms of the form zn_{ion} instead of merely n_{ion} , where z is the valence of the ion, implying that when, say, a divalent ion replaced two univalent ions, the other univalent ions could exchange places either with the divalent ion or with a vacancy which had been created by the replacement.

C. RESULTS

A review of the more important cryoscopic studies on systems of molten salts carried out before 1913 was made by Hoenen (116) to provide data for a test of his theories.

A list of the anhydrous salt systems studied by thermal analysis by Soviet workers was published recently (20), and reviews in English of the recent literature of freezing-point investigations will be found in the *Annual Review of Physical Chemistry* (235).

Compilations of data and references of value to the molten-salt cryoscopist will be found in several reference works (22, 118, 132, 133, 163, 167, 219, 228).

Both the original computations carried out by Hoenen and more recent investigations such as those of American, British, French, German, and Norwegian workers (44-46, 50, 54, 55, 57-59, 61, 68, 81, 82, 88, 102, 103, 108-110, 154-156, 190, 191, 203, 206-208, 211, 212, 223, 226, 227, 262, 277) have shown that the freezing-point behavior expected of various solute-solvent systems at low concentrations is in fact observed experimentally. Indeed, in several cases the claim has been made that the system behaves as predicted to quite a high concentration. This should not be taken too literally, however, as a ν -factor changing from, say, 1.9 to 1.5 over a concentration range of 0.1 molal would be regarded by some workers as satisfactory agreement with a predicted value of 2.0.

In general, the halides have been the most popular simple solvents, with nitrates next. Chlorates, nitrites, sulfates, carbonates, phosphates, borates, tungstates, thiocyanates, and many other salts have also been used. A considerable amount of interest has been focussed on mixtures of oxides, in particular those containing silica, because of their importance in metallurgy as slags and in the glass and ceramics industries. Compounds of the alkali and alkaline earth metals have received the greatest amount of attention, but many studies have been made of compounds of silver, zinc, mercury, boron, aluminum, lead, tin, phosphorus, arsenic, and antimony (the halides and oxyhalides of these latter in particular); there are apparently few common compounds on which no studies have been made.

The melting points, heats of fusion, and cryoscopic constants for several molten salts used as solvents in cryoscopic investigations have been collected in table 7. Since a number of these values are based on early data (116), the cryoscopic constants should be taken only as approximate values until more reliable data on heats of fusion are available. The heat of fusion of a eutectic mixture or solid solution used as a cryoscopic solvent may be estimated with moderate accuracy from the data for the pure components and Kirchhoff's equation (93). Thus, the value 3.9 kcal. mole⁻¹ predicted for the LiCl-KCl eutectic mixture may be compared with a recent experimental value (93) of 3.2 kcal. mole⁻¹ obtained calorimetrically.

Some data on heat of fusion and entropy of fusion are given in tables 7 and 8 for a variety of inorganic salts. Such data, both calorimetric and cryometric in origin, have been used (160, 164, 216, 222, 253, 254) to obtain information con-

TABLE 7
Melting points, heats of fusion, and cryoscopic constants for some molten-salt solvents

Solvent	Freezing Point	ΔH_f	k_f	References
	°C.	cal. mole ⁻¹	deg. mole ⁻¹ kg.	
NaCl.....	801	7230	19.4	(211, 116)
KCl.....	772	6410	27.6	(116)
KF.....	859.9	6290	25.6	(116)
NaF.....	992.2	7810	17.1	(116)
SrCl ₂	873	4060	51.3	(116)
CaCl ₂	765	6050	39.2	(116)
KNO ₃	334.5	4760	15.6	(116)
NaNO ₃	305.8	3860	15	(262)
AgNO ₃	208.5	2750	28.36	(155)
KCNS.....	177.9	2250	17.4	(155)
NaClO ₃	255	5150	11.5	(116)
HgBr ₂	238.5	3960	37.45	(122)

TABLE 8
Crystal structures, ionic radii, and entropies of fusion for salts of monovalent ions (228)

