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THE DISSOLUTION OF METALS IN FUSED HALIDES

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I. INTRODUCTION

The dissolution of metals in fused salts is of exceptional importance for many electrometallurgical and thermal processes, such as the production of titanium, magnesium, aluminium, sodium, etc. The ability of metals to dissolve in a fused electrolyte is the most important cause of decrease in current efficiency and deterioration of performance in electrolysis. Moreover, the kinetics of metal thermite processes, such as the magnesium thermite preparation of titanium, also appear to be related to interaction of the metals in the salt phase. Finally, in recent years a successful start has been made in the application of a method of refining metals, based on the reaction of the latter with a fused salt. There are reports of the use of this method for the purification of nickel, and a similar method for refining aluminium has already found general acceptance. All this indicates the considerable practical importance of the question of metal dissolution.

The theoretical side of the question is of no less importance, however. The study of solutions of metals in fused salts yields important information on the nature of reaction in ionic media and on characteristic features of the liquid state. Solutions of metals provide a clear illustration of Mendeleev's well-known hypothesis regarding the chemical nature of solutions.

The dissolution of metals in fused salts was discovered in 1807 by Davy[1,2], who established that during the electrolysis of fused KOH, or when metallic potassium is fused

with potassium hydroxide, the melt becomes coloured. Later an analogous phenomenon was observed when a number of other metals were fused with their salts, particularly in the Na + NaCl, K + KCl,[3-6] Rb + RbCl, Cs + CsCl,[7,8] Pb + $PbCl_2$,[9] and other systems[10,11]. It was established that lithium colours its salts black, lead brown, potassium violet, etc., and that all these colour changes are associated with dissolution of the metal in the fused salts. It was also shown that the solubility of metals in fused salts depends on the nature of the metal and salt, the composition of the metallic and salt phases, and the temperature[10]. When a melt containing dissolved metal is frozen, the metal is usually found as metallic particles of colloidal dimensions, and on this basis Lorenz[9] put forward the hypothesis that solutions of metals in fused salts are colloidal in character.

For a long time Lorenz's hypothesis had many supporters, so that in industry the terms "pyrosol" and "metal fog" are still used to describe solutions of metals. Later studies[10] showed, however, that solutions of metals in fused salts exhibit all the properties of true solutions and are moreover optically homogeneous[12-14], so that Lorenz's hypothesis should now be rejected. The appearance of colloidal metal particles when a melt freezes is probably due to displacement of the chemical equilibrium between metal and fused salt with decrease in temperature.

The established fact that true solutions are formed by metals in fused salts does not settle the question of the nature of these solutions. Three viewpoints exist.

1) It may be assumed that the metal dissolves in the salt in the form of atoms, which retain their individuality and are evenly distributed throughout the whole volume of the solution, for example, by introduction into vacancies in the quasi-crystalline structure of the liquid salt. The possibility of atomic dissolution of metals was first discussed by Hettich[15], and recently this hypothesis has been intensively developed by Cubicciotti and coworkers[16,17].

2) It may be assumed that the dissolution of metals in fused salts is due to chemical reaction between the electrolyte and the metal with the formation of ions of lower valency (sub-ions)[10,11,18]. In other words the dissolution of metals is assumed to involve equilibria of the type

$$Pb + Pb^{2+} \rightleftharpoons 2Pb^{+},$$
$$Hg + Hg^{2+} \rightleftharpoons Hg_2^{2+}, \text{ etc.}$$

Although in some cases (Hg, Tl, Al) sub-ions are undoubtedly formed, in others, particularly that of the alkali metals, the possibility that ions of lower valency exist is not so obvious, and it is necessary to assume[15] that "atom–ion" complexes are formed, for example

$$Na + Na^{+} \rightleftharpoons (Na{-}Na^{+}).$$

The majority of sub-compounds, if they do exist in fused salts, cannot be isolated in the pure state at room temperature.

3) Finally, we may start from the similarity in many properties of fused salts and ionic crystals and consider solutions of metals in fused salts as structural units similar to colour centres (*F*-centres). In this case it would be correct to describe solutions of metals as ion-electronic liquids, whose possible formation was first pointed out by Ol'shanskii[19,20]. This viewpoint has not yet been developed as fully as it should.

II. SUB-COMPOUNDS

Since most workers at present tend to attribute the dissolution of metals in fused salts to the formation of sub-ions, we shall in this section examine data on the formation of ions and compounds of lower valency.

The valency shown by elements in their compounds is determined by their electronic structures; for example, for Na $1s^2 2s^2 2p^6 3s^1$, for Mg $1s^2 2s^2 2p^6 3s^2$, and for Al $1s^2 2s^2 2p^6 3s^2 3p^1$. In ionic compounds these elements normally lose electrons from the outer *M* level and acquire the neon structure $1s^2 2s^2 2p^6$, showing valencies of 1, 2, and 3 respectively. The situation is more complex for metals of the sub-groups, such as Hg ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2$), Tl (...$6s^2 6p^1$), Pb (...$6s^2 6p^2$), and Bi (...$6s^2 6p^3$). The maximum valency of these elements corresponds to the loss of electrons from the outer *s* and *p* levels, so that ions with an outer shell of 18 electrons are formed. These metals can, however, form ions of lower valency in addition to the compounds with the highest degree of oxidation. Thus mercury with the Hg^{2+} ion in aqueous solutions forms a singly-charged ion with one 6*s* electron in the outer shell. The equilibrium constants for the reaction $Hg^{2+} + Hg \rightleftharpoons Hg_2^{2+}$, together with X-ray diffraction data for compounds of monovalent mercury[21], show that in this case there is formed a dimer Hg_2^{2+}, in which the bond between the two mercury atoms is formed by a pair of *s* electrons. Thallium forms compounds in which it shows valencies of either +3 or +1*. In the latter case the thallium atom loses the 6*p* electron and retains the two 6*s* electrons in its outer shell. Lead and bismuth, in addition to Pb^{4+} and Bi^{5+} ions, form Pb^{2+} and Bi^{3+} ions, which are much more stable in aqueous solution and which also have two 6*s* electrons in the outer shell.

If the term "sub-compounds" is used to describe compounds of lower valencies of metals, the Hg_2^{2+}, Tl^{+}, Pb^{2+}, and Bi^{3+} ions are sub-ions of the corresponding elements. The fact that the electronic structure of these ions are identical and that intermediate oxidation states (Tl^{2+}, Pb^{3+}, etc.) do not exist, indicates that stable ions of lower valency exist as a result of coupling of two 6*s* electrons. This is shown particularly clearly in the case of mercury, where a pair of 6*s* electrons is coupled by dimerisation.

From this viewpoint the existence of Al^{+}, Cd_2^{2+}, Ca_2^{2+} ions, etc., is quite probable, and spectroscopic studies show that monovalent halides of aluminium, the alkaline-earth metals, zinc, cadmium, etc., exist in the vapour state at high temperatures[22]. The most stable of these compounds appear to be the aluminium sub halides[23,24]. Russell *et al.*[25,26] studied the equilibrium between $AlCl_3$ vapour and liquid aluminium,

$$AlCl_3 + 2Al \rightleftharpoons 3AlCl, \qquad (a)$$

by a flow method involving the passage of a gaseous mixture of $AlCl_3$ and argon through molten aluminium with subsequent analysis of the gas composition. Analogous measurements were also made by Semenkovich[27,28], who determined the free energy of formation of aluminium sub-

* The existence of divalent thallium and its analogues (Ga and In) has been reported. As will be shown later, this is unlikely, since such compounds are probably complexes containing Tl^{+} and Tl^{3+}.

chloride according to reaction (a):

$$\Delta G = 76780 - 52.75\,T \text{ kcal mole}^{-1}. \quad (1)$$

Thus at ~1200° the subchloride predominates in the gas phase over aluminium ($\Delta G < 0$).

Gross *et al.*[29] showed that aluminium subchloride is formed when aluminium is heated in fused NaCl to 750°–1000°:

$$NaCl + Al \rightleftharpoons AlCl + Na. \quad (b)$$

The enthalpy of formation of AlCl at 298°K, calculated from experimental data, was given as 16.0 kcal mole^{-1} by Semenkovich[28] and as 17.0 kcal mole^{-1} by Weiss[30]. The entropy of formation of AlCl is +54.1 cal mole^{-1} deg^{-1}.

A phenomenon which has for long been known in electrochemistry is the negative difference-effect[31], that is, the liberation of hydrogen at the anode during the anodic dissolution of a number of metals in aqueous solutions. This phenomenon was first discovered by Beetz[32] for magnesium anodes and by Wohler and Buff for aluminium anodes[33]. Beetz established that the magnesium anode becomes covered by a black film which is decomposed by water with the evolution of hydrogen, and he suggested that the film contains magnesium suboxide Mg_2O. Later, Baborovsky[34] confirmed the evolution of hydrogen from a magnesium anode and established that the anodic current efficiency of the magnesium amounts to ~150% and depends only to a slight extent on the composition and concentration of the solution, the current density, or the temperature.

By studying the anodic current efficiency during the dissolution of metals in aqueous solutions, it is possible to determine the apparent valency $\tilde{n}$ of the metal dissolving. Recent studies[35–39] have shown that for many metals the values are unusually low and may even be non integral (Table 1), indicating that the difference-effect is not such a rare phenomenon.