Cation	Radius of Cation A.	F ⁻ $r_{\text{anion}} = 1.4 \text{ \AA.}$		Cl ⁻ $r_{\text{anion}} = 1.8 \text{ \AA.}$		Br ⁻ $r_{\text{anion}} = 2.0 \text{ \AA.}$		I ⁻ $r_{\text{anion}} = 2.2 \text{ \AA.}$		NO ₃ ⁻ $r_{\text{anion}} = 1.9 \text{ \AA.}$		SO ₄ ²⁻	
		Crystal structure	$\Delta S_f/2^*$	Crystal structure	$\Delta S_f/2$	Crystal structure	$\Delta S_f/2$	Crystal structure	$\Delta S_f/2$	Crystal structure	$\Delta S_f/2$	Crystal structure	$\Delta S_f/3$
Cs...	1.65	Cubic	1.8	Cubic†	2.0	Cubic	1.0	Cubic	—	†	2.4	Rhombic or hexagonal	—
Rb...	1.5	—	2.0	Cubic	2.2	Cubic	2.0	Cubic	1.6	Hexagonal cubic†	1.1	Rhombic hexagonal	—
K...	1.3	Cubic	3.0	Cubic	2.9	Cubic	3.5	Cubic	—	Rhombic trigonal†	2.3	Rhombic hexagonal	2.2
Na...	1.0	Tetragonal or cubic	3.1	Cubic	3.15	Cubic	3.0	Cubic	2.8	Trigonal or rhombic	3.3	Hexagonal	2.7
Li...	0.8	Cubic	1.6	Cubic	1.8	Cubic	1.8	Cubic	—	Trigonal	5.8	Cubic	0.9
Ag...	1.1	Cubic	—	Cubic	2.2	Cubic	1.6	Hexagonal	1.4	Rhombic	2.9	Rhombic	2.0
Cu...	1.0	‡	—	Cubic†	1.7	Cubic†	—	Cubic†	—	—	—	—	—
Tl...	1.5	Cubic octagonal	—	Cubic	2.8	Cubic	2.5	Cubic (red) Octagonal (yellow)	1.9	Cubic†	2.4	Rhombic	2.0

* Entropy of fusion per gram-ion.

† Displays one or more transitions below the melting point.

‡ Considered to exist as Cu₂X₂.

cerning the change in structure of solids on melting. The differences observed in the entropy of melting between salts such as alkali halides and alkali hydrogen sulfates have been attributed (216, 225) to contributions from rotational and vibrational motions of the ions which are "frozen in" on solidification and from the break-up of association complexes, which occur in the polyatomic salts but not in the diatomic salts.

TABLE 9
Results of some cryoscopic studies on molten-salt systems

Solvent	Solute			Reference	Solvent	Solute			Reference
	Observed freezing-point depression factors					Observed freezing-point depression factors			
	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3			<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	
AgNO ₃	KNO ₃	KClO ₄	HgCl ₂	(155)	KCl.....	KF			(116)
	Pb(NO ₃) ₂	PbSO ₄	HgBr ₂			K ₂ SO ₄			
KCNS.....	Ag ₂ SO ₄	ZnSO ₄	HgI ₂	(155)	SrCl ₂	K ₂ CO ₃			(116)
	AgCN		PbCl ₂		CaCl ₂	K ₂ CrO ₄			
	AgCNS		K ₂ Cr ₂ O ₇			SrSO ₄			
	KBr					CaSO ₄	BaSO ₄		
	KI					CaO			
NaCl.....	KCN			(211)	NaNO ₂	NaCl	LiCl	CaCl ₂	(262)
	AgCNS					Na ₂ CO ₃	CsCl	SrCl ₂	
	KNO ₃		BaF ₂			Na ₂ SO ₄		BaCl ₂	
	NaF	KF				NaBrO ₄			
KNO ₃	KCl			(116)					
	NaF	BaSO ₄				Na ₂ WO ₄			
	Na ₂ SO ₄	SrCO ₃				Na ₂ MoO ₄			
	Na ₂ CO ₃					Pb(NO ₃) ₂			
	AgNO ₃	NaCl	SrCl ₂		(116)	LiNO ₃			
	KCl		BaCl ₂						
	Ba(NO ₃) ₂								
	Sr(NO ₃) ₂								

The results of some of the more important cryoscopic studies on simple salts are collected in table 9, while figure 4 shows some of the results obtained (155) for solutions in the solvent silver nitrate.

The successful prediction of the cryoscopic behavior of many types of solute-solvent systems has led to the use of cryoscopy as a diagnostic procedure. One example of this is the explanation of the behavior of K₂[Hg(Cr₂O₇)Cl₂] in silver nitrate (155). The complex salt gives a sixfold freezing-point depression; mercuric chloride and potassium dichromate give threefold depressions. Potassium