The mechanism of the negative difference-effect has not yet been finally established, and different workers give different explanations. This phenomenon has perhaps been best studied for the case of magnesium, so that we shall examine the data for this metal in more detail*.

Bodfross[40,41] established that the potential of a magnesium electrode is independent of the Mg^{2+} ion concentration in the solution but changes considerably with change in the acidity of the solution. With mechanical displacement of the electrode its potential is shifted to more negative values.

TABLE 1. Apparent valency during the anodic dissolution of metals in aqueous solutions[38].

M	Be	Al	Mg	Zn	Ti	Ga	U	In	Mn	Hg
Normal valency	2	3	2	2	3	3	4	3	3	2
$\tilde{n}$	1	1.3	1.2	1.4	1.5	1	1.4	1	1.7	1

* Work on aluminium has been reviewed by Belyaev and Firsanova[24].

TABLE 2. Dependence of $\tilde{n}$ on the nature of the solution and on the anode potential[44,45].

Solution	Concentration, N	i_a, mA cm^{-2}	ψ_a, V	$\tilde{n}$
$MgCl_2$	0.1–4.0	150	–1.7	1.26
$MgBr_2$	0.1–1.0	100	–1.62	1.30
$MgSO_4$	0.01–1.0	100	–1.55	1.35
$MgSO_4$ + K_2CrO_4	1.0	100	–1.5	1.30
	0.05			
$KClO_3$	1.5	6.4	–1.3	1.64

Bodfross related these properties of the magnesium electrode to the potential-determining reactions

$$Mg \rightleftharpoons Mg^+ + \varepsilon,$$
$$Mg^+ + H^+ \longrightarrow Mg^{2+} + {}^1/_2H_2.$$

Faivre and Michel[42] and Brouchere[43] showed by X-ray structure analysis that the dark-grey film formed on a magnesium anode during dissolution is magnesium oxide containing excess Mg atoms in the lattice.

Petti *et al.*[37] and Kokoulina and Kabanov[44,45] studied the apparent valency of magnesium during its anodic dissolution and established that the values of $\tilde{n}$ are independent of the current density and concentration of the solution, but are determined by the potential of the anode (Table 2).

Kokoulina and Kabanov explained the dependence of the apparent valency of the dissolving magnesium on the potential by assuming that the anodic process takes place according to the scheme

$$Mg \longrightarrow Mg^+_{ads} \xrightarrow{+\varepsilon} \begin{cases} \nearrow Mg^{2+} \\ \searrow Mg^+ + H_2O \longrightarrow Mg^{2+} + {}^1/_2H_2 + OH^-, \end{cases}$$

in which the slowest stage is the oxidation of Mg to Mg^+. They showed that in this case the apparent valency is given by the equation

$$\tilde{n} = \frac{1 + 2k\,(\exp \beta\varphi F/RT)}{1 + k\,(\exp \beta\varphi F/RT)}, \quad (2)$$

which shows qualitative agreement with experiment.

Other authors[46–48] reached an analogous conclusion, and it has been suggested that monovalent magnesium is formed as Mg_2^{2+}, although no experimental data in support of this were given.

Other data indicate the possible formation of extremely unstable compounds of monovalent magnesium. Thus McEwen *et al.*[49] showed that during the electrolysis of solutions containing various organic compounds with magnesium electrodes, reduction processes take place in the anolyte. For example, dimethylbenzophenone and azoxybenzene are reduced to tetra-*p*-tolylethylene and azobenzene respectively. This phenomenon is also attributed to the formation of Mg^+ ions with strong reducing properties. Runge[50] pointed out that the formation of subhalides explains the reduction of many organic compounds by a mixture of Mg + MgI_2 (2MgI) and organomagnesium compounds RMgX, which apparently dissociate according to the scheme

$$RMgX \rightleftharpoons R + MgX,$$

where X is a halogen atom and R an organic radical.

Some idea of the stability of the subhalides of different metals can be obtained by calculating their heats of formation from the elements, and this has been done by Grimm and Herzfeld[51], Belozerskii[10], and Irmann[52]. Thus the formation of aluminium monochloride

$$Al(solid) + \tfrac{1}{2}Cl_2(gas) = AlCl(solid)$$

can be broken down into the following stages: (1) dissociation of the gaseous chlorine molecules to atoms (heat of dissolution $\frac{1}{2}D$); (2) sublimation of solid aluminium (heat of sublimation σ); (3) ionisation of aluminium atoms (ionisation potential I); (4) attachment of electrons to gaseous chlorine atoms (electron affinity E); and (5) formation of the AlCl crystal lattice from the ions (lattice energy of the subchloride U); the heat of formation of the subchloride is then

$$W = U + E - I - {}^1/_2D - \sigma. \qquad (3)$$

Values of the heats of stages 1–4 are known. The greatest difficulty is encountered in the determination of the lattice energy of the subchloride. Earlier, this involved not only the use of extremely approximate relationships but also the tacit assumption that laws derived for purely ionic lattices were applicable to sub-compounds. It is, however, possible to determine the lattice energy of a subhalide with sufficient accuracy using the equation put forward by Yatsimirskii[53] for the energy of a lattice in which the bonds have a high degree of covalent character:

$$U - U_0 + 250\{0.5 + 2\cdot 10^3(I - E - U_0)\}, \qquad (4)$$

where U_0 is the lattice energy of the corresponding compound, calculated from Kapustinskii's equation

$$U_0 = \frac{574.4}{r_C + r_A}\left(1 - \frac{0.345}{r_C + r_A}\right), \qquad (5)$$

where r_C and r_A are radii of cation and anion.

In calculations with formula (4) it is necessary to know the radii of the sub-ions. These may be found on the assumption that the radius of a sub-ion is equal to the radius of the atom with the same electronic structure. This is confirmed for the case of the Tl^+ ion (1.49 Å), whose radius is equal to that of the isoelectronic mercury atom Hg (1.50 Å).

The data for calculating the heats of formation of subhalides are given in Table 3. The values of I and σ are taken from Mishchenko and Ravdel'[54] and of E and D from Latimer[55]. The values obtained for the lattice energies and heats of formation of the subhalides are given in Table 4, which also gives for comparison the heats of formation of the normal halides of the corresponding metals (W^*). The reliability of these results is confirmed by comparison of the calculated data in Tables 4 with the experimental values of the heats of formation[28,29,55]:

	TlCl	TlBr	TlI	InCl	AlCl
W_{exp}, kcal mole^{-1}	48.99	41.2	29.7	44.5	16.0–17.0

in which the discrepancy does not exceed 10%.

Comparison of the values of W and W^* in Table 4 shows that in most cases the subhalides cannot be stable at room temperature and should decompose into the corresponding metal and normal salt, the only exceptions being the subhalides of Tl, In, and Ga. With increase in temperature, however, the stability of the subhalides can apparently increase, as in the case of aluminium subchloride[28].

The experimental detection of subhalides has also been reported. Thus Borchers[56] reports the formation of the salts CaCl, SrCl, and BaCl; and Frary and Berman[57] and Ravier[58], in a study of the composition of the violet cathodic deposit formed during the electrolysis of fused magnesium chloride, concluded that it consisted of Mg_2O and MgCl. Guntz and Benoit[18] reported the preparation of strontium, barium, and calcium subhalides and gave the following data for the heats of reaction at room temperature:

$$Ca + CaCl_2 \longrightarrow 2CaCl \qquad Q = 2.7 \text{ kcal},$$
$$Sr + SrCl_2 \longrightarrow 2SrCl \qquad Q = 14.6 \text{ kcal},$$
$$Ba + BaCl_2 \longrightarrow 2BaCl \qquad Q = 16.5 \text{ kcal},$$

but these results differ considerably from those obtained by the above calculations.

There are also reports[59] of the isolation of almost pure bismuth subchloride, which can be kept *in vacuo* at 180° for a prolonged period but which decomposes rapidly in air or on cooling.

Many authors have noted the marked influence of temperature on the stability of subhalides. Thus Guntz[60] states that lithium subchloride is stable in the narrow temperature range 500°–700°. According to Wöhler and Rodewald[61], calcium subchloride is stable above 800°, while silver subfluoride Ag_2F decomposes above 90°.

TABLE 3. Thermochemical characteristics of ions, kcal mole^{-1}.

Ion	I	σ	r, Å	Ion	I	σ	r, Å	Ion	E	$^1/_2D$	r, Å
Mg^+	177.7	35.9	1.91	Zn^+	216.0	31.0	1.27	F^-	93.5	32.2	1.33
Ca^+	142.2	46.0	2.36	Cd^+	206.0	27.0	1.44	Cl^-	88.2	28.9	1.81
Sr^+	132.8	39.2	2.53	In^+	134.8	58.2	1.49	Br^-	81.6	26.9	1.96
Ba^+	121.6	42.0	2.74	Ga^+	139.8	66.0	1.33	I^-	74.6	25.4	2.20
Tl^+	142.3	44.5	1.49	Sn^+	140.6	72.0	1.62				
Al^+	139.5	75.0	1.60	Pb^+	172.5	46.3	1.70				
Hg^+	242.6	14.5	1.44	Sb^+	200.7	60.8	1.40				
Bi^+	169.4	49.7	1.75								

TABLE 4. Lattice energies and heats of formation of subhalides and normal salts (198° K).