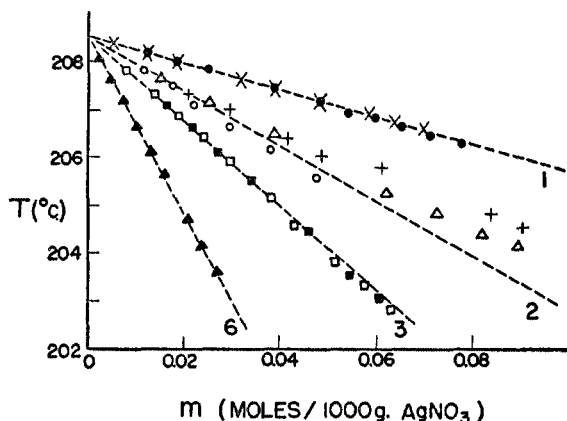


FIG. 4. Freezing-point depressions in the solvent silver nitrate (155). - - - are theoretical lines for *n* = 1, 2, 3, and 6. The experimental points are: X, Ag₂SO₄; ●, Pb(NO₃)₂; +, ZnSO₄; ○, PbSO₄; △, KClO₄; ■, K₂Cr₂O₇; □, PbCl₂; ▲, K₂[Hg(Cr₂O₇)Cl₂].

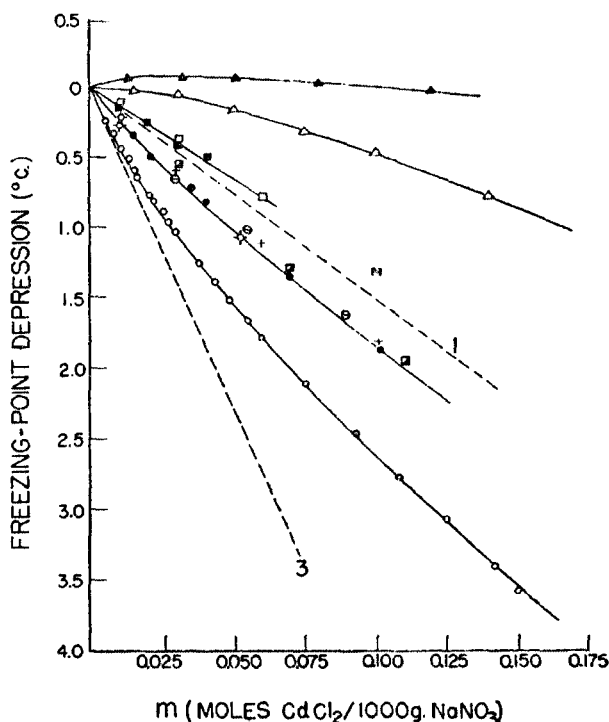


FIG. 5. Freezing-point depressions of sodium nitrate by cadmium chloride in the presence of added chlorides (262). --- are theoretical lines for $n = 1$ and 3. The experimental points are: \circ , + pure CdCl_2 ; \bullet , + 0.10 m NaCl ; \blacksquare , + 0.54 m CaCl_2 ; \ominus , + 0.10 m KCl ; \oplus , + 0.10 m CsCl ; $+$, + 0.110 m LiCl ; \blacksquare , + 0.2 m NaCl ; \square , + 0.109 m CaCl_2 ; \triangle , + 0.4 m NaCl ; \blacktriangle , + 0.627 m NaCl .

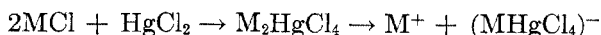
chloride was not studied, but would be expected to give a twofold depression. Thus the sixfold depression given by the complex can be satisfactorily explained as being caused by the dissociation:



The association of ions in molten salts to form complexes, as well as the dissociation of molecules, can be shown by cryoscopy. Figure 5 shows some of the results obtained by Van Artsdalen (262) for the freezing points of solutions of cadmium chloride in sodium nitrate solvent in the presence of added chloride. As the concentration of the added chloride is increased, the effect on the freezing point produced by a given concentration of cadmium chloride decreases; this is interpreted as a removal of chloride ions by the cadmium ion. The data have been interpreted as showing that the important species in the melt are Cd^{2+} , CdCl_2 , and CdCl_4^{2-} . Similar results were obtained with other salts. Some of the results which have been obtained are collected in table 10.

The behavior of alkali metal chlorides in mercuric chloride (18) is of interest. The "apparent molecular weight" increases with increasing concentration; i.e.,

the depression factor decreases with concentration. Furthermore, the depression factor for, say, the solute potassium chloride is initially greater than unity. It was seen, above, that for a fully or partially dissociated solvent, addition of a binary salt with an ion in common with the solvent should give an initial depression factor of unity. The depression factor would also increase with concentration. These anomalous results were explained (84) on the basis of the reaction:



Confirmation for this suggestion was obtained from conductance measurements.