Subhalide	U, kcal mole^{-1}	W, kcal mole^{-1}	Halide	W^*, kcal mole^{-1}	Subhalide	U, kcal mole^{-1}	W, kcal mole^{-1}	Halide	W^*, kcal mole^{-1}
MgF	189.4	37.1	MgF_2	263.5	AlF	187.7	34.5	AlF_3	311.0
MgCl	179.3	25.0	$MgCl_2$	153.4	AlCl	173.8	18.6	$AlCl_3$	166.2
MgBr	179.8	21.6	$MgBr_2$	123.7	AlBr	170.2	10.4	$AlBr_3$	125.8
MgI	178.6	14.2	MgI_2	86.0	AlI	168.8	3.0	AlI_3	75.2
CaF	168.2	41.0	CaF_2	290.3	TlF	193.3	67.8	TlF_3	—
CaCl	157.9	29.0	$CaCl_2$	190.0	TlCl	177.5	50.0	$TlCl_3$	—
CaBr	157.9	24.4	$CaBr_2$	161.3	TlBr	175.5	43.4	$TlBr_3$	—
CaI	156.7	17.7	CaI_2	127.8	TlI	171.5	33.9	TlI_3	—
SrF	159.1	48.4	SrF_2	290.3	ZnCl	210.7	23.0	$ZnCl_2$	99.4
SrCl	151.8	39.1	$SrCl_2$	198.0	CdCl	202.1	28.4	$CdCl_2$	93.0
SrBr	151.7	34.4	$SrBr_2$	171.1	InCl	175.5	41.8	$InCl_3$	128.4
SrI	153.7	30.9	SrI_2	135.5	GaCl	181.9	35.4	$GaCl_3$	125.4
BaF	151.4	49.1	BaF_2	286.9	SnCl	173.8	20.5	$SnCl_2$	83.6
BaCl	144.5	40.2	$BaCl_2$	205.6	PbCl	182.4	22.9	$PbCl_2$	85.8
BaBr	144.6	35.7	$BaBr_2$	180.4	SbCl	200.9	−1.3	$SbCl_3$	91.6
BaI	144.0	29.6	BaI_2	144.0	BiCl	180.1	20.3	$BiCl_3$	90.8

Analysis of the available experimental material on the existence of sub-compounds shows that much of it is unreliable. The calculated values of the heats of formation, however, cannot form the basis for a complete rejection of the possible formation of sub-compounds. In the case of mercury, for example, calculation of the heats of formation of the subhalides gives the values

	HgCl	HgBr	HgI	
W =	30	25	15	kcal mole^{-1},

whereas the actual values of the heats of formation of Hg_2Cl_2, Hg_2Br_2, and Hg_2I_2 are double these (kcal mole^{-1}): 63.3, 49.4, and 28.9, due to dimerisation of the monovalent ions. This dimerisation is not exceptional. As is shown below, analogous dimers appear to be formed by bismuth (Bi_2^{2+}), cadmium (Cd_2^{2+}), and possibly the alkaline-earth metals (Ca_2^{2+}. etc.).

III. COLOUR CENTRES IN IONIC CRYSTALS

Most solid salts, and in particular almost all halides, exhibit a slight ionic conductivity due to the presence of lattice defects. As early as 1903, however, Ioffe[62] discovered that, when irradiated with X-rays, crystals of sodium chloride become coloured and acquire the property of photoconductivity. This phenomenon was later studied in detail by Roentgen and Ioffe[63], Tartakovskii[64], and others[65,66]. It was established that the production of colour under the influence of X-rays is shown not only by crystals of all alkali-metal halides[67], but also by the halides of the alkaline-earth metals (CaF_2,[68,69] SrF_2, $SrCl_2$, and BaF_2[70,71]) and transition metals (CdF_2[72]).

This phenomenon has now been studied in considerable detail and a large quantity of experimental data and theoretical work on the nature of colour production in crystals has been reviewed in detail by Seitz[73,74], Pohl[75], and Saint-James[76]. Since this work has been published chiefly in specialised physical literature, we shall give the chief results below.

The cause of the production of colour in crystals is the appearance of electrons in the conduction band, as a result of which a new light-absorption band is produced and the crystal acquires colour. Under certain conditions this colour may be retained for several years.

Experiment shows that colour can be produced in crystals by various methods, which can be conveniently divided into two groups[66]: (A) irradiation of the crystal with X-rays or with beams of electrons or neutrons; this is accompanied by excitation of electrons and their transfer to the conduction band; (B) introduction into the crystal of excess metal atoms, by heating the salt in metal vapour or by passing direct current through the crystal. In the former case the metal atoms absorbed by the crystal are ionised and the electrons enter the conduction band. In the latter case the electrons enter the crystal from the metal cathode, which is usually sharply pointed.

The production of colour in crystals takes place fairly rapidly at elevated temperatures. The rate of production of colour and its intensity increase exponentially with temperature [proportional to $\exp(-\frac{\text{const.}}{T})$]. At low temperatures the coloured crystals are dielectrics, but on heating or illumination they acquire considerable electronic conductivity. The electrical conductivity of coloured crystals

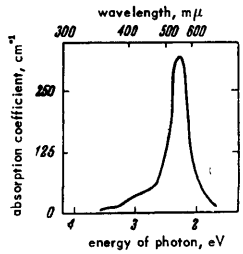


Fig. 1. F-absorption band for a KCl crystal; concentration of colour centres 1.15×10^{18} cm^{-3}; K_{max} = = 310 cm^{-1}.

TABLE 5. Position of absorption band maxima for alkali-metal halide crystals.

Crystal	Maximum of F-band	Crystal	Maximum of F-band	Crystal	Maximum of F-band
LiF	257	NaF	340	KF	455
LiCl	395	NaCl	470	KCl	556
LiBr	452	NaBr	500	KBr	630
LiI	531	NaI	609	KI	720

also increases exponentially with temperature. If a direct current is passed through a heated coloured crystal, the colour front moves to the anode and disappears there, and both the conductivity of the crystal and the current at constant voltage decrease.

The colour of the crystal and the appearance of the new absorption band, and also the electronic conductivity, which increases with increase in temperature, result from the localisation, in energy levels lying below the conduction band, of the electrons introduced into the crystal by one of the above methods. These local electronic states are usually called F-centres or colour centres. Their properties are independent of the means by which the crystals are coloured. An absorption band for a coloured KCl crystal is shown in Fig. 1. The maximum at 556 mμ corresponds to the absorption by the F-centres. The position of the maximum depends on the nature of the salt. Table 5 gives the positions of the F-absorption band maxima for alkali-metal halide crystals[76]. The position of the maximum of the F-absorption band is independent of the nature of the alkali metal in whose vapour the crystal is heated.

If the crystal is coloured by irradiation, holes, that is, vacant levels from which electrons have moved, are produced, and electrons are promoted to the conduction band. With the passage of time, the excited electrons recombine with the holes, that is, they return to the ground state and the crystal loses its colour. The decolorisation of the crystal is accelerated considerably when the crystal is heated or illuminated. If the crystal is coloured by the introduction of electrons from outside (by heating in metal vapour or by electrolysis), the colour is extremely stable,

since recombination in this case is impossible. These crystals can be decolorised either by heating in vacuum, causing the alkali metal to volatilise from the crystal, or by heating followed by slow cooling, which leads to coagulation of the alkali metal. In the latter case the F-absorption band disappears and the colour of the crystal changes to that due to the colloidal metal.

The concentration of colour centres varies with the method by which the colour is produced. Under certain conditions it may reach 10^{19}–10^{20} centres/cm^3, which corresponds to an excess metal atom concentration of 0.1–1.0 at.%. Particularly high concentrations of F-centres are attained by introducing electrons from outside. Buckel and Hirsch[77] raised the concentration of alkali metal in the crystal (KCl, NaCl, KBr) to 10 at.%. The concentration of F-centres, however, was not more than 1.1%, the rest of the metal being present in the colloidal state.

The properties of F-centres are readily explained[65,66] if it is assumed that they are electrons which have replaced halide ions at the crystal lattice sites. This localisation of current carriers takes place not only in purely ionic crystals, but also in typical semiconductors. There is no essential difference between an NaCl crystal heated in sodium vapour and containing excess Na^+ ions and F-centres, and a crystal of cuprous oxide heated in oxygen and containing excess O^{2-} ions and conductivity holes. The only difference is that the absorption band for the cuprous oxide lies in the infra-red and not in the visible region of the spectrum, and its formation does not change the colour of the crystal.

The conditions for equilibrium between a crystal and metal vapour were examined by Mott and Gurney [65]. By calculating the free energy change for the removal of one metal atom from the vapour (ΔF_v) and for the introduction of one atom of metal into the crystal (ΔF_c) and equating the two, they obtained an approximate equation for calculating the equilibrium concentration of F-centres in unit volume (n_F):

$$n_F = n_M \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-W_F/kT}, \qquad (6)$$

where n_M is the concentration of metal atoms in the vapour, m the mass of a metal atom, h and k are Planck's and Boltzmann's constants, and W_F is the work done in introducing one metal atom into the crystal, that is the work of formation of an F-centre.