More recent investigations (122), using mercuric bromide as the solvent, have shown that solutes such as potassium bromide, sodium bromide, and thallos bromide give depression factors of 2 at very low concentrations, falling to about

TABLE 10
Cryoscopic evidence for the existence of complex ions in molten-salt systems

Solvent	Solute	Cryoscopic n (Foreign Particles)	Ionizations	Reference
KCNS	HgX ₂ (X = Cl, Br, I)	2	HgX ₂ = HgX ⁺ + X ⁻	(155)
	AgX (X = Cl, Br, I)	1.5	3KCNS + 2AgX = [Ag(CNS)X] ⁻ + [Ag(CNS) ₂] ⁻ + X ⁻ + K ⁺	
	AgCN	1	2KCNS + 2AgCN = [Ag(CNS) ₂] ⁻ + [Ag(CN) ₂] ⁻ + 2K ⁺	
	MI ₂ (M = Cd, Zn)	2	(a) MI ₂ = MI ⁺ + I ⁻ or (b) 3KCNS + MI ⁺ = [M(CNS) ₃ I] ²⁻ + 3K ⁺	
	Ag ₂ HgI ₄	5	(a) Ag ₂ HgI ₄ = 2AgI + HgI ⁺ + I ⁻ (b) 3KCNS + 2AgI = [Ag(CNS)I] ⁻ + [Ag(CNS) ₂] ⁻ + I ⁻ + 3K ⁺	
	K ₃ Cu(CN) ₄	5 (very dilute solution)	K ₃ Cu(CN) ₄ = 3K ⁺ + Cu ⁺ + 4CN ⁻	
	K ₃ Cr(CNS) ₆ (violet)	1	K ₃ Cr(CNS) ₆ = 3K ⁺ + [Cr(CNS) ₄] ⁻ + 2(CNS) ⁻ (melt green)	
	NiBr ₂ (brown)	3	(a) 6KCNS + NiBr ₂ = [Ni(CNS) ₄] ²⁻ + 6K ⁺ + 2(CNS) ⁻ + 2Br ⁻ (melt light green) (b) 6KCNS + NiBr ₂ = [Ni(CNS) ₆] ⁴⁻ + 6K ⁺ + 2Br ⁻ (crystals light blue)	
CoCl ₂ (greyish blue)	3	4KCNS + CoCl ₂ = [Co(CNS) ₄] ²⁻ + 4K ⁺ + 2Cl ⁻ (melt and crystals dark blue)		
AgNO ₃	HgI ₂	1.5 (concentrated solution)	May form Ag ₂ HgI ₄ by reaction with the solvent	(155)
	K ₂ [Hg(Cr ₂ O ₇)Cl ₂]	6	K ₂ [Hg(Cr ₂ O ₇)Cl ₂] = 2K ⁺ + Hg ²⁺ + (Cr ₂ O ₇) ²⁻ + 2Cl ⁻	
KNO ₃	K ₂ MF ₆ (M = Ti, Zr)	5	K ₂ MF ₆ = 2K ⁺ + 2F ⁻ + MF ₄	(155)
	K ₂ MF ₆ (M = Ti, Zr)	1	K ₂ MF ₆ = 2K ⁺ + [MF ₆] ²⁻	
NaCl	K ₂ ZrF ₆	(a) 9 (very dilute solution) (b) 5 (dilute solution)	(a) K ₂ ZrF ₆ = 6F ⁻ + Zr ⁴⁺ + 2K ⁺ (b) K ₂ ZrF ₆ = (ZrF ₄) + 2F ⁻ + 2K ⁺	(211)
	K ₂ TiF ₆	(a) 5 or 6 (b) 8 (higher temperatures)	(a) K ₂ TiF ₆ = (TiF ₄) + 2F ⁻ + 2K ⁺ (b) (TiF ₄) + 2F ⁻ + 2K ⁺ + 4NaCl = (TiCl ₄) + 6F ⁻ + 2K ⁺ + 4Na ⁺	
	Na ₃ AlF ₆	(7 very dilute); decreases steadily with rise of concentration	Na ₃ AlF ₆ = 3Na ⁺ + Al ³⁺ + 6F ⁻ = [AlF ₆] ³⁻ + 3Na ⁺	
	AlF ₃	(a) 4 (dilute solution) (b) 2 (less dilute)	(a) AlF ₃ = Al ³⁺ + 3F ⁻ (b) AlF ₃ = (AlF ₂) ⁺ + F ⁻	

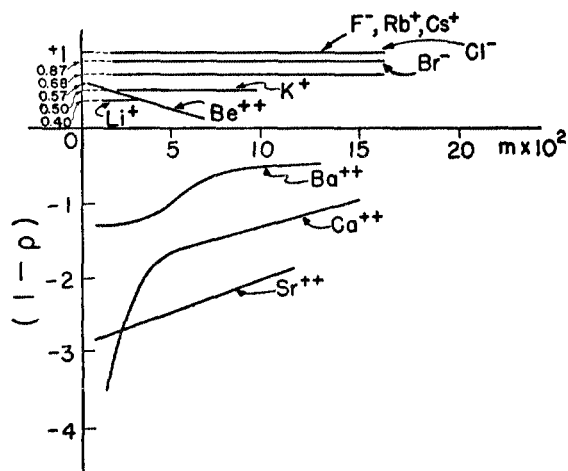


FIG. 6. Formation of solid solutions in sodium sulfate (203, 208)

unity at higher concentrations. The suggestion is made that at these low concentrations complexes of the type $M[\text{HgBr}_3]$ are formed.



Information about the extent of solid-solution formation from sodium sulfate solutions has been obtained by cryoscopy (203, 208).

Figure 6 shows that for rubidium ion, cesium ion, and fluoride ion the value of $(1 - \rho)$ is unity, i.e., ρ , the coefficient of distribution of solute between solid and liquid, is zero, corresponding to the absence of solid-solution formation from solutions of sodium fluoride or rubidium or cesium sulfates in sodium sulfate. Increasing amounts of solid-solution formation occur from solutions containing sodium chloride, sodium bromide, potassium sulfate, and lithium sulfate. The plots for sulfates of the divalent ions Be^{2+} , Ba^{2+} , Ca^{2+} , and Sr^{2+} show a change in slope as the concentration varies. It has been suggested (205) that this might be caused by the formation of new solute species having different values of ρ from those originally present.

The cryoscopic constant, k_f , has to be known before any interpretations of solute behavior can be made from freezing-point measurements. It may be found empirically, by the use of compounds expected to behave as inert solutes or as solutes dissociating to give known numbers of foreign particles, or it can be calculated from the heat of fusion of the solvent obtained calorimetrically. Many empirical cryoscopic constants used in investigations appear to be "calculated" constants, because they have been computed from literature values of heats of fusion, but many of these latter were actually derived from phase-rule studies, as in the case of those compiled by Kelley (132).

The basic freezing-point equation, equation 22, may be integrated to give

$$\ln a_1 = -(\Delta H_f^\circ/R)(1/T - 1/T_f^\circ)$$

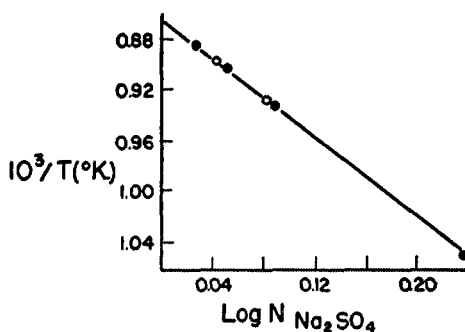


FIG. 7. Cryoscopic behavior of solutions in sodium sulfate (81): ●, NaCl; ○, NaBr

by assuming that the heat of fusion of the pure solvent, ΔH_f° , is constant over the range of temperature from T_f° , the freezing point of the pure solvent, to T , the freezing point of the given solution.

Usually, "cryoscopic" values of heats of fusion given in the literature have been obtained by plotting $\log x_1 = \log(1 - x_2)$ against $1/T$, the assumption being made that the solution is ideal so that the activity of the solvent may be replaced by the mole-fraction, which in turn may be calculated from the known composition of the solution. Recently, a method was described (81) by means of which the composition of the liquidus may be determined directly by analysis after filtration in situ. Figure 7 shows some of the results obtained (81) for solutions of sodium chloride and sodium bromide in molten sodium sulfate. The linearity of the plot is said to show that both systems are essentially ideal. The value of the heat of fusion of sodium sulfate was found, after correction for the difference in the heat capacities of the liquid and solid states, to be 6.1 kcal. mole⁻¹. In these experiments the temperatures were measured to an accuracy of 0.1–0.2°C. For these systems, however, as mentioned earlier, Petit (203) has claimed that solid solutions are formed, the distribution functions, ρ , of the solutes between liquid and solid phases being 0.87 for sodium chloride and 0.68 for sodium bromide, as shown in figure 6.

The most direct, and usually the most accurate, method of measuring heats of fusion is by calorimetry. An apparatus for the measurement of heats of fusion of inorganic compounds to an accuracy of about ± 2 per cent has been described recently in a paper (94) which includes a critical review of earlier designs.

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