This relationship has been confirmed experimentally. From experimental data, Pohl[67] calculated W_F for different crystals and obtained the values -0.10 eV (-2.3 kcal) for KCl and -0.25 eV (-5.4 kcal) for KBr. Thus the dissolution of a metal atom in a halide crystal is accompanied by a gain of energy.

The mechanism of formation of F-centres when crystals are heated in the vapour of the corresponding metals was explained by Mott and Gurney as follows. One of the metal atoms is adsorbed on the surface of the crystal, and after a time interval this atom loses its electron, which enters the conduction band and begins to drift into the interior of the crystal. At the same time one of the negative ions is successively displaced from the internal layers of the crystal to the surface and occupies a position next to the positive ion. The anionic vacancy thus produced captures the electron and forms an F-centre. The localised electron can be regarded as being shared by six positive ions (in the NaCl lattice). On heating, the localised electrons are lifted from their positions (dissociation of the F-centres) and give the crystal electronic conductivity.

An important property of F-centres is that if an alkali metal is dissolved in any fused alkali-metal halide and the melt is cooled, typical F-absorption bands, characteristic of the given salt, are formed on freezing. This means that the F-centres can exist only in the presence of standard lattice defects, which do not occur in the liquid salt.

It is also apparent, however, that there is a direct link between the F-centres and the metal dissolved in the salt. We shall examine this question in more detail below, in discussing the absorption spectra of solutions of metals in fused salts.

IV. SOLUBILITY OF METALS IN PURE SALTS

It is convenient to examine the solubility of metals in fused salts with reference to their position in the Periodic Table.

(a) The solubility of alkali metals. The dissolution of alkali metals in fused halides has been studied by a number of workers. Lorenz and Winzer[78] found that the solubility of sodium in fused NaCl increases from 10 mole % to 15 mole % when the temperature increases from 810° to 850°. Similar results were obtained by Belozerskii[10,11], who found that the solubility of potassium in potassium chloride is ~8 mole % at 800°.

The most complete study of the solubility of alkali metals in fused halides was made by Bredig *et al.*[79–82], who recorded the fusion diagrams for the Na–NaX, K–KX, and Cs–CsX systems (where X = F, Cl, Br, or I). Some of these are given in Fig. 2, which shows horizontal lines corresponding to monotectic reactions and indicates complete miscibility of metal and salt above certain limiting temperatures, given in Table 6, which also gives the temperatures of the monotectic reactions. In general the limiting temperature decreases for a given metal in the halide series

$$MF > MCl > MBr > MI.$$

The monotectic temperature changes in the same direction. The solubility increases on going from sodium to caesium, and caesium is completely miscible with liquid sodium fluoride in all proportions.

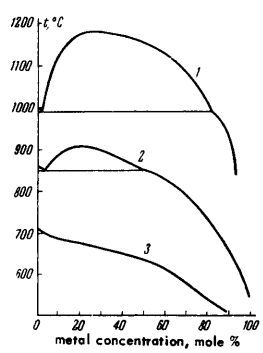


Fig. 2. Fusion diagrams for the systems: 1) Na–NaF; 2) K–KF; 3) Cs–CsF.

TABLE 6. Limiting temperatures (t_{lim}) for the existence of two liquid phases and monotectic temperatures for the K–KX and Na–NaX systems [69, 70].

System	t_{lim}, °C	Monotectic temp., °C
Na — NaF	1180	990
Na — NaCl	1080	795
Na — NaBr	1026	740
Na — NaI	1033	657
K — KF	904	849
K — KCl	790	752
K — KBr	728	708
K — KI	717	658

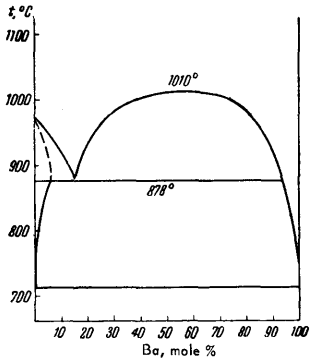


Fig. 3. Fusion diagram for the Ba–$BaCl_2$ system.

TABLE 7. Solubility of the alkaline-earth metals in fused halides.

Metal	Salt	t, °C	Solubility, at.%	
			Cubicciotti's data	Guntz and Benoit's data
Mg	$MgCl_2$	720	—	0.55**
		800	0.92*	0.82**
		900	1.20*	1.28**
	MgI_2	900	1.25*	
		1000	1.31*	
Ca	$CaCl_2$	900	16	—
		1000	13	5.7
	CaI_2	1000	—	9.6
Sr	SrF_2	1000	—	20.0
	$SrCl_2$	1000	—	24.6
	$SrBr_2$	900	21	—
		1000	22	35
	SrI_2	900	27	—
		1000	35	40
Ba	BaF_2	1050	—	22
	$BaCl_2$	900	30	—
		1000	28	—
		1050	—	28
	$BaBr_2$	900	18	—
		1000	22	—
		1050	—	37
	BaI_2	1050	—	39

* Zhurin's data [83, 84].

** Bukun and Ukshe's data [85].

(b) The solubility of the alkaline-earth metals. The dissolution of the alkaline-earth metals in fused halides has been studied by Wöhler and Rodewald [61], Guntz and Benoit [18], Zhurin [83,84], and others [85]. Recently, Cubicciotti *et al.* [16,86,87] studied the fusion diagrams for the alkaline-earth metal–halide systems Ba–$BaCl_2$, Ba–$BaBr_2$, Sr–$SrCl_2$, Sr–SrI_2, and Ca–$CaCl_2$. In this work it was noted that at certain concentrations, solutions of salt in metal and of metal in salt form two immiscible layers. The solid formed when the salt-rich phase freezes, reacts violently with water evolving hydrogen. Complete mutual solubility of the metal and salt was not observed even at high temperatures (1100°), in contrast to the case of the alkali metals. Later, however, Schäfer and Niklas [88] showed that Cubicciotti's studies were inexact, and that in the Ba–$BaCl_2$ system, for example, complete mutual solubility can be attained at 1010°. The corresponding fusion diagram (Fig. 3) is very similar to those of the alkali metal–halide systems.

Table 7, which is compiled from various sources, gives values for the solubility of the alkaline-earth metals in the fused halides, and shows that these solubilities can be measured only approximately. Some conclusions can, however, be reached. Thus it is undoubtedly true that the solubility of the alkaline-earth metals increases in the series

$$Mg < Ca < Sr < Ba$$

and decreases in the series

iodide > bromide > chloride > fluoride,

in agreement with the corresponding data for the alkali metals.

(c) The solubility of heavy metals. Data on the solubility of metals in fused halides have been published. The solubilities of lead [89–91], cadmium [90,92–96], bismuth [88,97–100], cerium [101–103], and others have been studied in detail, and for many of these the fusion diagrams of the metal–salt systems have been obtained (Figs. 4 and 5). Collected solubility data are given in Table 8.

In most cases, increase in temperature is accompanied by an increase in the solubility of the metal in the fused salt. Corbett, von Winbush, and Albers [96] showed that for systems with a solubility < 2%, the logarithm of the solubility is a linear function of $1/T$. [83,84]

The Bi–$BiCl_3$ system is a special case, since Bi and $BiCl_3$ show complete mutual solubility above 780°. [104] The solubility of Bi in $BiCl_3$ increases with increase in temperature from 200° to 320°, then decreases with further

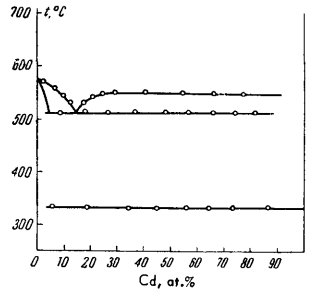


Fig. 4. Fusion diagram for the $Cd-CdCl_2$ system.

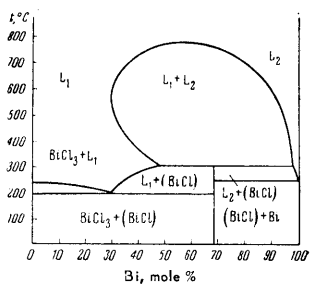


Fig. 5. Fusion diagram for the $Bi-BiCl_3$ system.

TABLE 8. Solubility of heavy metals in fused halides.

Metal	Salt	t, °C	Solubility, at.%	References
Zn	$ZnCl_2$	500 600 700	0.182 0.61 1.64	95
	ZnI_2	500 600 670	0.28 0.87 1.65	95
Cd	$CdCl_2$	530 600 690	12.5 16.0 15.6	92, 93, 105
	$CdBr_2$	600	14.0	92
	CdI_2	410 610	0.63 1.5 5.7	95 92
Hg	$HgCl_2$ HgI_2	500 500	50 25	92 92
Ga	$GaCl_3$ $GaBr_3$ GaI_3	230	2 9 40	95
In	InX_3	230	50	95
Tl	TlX_3	230	50	95
Sn	$SnCl_2$ $SnBr_2$	500 500	0.003 0.009	95 95
Pb	$PbCl_2$	500 700	0.060 0.056	95 106
	PbI_2	500 600 700	0.05 0.15 0.41	92 95 94
Sb	$SbCl_3$ SbI_3	273 300 400	0.018 3.5 5.8	95
Ce	$CeCl_3$	800	9.5	103
Bi	$BiCl_3$ $BiBr_3$	270 270	33 40	104 95

increase in temperature to 550°, and increases again above 550°.

For a series of metals in the same Group of the Periodic System at constant temperature, the solubility (Table 8) increases with increase in the atomic weight of the metal, that is for a given halide the solubility increases in the series

$$Zn < Cd < Hg$$
$$Ga < In, Tl$$
$$Sn < Pb$$
$$Sb < Bi,$$

in agreement with the analogous relationships for the alkali and alkaline-earth metals.

For metals of the Third, Fourth, and Fifth Groups, changing the anion increases the solubility in the series

chloride < bromide < iodide,

in agreement with the corresponding change for the alkali and alkaline-earth metals. The same order is observed for zinc solutions, but in the case of cadmium the reverse order is shown and the solubility increases from the iodide to the chloride.

Corbett, von Winbush, and Albers[95] noted that the standard free energy changes for the disproportionation of solid mercurous halides are 8.0 kcal mole^{-1}, 6.6 kcal mole^{-1}, and 2.5 kcal mole^{-1} for the chloride, bromide, and iodide respectively, indicating that the order of stability of the mercury sub-compounds is similar to the order of solubilities for cadmium. A characteristic feature is that although the stability of the halide complexes of most metals in aqueous solution decreases from the fluoride to the iodide, the reverse order is shown by complexes of cadmium and mercury[107]. This is attributed to the tendency of mercury and cadmium to form covalent donor π-bonds whose strength increases in the series chloride < bromide < iodide. In this case we can assume that both the solubility and the stability of the sub-compounds should decrease with increase in the stability of the bond between the "normal" cation and the anion.

Data on the dissolution of a number of other heavy metals have recently been published. Cubicciotti and Johnson[108,109] reported the high solubility (up to 7.5 at.%) of nickel in nickel chloride. Corbett *et al.*[94,110-113] studied the fusion diagrams of gallium halides and established the

existence of the compounds GaX, GaX_2, and GaX_3. A mixture of gallium iodides was formed when gallium was heated with elementary iodine to 350°–500°. On fusion the gallium di-iodide (m.p. 211°), disproportionated to GaI and GaI_3.

Clark, Griswold, and Kleinberg[114] obtained the InCl–$InCl_3$ phase diagram and noted the formation of a congruently melting compound, In_2Cl_3, which they assumed to be the complex salt $In_3^{(I)}[In^{(III)}Cl_6]$.

Corbett[113,115] also studied the Pr–$PrCl_3$, Nd–$NdCl_3$, and Nd–NdI_3 equilibria. The fusion diagrams indicate that the compounds $PrCl_{2.34}$ (978°), $NdCl_2$ (950°), NdI_2 (970°) and the compound $NdCl_{2.3}$, melting incongruently at 700°, are formed in these systems. Their structures are not yet clear.

V. INFLUENCE OF FOREIGN CATIONS ON THE SOLUBILITY OF METALS

In this section we shall examine the influence of foreign cations of less noble metals on the solubility. Only a few data are available.

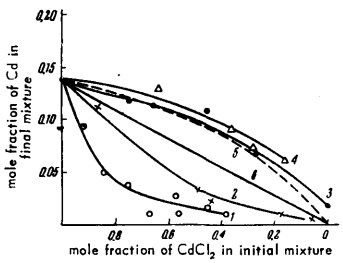


Fig. 6. Solubility of cadmium in binary salt systems: 1) $CdCl_2$–KCl; 2) $CdCl_2$–$CaCl_2$; 3) $CdCl_2$–$MgCl_2$; 4) $CdCl_2$–$CeCl_3$; 5) calculated curve for a regular solution; 6) calculated curve for an ideal solution.

TABLE 9. Polarising power of cations (P)*

M^{n+}	R, Å	$P=\frac{z}{R^2}$
Cd^{2+}	1.03	(1.90)
K^+	1.33	0.56
Ca^{2+}	1.06	1.76
Mg^{2+}	0.78	3.28
Ce^{3+}	1.01	(2.94)

* The polarising power of Cd^{2+} and Ce^{3+}, generally speaking, is greater than z/R^2, since these ions do not have the electronic structure of an inert gas.

Cubicciotti[17] studied the dissolution of cadmium in binary salt melts containing KCl, $CaCl_2$, $MgCl_2$, and $CeCl_3$, all of which decrease the solubility of cadmium, the efficiency of the additives decreasing in the series (Fig. 6)

$$KCl > CaCl_2 > MgCl_2, \quad CeCl_3.$$

The influence of a foreign cation on the solubility of cadmium in cadmium chloride depends on its polarising power (Table 9). The K^+ and Ca^{2+} ions, whose polarising powers are much less than that of Cd^{2+}, decrease the solubility to a much greater extent than might be expected if the effect of the foreign salt were merely simple dilution of the salt phase in accordance with the law of mass action (curve *6* in Fig. 6). The reverse is true of Mg^{2+} and Ce^{3+}, which have a greater polarising power than Cd^{2+}.

Since the polarising power characterises quantitatively the interaction between the cations and anions in the salt, the observed relationship indicates a direct link between this interaction and the solubility. The "stronger" Mg^{2+} and Ce^{3+} cations decrease the energy of the Cd^{2+}–Cl^- bond and thus increase the solubility of cadmium compared with that in an ideal ionic solution, whereas the "weaker" cations, by increasing the energy of the Cd^{2+}–Cl^- bond, decrease the solubility.

These ideas lead to the suggestion that the solubility of cadmium should be proportional to the activity of $CdCl_2$ in the salt phase. This can be verified if the $CdCl_2$ solutions are regular. Denoting the solubility of cadmium by s and the cadmium chloride concentration by x_1, we obtain by the law of mass action

$$K = \frac{s\gamma_s}{x_1\gamma_1}, \tag{7}$$

where γ_s and γ_1 are the corresponding activity coefficients. Assuming γ_s = const. and, in accordance with the theory of regular ionic solutions[116],

$$\log\gamma_1 = A(1-x_1)^2, \tag{8}$$

we find

$$\log\frac{s}{x_1} = \log\frac{k}{\gamma_s} + A(1-x_1)^2, \tag{9}$$

where A is a constant. The broken line in Fig. 6 gives the solubility curve for Cd in $CdCl_2$–$MgCl_2$ with appropriate choice of the constants k/γ_s and A, and shows that satisfactory agreement with experiment can be obtained. Analogous results can also be obtained for the $CdCl_2$–$CeCl_3$ system, but for $CdCl_2$–KCl and $CdCl_2$–$CaCl_2$ mixtures this relationship is not confirmed, probably because these solutions are not regular. The results obtained by Cubicciotti[17] were explained in terms of his own theory, which does not, however, agree with a number of facts, particularly the difference in the influence of $CaCl_2$ and $MgCl_2$ on the solubility of cadmium.

Analogous results were obtained[86] in a study of the solubility of Bi in $BiCl_3$–NaCl and $BiCl_3$–$CaCl_2$ mixtures. The Na^+ cation, which has a lower polarising power, decreased the solubility of bismuth to a greater extent than the Ca^{2+} cation.

The influence of foreign cations on the solubility of magnesium in a chloride melt was studied by Zhurin[83,84] and in more detail by Bukun and Ukshe[85], who showed that at a given magnesium chloride concentration the solubility decreases with decrease in the polarising power of the foreign cation (Table 10).

The influence of cations of metals more noble than the metal dissolving is complicated by equilibria of the type $Mg + PbCl_2 \rightleftharpoons MgCl_2 + Pb$, which are outside the scope of the present article. It is nevertheless of interest to examine how the solubility is affected by dilution of the metallic phase by a more noble metal. Heymann *et al.*[116-119] showed that for the Cd–Bi–$CdCl_2$ system the solubility is proportional to the concentration of dissolving metal in the alloy:

$$s = k_0 x_M \quad (10)$$

Similar results were obtained by Zhurin[84] for the Mg–Al–$MgCl_2$ system (Table 11). A deviation from Eqn. (10) was observed[105] for Na–Pb(Cd) alloys, and the authors attributed this to the non-ideal nature of the metal solutions.

VI. CRYOSCOPIC STUDIES OF SOLUTIONS OF METALS IN FUSED SALTS

Since solutions of metals are true solutions, the application of the Raoult–Van't Hoff law for the dependence of the freezing point depression on the concentration of solute should give information on the structure of the dissolved species. Since

$$\Delta T_f = \nu K_f m, \quad (11)$$

where T_f is the m.p. of the pure solvent, m the molal solute concentration, $K_f = \frac{RT_f^2 M_0}{1000\, L_f}$ the cryoscopic constant; L_f is the heat of fusion of the pure solvent, and M_0 its molecular weight, we can, by comparing the experimental value of the cryoscopic constant K_f with the calculated value, find the number of particles of new species formed when one atom of metal dissolves (ν).

TABLE 10. Solubility of magnesium at 800° in a melt of 50 mole % $MgCl_2$ + 50 mole % MCl_n[85].

MCl_n	KCl	NaCl	$BaCl_2$	$SrCl_2$	$CaCl_2$	LiCl
z_M/R_M^2	0.56	1.04	0.98	1.34	1.76	1.64
$s \times 10^2$, at.%	15.2	17.4	34.2	37.2	42.0	40.4

TABLE 11. Solubility at 800° of magnesium diluted with aluminium[84].

Metal phase compn., %		s, at.% × 10	$k_0 \times 10^4$
Mg	Al		
100	0	94	47
79	21	82	51
67	33	56	42
49	51	45	46
		average	46.5

This calculation can be carried out, for example, for solutions of potassium and sodium in their halides (Table 12). The data of Bredig and coworkers were used for the heats of fusion, melting points[120], solution concentrations x (mole fractions), and ΔT_f.[79,80,82] In all cases $\nu = 0.5$–0.7, indicating that one species is formed in solution for every two atoms of dissolved metal. In other words, the dissolution of sodium and potassium is accompanied by the formation of Na_2 and K_2 molecules. It should be emphasised that these are molecules and not double ions, since reaction of the type

$$Na^+ + Na \longrightarrow Na_2^+,$$

corresponds to the formation of one dissolved species for every metal atom. The fact that the value of ν, particularly for sodium, is greater than 0.5 was attributed by Bredig and Bronstein[82] to partial dissociation of the molecule

$$Na_2 \rightleftharpoons 2Na.$$

Dissociation according to the scheme

$$Na_2 + 2Na^+ \rightleftharpoons 2Na_2^+.$$

is also possible.

Similar calculations by Cubicciotti and coworkers[108] showed that when nickel dissolves in $NiCl_2$, up to Ni concentrations of 7.4 at.%, the freezing point depression corresponds to the formation in solution of two new species for every dissolved nickel atom, indicating that the dissolution of nickel involves the reaction

$$Ni + Ni^{2+} \rightarrow 2Ni^+.$$

Another method of interpreting the results of cryoscopic measurements involves the use of the approximate Schröder equation for the liquidus line

$$\ln x = -\frac{L_f \Delta T_f}{RT_f(T_f + \Delta T_f)}, \quad (12)$$

where x is the mole fraction of the solvent.

Grjotheim, Gronvold, and Krogh-Moe[121] investigated freezing point depressions for the dissolution of cadmium in cadmium chloride. The value of x depends on the structural model of the solution. By assuming different structural models, it is possible to calculate the heat of fusion L_f and compare it with experimental data. Thus for Cd–$CdCl_2$ we have:

1. For the reaction $Cd + Cd^{2+} = Cd_2^{2+}$

$$x_{Cd^{2+}} = (n_{CdCl_2} - n_{Cd})/n_{CdCl_2}, \quad L_f = 5.4 \text{ kcal mole}^{-1},$$

where n_i is the number of moles of the i-th component.

TABLE 12. Structure of sodium and potassium dissolved in halides.

Salt	T_f, °K	L_f, kcal × × mole^{-1}	ΔT_f, °K	$x \cdot 10^2$	K_f	ν	Salt	T_f, °K	L_f, kcal × × mole^{-1}	ΔT_f, °K	$x \cdot 10^2$	K_f	ν
NaF	1268	7.8	5	2.5	13.7	0.60	KF	1131	6.75	9	45	18.8	0.60
NaCl	1073	6.7	5	2.1	18.5	0.73	KCl	1043	6.34	18	10	26.6	0.54
NaBr	1020	6.24	7	2.9	33.2	0.72	KBr	1007	6.10	26	17	32.4	0.46
NaI	933	5.64	3	1.6	49.0	0.55	KI	954	5.74	23	12	48.5	0.57

2. For the reaction $Cd + Cd^{2+} = 2Cd^{+}$

$$x_{Cd^{2+}} = (n_{CdCl_2} - n_{Cd})/(n_{CdCl_2} + n_{Cd}), \quad L_f = 10.4 \text{ kcal mole}^{-1}.$$

3. For the atomic dissolution of cadmium

$$x_{Cd^{2+}} = n_{CdCl_2}/(n_{CdCl_2} + n_{Cd}), \quad L_f = 4.3 \text{ kcal mole}^{-1}.$$

The experimental value is L_f = 5.3 kcal mole^{-1}, indicating that Cd_2^{2+} ions are formed in solution.

Analogous calculation from published data[108] for Ni in $NiCl_2$ gives a value ~10 kcal mole^{-1} for L_f assuming that Ni_2^{2+} is formed and ~20 kcal mole^{-1} assuming that Ni^{+} is formed. This confirms that the Ni dissolves as singly-charged Ni^{+} ions, since the experimental heat of fusion of nickel chloride is 18.5 kcal mole^{-1}.

Mellors and Senderoff[103] carried out an analogous analysis of the dissolution of Ce in $CeCl_3$. The calculated values of the heat of fusion of $CeCl_3$, assuming the formation of an atomic solution, Ce^{+} ions, and Ce^{2+} ions, are 6.0 kcal mole^{-1}, 9.0 kcal mole^{-1}, and 18.0 kcal mole^{-1} respectively. Comparison with the actual heat of fusion $L_f \simeq$ $\simeq$ 8 kcal mole^{-1}, shows that Ce^{+} ions are formed.

Bredig[122] and Mayer *et al.*[123] examined the structure of solutions of Bi in $BiCl_3$ on the basis of cryoscopic data. The following dissolution reactions were assumed:

Bi → atomic Bi	$2Bi + BiCl_3 \rightarrow Bi_3Cl_3$,
$2Bi \rightarrow Bi_2$,	$8Bi + 4BiCl_3 \rightarrow 3Bi_4Cl_4$,
$2Bi + BiCl_3 \rightarrow 3BiCl$,	$Bi + 2BiCl_3 \rightarrow 3BiCl_2$,
$4Bi + 2BiCl_3 \rightarrow 3Bi_2Cl_2$,	$Bi + BiCl_3 \rightarrow Bi_2Cl_3$.

The heat of fusion of $BiCl_3$, was found to be 5.5 kcal mole^{-1} by Bredig[122], and 5.7 kcal mole^{-1} by Mayer *et al.*[123], and best agreement with experimental data is obtained assuming the formation of Bi_2Cl_2 (Fig. 7) or the dimeric ion $(:Bi::Bi:)^{2+}$, by analogy with the $(Hg:Hg)^{2+}$ ion. Dissociation of the dimer above 400° is possible.

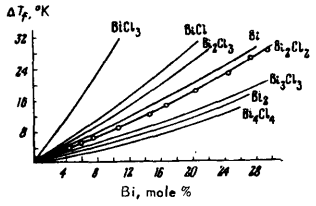


Fig. 7. Comparison of experimental data for the depression of the freezing point of $BiCl_3$ by Bi with the calculated values obtained for different structural schemes for the solutions.

VII. INFLUENCE OF THE DISSOLUTION OF METALS ON THE VAPOUR PRESSURE OF FUSED SALTS

Cubicciotti *et al.*[124] studied the vapour pressure of $BiCl_3$ in equilibrium with Bi in the range 210°–410° and showed that the vapour consisted of monomeric $BiCl_3$ and that the vapour pressure is related to the temperature by the expression

$$\log p = p_0 + \frac{b}{T}. \qquad (13)$$

The dependence of the vapour pressure on concentration shows positive deviations from Raoult's law, indicating that the bismuth dissolves as neutral aggregates of the type Bi_n or as polymeric ions, for example

$$2Bi + Bi^{3+} \rightleftarrows 3Bi^{+},$$
$$3n\,Bi^{+} \rightleftarrows 3Bi_n^{n+}.$$

The nature and structure of the dissolved bismuth were discussed by Corbett[59,125] and Bredig[122]. Corbett concluded that the deviations from ideal behaviour can be attributed to the formation of the polymer Bi_4Cl_4 at temperatures up to 360° and of more complex polymers at higher temperatures. According to Bredig[122], the data can be explained equally readily by assuming the formation of the dimer Bi_2Cl_2, which is converted to Bi_2 at higher temperatures. Analogous results have been obtained for Bi–$BiBr_3$.[126] The equilibrium

$$3Bi_2X_2 \rightleftarrows 2Bi_2 + 2BiX_3,$$

according to Bredig, exists at all temperatures but is displaced to the right with increase in temperature. The equilibrium constant of this reaction for Bi–$BiBr_3$, for example,

$$K = \frac{[Bi_2X_2]^3}{[BiX_3]\,[Bi_2]^2} \qquad (14)$$

decreases from 0.05 at 300° to 10^{-4} at 400°.

This explanation does not contradict cryoscopic data and also explains the complete miscibility of Bi and $BiCl_3$ at high temperatures[104], for if the dissolution of the bismuth involved merely the formation of singly-charged ions, the solubility could not exceed 33 at.%, whereas Bredig's hypothesis postulates that the complete miscibility is due to mixing of the Bi_2 dimers with the subhalide Bi_2X_2, no Bi^{3+} ions apparently remaining.

Cubicciotti and Keneshea[127] also studied the vapour pressure BiI_3 over Bi–BiI_3 solutions. Unlike the chloride and bromide systems, this system shows ideal behaviour up to Bi concentrations of 30–35 at.%. The equilibrium

$$BiI_3 \rightleftharpoons \tfrac{3}{2}I_2(\text{gas}) + Bi(\text{soln.})$$

is established. No explanation for the unique behaviour of this system has been given.

VIII. VOLUME EFFECTS ACCOMPANYING THE DISSOLUTION OF METALS IN FUSED SALTS

The influence of the dissolution of metals on molar volume was also studied by Cubicciotti and Keneshea[126–130] in the case of bismuth solutions. They established that in all cases the density of the solutions decreases linearly with temperature

$$\rho = \alpha - \beta t.$$

The quantity α increases and the temperature coefficient β decreases slightly with increasing concentration of bismuth (Table 13).

TABLE 13. Change in density of $Bi-BiX_3$ solutions with change in concentration (by interpolation from Cubicciotti's data).

x_{Bi}, at.%	$BiCl_3$		$BiBr_3$		BiI_3	
	α	$\beta \times 10^3$	α	$\beta \times 10^3$	α	$\beta \times 10^3$
0	4.42	2.20	5.25	2.40	5.56	2.22
10	4.58	2.06	5.39	2.20	5.67	2.10
20	4.85	2.08	5.54	2.00	5.79	1.95
30	5.19	2.15	5.71	1.85	5.94	1.75

If we assume that the subchloride Bi_2Cl_2 is formed in solution of the molar volume of the solution can be calculated from the formula

$$\bar{V} = \frac{x_{Bi_2Cl_2} M_{Bi_2Cl_2} + (1 - x_{Bi_2Cl_2}) M_{BiCl_3}}{\rho} = \frac{489 x_{Bi_2Cl_2} + 315.4 (1 - x_{Bi_2Cl_2})}{\rho}, \quad (15)$$

where x is the mole fraction and M the molecular weight. Here

$$x_{Bi_2Cl_2} = \frac{3x_{Bi}}{4 - 3x_{Bi}}, \quad (16)$$

where x_{Bi} is the mole fraction of dissolved metal and the molar volume of the Bi_2Cl_2 dimer in the solution is defined as

$$\varnothing_{Bi_2Cl_2} = \frac{\bar{V} - (1 - x_{Bi_2Cl_2}) \bar{V}_{BiCl_3}}{x_{Bi_2Cl_2}}, \quad (17)$$

where $\bar{V}_{BiCl_3}$ is the molar volume of pure bismuth chloride. Analogous equations can be written for the other halides. Calculation shows that in the concentration range $x_{Bi} = 0.05-0.20$ ($x_{Bi_2X_2} = 0.04-0.18$) the partial molar volume of the dimer is almost independent of the concentration of the solution and is close to $\bar{V}_{BiX_3}$. The fact that the partial molar volume of Bi_2X_2 is constant indicates that solutions of Bi in BiX_3 approximate to ideal behaviour if they are regarded as $Bi_2X_2-BiX_3$ mixtures.

Thus measurements of the density of $Bi-BiX_3$ solutions agree with the assumption that Bi_2X_2 is formed. Analogous calculations can also be made, however, assuming that bismuth dissolves as atoms. There are no grounds for rejecting the latter hypothesis.

IX. POTENTIOMETRIC STUDIES OF SOLUTIONS OF METALS

Karpachev and Stromberg[106,131] were the first to make a potentiometric study of solutions of metals in fused salts. The procedure involves the determination of the dependence of the potential of an inert carbon electrode on the concentration of dissolved metal. The electrode potential, like an ordinary redox potential, is determined by the ratio of the concentrations of dissolved metal to that of normal chloride and if the latter remains constant, the potential obeys the Nernst equation

$$\varphi = \varphi_0 - b \log x.$$

The value of the prelogarithmic coefficient b is determined by the mechanism of the dissolution. If this involves the formation of M^+ ions, $b = 2.3\,RT/F$, if M_2^{2+} ions or M atoms are formed, $b = 2.3\,RT/2F$, etc. For solutions of cadmium in $CdCl_2$ + KCl–NaCl (1 : 1) at 700° the experimental value of $b = 0.092$, indicating that dissolution of cadmium takes place according to the reaction

$$Cd + Cd^{2+} \longrightarrow Cd_2^{2+}$$

or

$$Cd_M \longrightarrow Cd_{diss}$$

For solutions of lead in $PbCl_2$ at 700°, $b = 0.185$, *i.e.*

$$Pb + Pb^{2+} \longrightarrow 2Pb^+,$$

which agrees with the results of cryoscopic measurements.

Using potentiometric measurements, Karpachev and Stromberg determined the composition of a saturated solution from the point at which the potential of the carbon electrode ceased to change when the metal was introduced into the cell by cathodic deposition. The quantity of metal liberated was calculated from the quantity of electricity passed. The results of the solubility measurements made in this way are given in Table 14. The solubility of lead in $PbCl_2$ at 700° is 0.056 mole%, which agrees well with other data.

Although the solubility of Cd in a KCl–NaCl (1 : 1) melt is very small, it is nevertheless significant and when recalculated in volume units amounts to ~0.0059 M. The Cd concentration in the vapour above the metal at 1 atm and 700° also amounts to ~0.006 M, so that it is natural to assume that part of the cadmium "volatilises" into the melt in atomic form.

Senderoff and Mellors[132] made a potentiometric study of solutions of cerium in cerium chloride and found that the e.m.f. of the cell

$$Ce \mid CeCl_3, \text{ sat. with } Ce \parallel CeCl_3 \mid Ce$$

in the temperature range 820°–920° exceeds the calculated value by 0.7 V. Since in the authors' opinion the junction potential in the cell cannot exceed 60 mV, this difference can only be ascribed to an equilibrium of the type

$$4CeCl_3 + 2Ce \rightleftarrows 3Ce^+ + 3CeCl_4^-.$$

Analogous e.m.f. values were obtained with inert Mo electrodes. The e.m.f., for Ce concentrations in the melt between 8.7 mole % and zero, was related to x_{Ce} by the equation

$$\varphi = \varphi_0 + b \log \frac{[Ce^{3+}]}{[Ce^+]}, \quad (18)$$

with a prelogarithmic factor equal to 0.115 V, indicating that Ce^+ ions are formed. In Senderof and Mellors'

TABLE 14. Solubility of cadmium in $CdCl_2-KCl-NaCl$ at 700°.

Concn. of $CdCl_2$ in NaCl–KCl, mole %	0	1.0	2.0	3.0	5.0	6.5	10.0	25.0	50.0
Solubility of Cd, at.%	0.025	0.034	0.042	0.053	0.071	0.081	0.110	0.465	2.34

opinion, the dissolution of cerium should lead to formation of the complex

$$Ce^{(I)}[Ce^{(III)}Cl_4].$$

Finally, Smirnov and Chukreev[133,134] made a potentiometric study of the dissolution of beryllium in $BeCl_2$ + + KCl–LiCl at 400°–900°. Assuming that Be on dissolution forms singly-charged Be^+ ions, they measured the potential of an inert molybdenum electrode in the melt and found the equilibrium constant of the reaction

$$Be(solid) + Be^{2+} \rightleftharpoons 2Be^+$$

to be given by

$$k = \exp\left(2.36 - \frac{4904}{T}\right). \qquad (19)$$

X. ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF METALS IN FUSED SALTS

The electrical conductivity of solutions of metals in fused salts was studied by Aten[93,135,136] and Bredig and Bronstein[137]. The latter made a systematic study of the electrical conductivity of solutions of sodium and potassium in their fused chlorides and bromides (Figs. 8 and 9).

The dissolution of the alkali metals in all cases leads to an increase in the conductivity. Bredig and Bronstein calculated the equivalent conductance of the dissolved metal, assuming additivity of the molar volumes, from the equation

$$\lambda_M = \frac{\kappa_{soln}\tilde{V} - x_1\lambda_{salt}}{x_2}, \qquad (20)$$

where x_1 and x_2 are the mole fractions of the metal and salt, λ_{salt} is the molar conductance of the pure salt, κ_{soln} the specific conductivity of the solution, and $\tilde{V}$ the molar volume of the solution. With increase in the concentration of dissolved metal, λ_{Na} decreases whereas λ_K increases (Fig. 9).

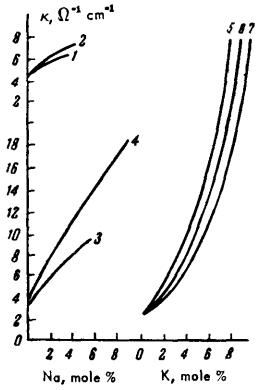


Fig. 8. Specific conductance of solutions of metals in fused salts:
1) Na–NaCl, 845°; 2) Na–NaCl, 890°;
3) Na–NaBr, 805°; 4) Na–NaBr, 895°;
5) K–KBr, 870°; 6) K–KBr, 760°;
7) K–KCl, 820°.

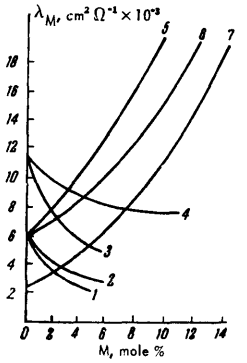


Fig. 9. Equivalent conductance of metal dissolved in a fused salt. Numbering same as in Fig. 8.

These facts require special explanation. In Bronstein and Bredig's opinion, the electrons should be relatively weakly bound to the dissolved metal atoms, so that the conductivity of the solution becomes partly electronic in character, and increases with increase in concentration. In addition, however, association of dissolved particles (Na_2) is possible, and this apparently leads to a decrease in λ_{Na} with increase in the Na concentration in the solution. The decrease in the equivalent conductance of the solution due to association can hardly be more than 1–2 $cm^2\,\Omega^{-1}$ per mole % of dissolved metal, whereas the increase in the equivalent conductance due to the electronic contribution reaches 100 $cm^2\,\Omega^{-1}$ per mole % of metal. It is assumed that almost no association of potassium takes place in solution, although this does not agree with cryoscopic data. Bronstein and Bredig assumed that the electronic conductance in the melt involved the transfer of electrons between ions of different states of oxidation. This mechanism is similar to proton transfer in aqueous solution.

Aten studied the electrical conductivity of solutions of Bi in $BiCl_3$ and of Cd in $CdCl_2$ (Table 15). The decrease in the conductivity produced by the dissolution of cadmium increases with increase in the metal concentration. On dissolution of bismuth, the conductivity of the solution at first increases, but starts to decrease when the concentration is increased above 15 at.%.

Aten calculated the molar conductance (λ_{Cd}) of dissolved cadmium and found the value 8 $\Omega\,cm^{-2}$ at 600°, whereas the molar conductance of pure $CdCl_2$ is higher by one order of magnitude (110 $\Omega\,cm^{-2}$). According to Bronstein and Bredig, this is due to formation of the dimer Cd_2^{2+}; there

TABLE 15. Electrical conductivity of solutions of Bi in $BiCl_3$ and of Cd in $CdCl_2$.

Bi, at.%	κ, Ω⁻¹ cm⁻¹		Cd, at.%	κ, Ω⁻¹ cm⁻¹	
	300°	350°		580°	600°
0	0.498	0.554	0	1.907	1.968
5.2	0.506	0.585	2.5	1.898	1.959
10.1	0.507	0.605	5.0	1.884	1.945
20.5	0.481	0.607	7.5	1.867	1.928
31.1	0.405	0.549	10.0	1.845	1.906

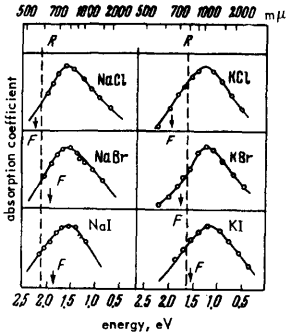


Fig. 10. Absorption bands of Na and K dissolved in their fused halides. *R* gives the position of the absorption lines of gaseous Na and K atoms.

is apparently no electronic contribution to the conductivity in this case. The mechanism of conduction in bismuth solutions is more complicated. It may be assumed that at low concentrations of dissolved metal, there is a slight electronic conductivity, which disappears at high concentrations due to association or to the change

$$2Bi_2^{2+} \longrightarrow Bi^{2+} + Bi_2.$$

Senderof and Mellors[132] measured the electrical conductivity of solutions of Ce in $CeCl_3$ and found that at 840° the conductivity of the melt increases from 0.92 $\Omega^{-1}\,cm^{-1}$ for pure $CeCl_3$ to 3.76 $\Omega^{-1}\,cm^{-1}$ for a saturated solution of Ce in $CeCl_3$. This fourfold increase in the conductivity for a Ce content of ~9% can hardly be due to the higher mobility of the Ce^+ ions and in this case it is most probable that the increase in conductivity is due to electron transfer.

Since Aten, on the basis of measurements of the electrical conductivity of Cd–$CdCl_2$, concluded that cadmium dissolves as uncharged species, it is of interest to describe the experiments of Grjotheim[121], who showed that the dissolved metal takes part in the transfer of current. Electrolysis was carried out in a quartz U-tube, fitted with a porous alundum partition impregnated with pure $CdCl_2$. Both sections of the vessel were filled with Cd–$CdCl_2$ solution and on application of a direct current the colour front entered the partition and moved rapidly towards the cathode, indicating that the colour of the cadmium solutions is due to positively charged species.

XI. MAGNETIC AND SPECTROSCOPIC STUDIES OF SOLUTIONS OF METALS IN FUSED SALTS

The effect of a magnetic field on a body is determined by the electronic structures of the atoms or ions[138]. When the magnetic field influences only the movement of the electrons in the atoms and ions, the substance is diamagnetic, that is, it is repelled by the magnetic field. When the atoms or ions have a permanent magnetic moment, the substance is attracted towards the magnetic field, that is, it exhibits paramagnetic properties.

Paramagnetism is caused by the presence of unpaired electrons, so that the presence of ions such as Cd^+, Bi^+, and Ga^{2+} should be detectable by the appearance of paramagnetic properties when metals dissolve in fused salts. Unfortunately, there are few data on the magnetic properties of such systems.

Erlich and Gentsch[139,140] isolated calcium subchloride as pale-yellow crystals with density 2.45. The product, however, did not show paramagnetic properties, indicating the formation of Ca_2^{2+} ions. The magnetic susceptibility of solutions of Cd in $CdCl_2$ has been studied[121,141]. Since the cadmium solutions were found to be diamagnetic, the measurements confirmed that Cd_2^{2+} ions are formed. McMullan and Corbett[111] showed that gallium dichloride, $GaCl_2$, is diamagnetic, indicating that the Ga_2^{4+} ion or the complex $Ga^{(I)}[Ga^{(III)}Cl_4]$ is formed. Corbett[59] also noted the diamagnetism of bismuth monochloride, which agrees with the hypothesis that Bi_2^{2+} dimers are formed. Thus in all these cases the sub-ions are diamagnetic, confirming the tendency towards the formation of stable ions with filled *s*-orbitals.

The most important data on the nature of solutions in fused salts are probably obtainable from spectroscopic studies. The absorption spectra of alkali metals dissolved in fused halides have been studied[67,71,142]. Broad absorption bands (Fig. 10) were obtained with maxima at $\lambda = 790$ mμ for Na and 980 mμ for K. It may be assumed that these bands are produced from the first absorption lines of the atoms, with wavelengths 590 mμ for Na and 770 mμ for K. The displacement of the centre of the absorption band is ~200 mμ and the broadening of the bands is ~700 mμ (1 eV). The fact that there is no splitting of the energy levels of the alkali-metal atoms indicates that the perturbing field (due to the salt ions) is spherically symmetrical. In other words, the nature of the absorption spectra in these cases indicates that the solutions contain no stable compounds of dissolved atoms and normal ions (Na_2^+, K_2^+). The displacement of the maximum and the broadening of the absorption band indicate a marked expansion of the outer electronic orbital, that is a weakening of the bond between the electron and the metal atom. As already mentioned, *F*-centres are formed in the melt on freezing. If this is related to the appearance of lattice defects in the solid crystal, we would also expect that the electrons may be fairly readily displaced from ion to ion in the liquid salt, since the potential well for an electron is shallow in both solid and liquid salt.

Woodward *et al.*[143] recorded the Raman spectrum for molten gallium dichloride at 190° and showed that it has the structure $Ga^+[GaCl_4^-]$, and not $Cl_2Ga–GaCl_2$ as previously suggested[144]. An analogous conclusion was reached by Garton and Powell[145] on the basis of an X-ray diffraction study of $GaCl_2$ crystals. The study of the Raman spectra confirmed the existence of Hg_2^{2+} ions, containing a metal-to-metal bond, in mercurous chloride[146]. A similar structure for the calcium sub-ion was suggested by Erlich and Gentsch[140] on the basis of an X-ray analysis of CaCl.

XII. DISSOLUTION OF METALS IN ELECTROCHEMICAL PROCESSES

The dissolution of metals in fused salts has a significant effect on the current efficiency during electrolysis. Lorenz[9,147] suggested that the main reason for the deviation from Faraday's law during the electrolysis of fused salts is the dissolution of the metal being deposited at the

cathode and its subsequent oxidation at the anode. For example, during the electrolysis of lead chloride the overall cathodic processes are

$$Pb^{2+} + 2\varepsilon \longrightarrow Pb$$

$$Pb + Pb^{2+} \longrightarrow 2Pb^{+},$$

and the anodic process involves the reaction

$$Pb^{+} - \varepsilon \longrightarrow Pb^{2+}.$$

The decrease in the cathodic current efficiency is determined by the conditions for the transport of dissolved metal from the cathode to the anode and therefore depends to a considerable extent on the geometry of the electrolytic cell, the shape and size of the electrodes, the distance between them, and other factors determining the hydrodynamics of the electrolyte[148-154]. The most complete analysis of the influence of electrolysis conditions on the current efficiency in fused electrolytes was made by Bukhbinder[155].

Aten[136] suggested that the mechanism of metal loss can be related to electron transfer in solutions of metals in fused salts. Yanagase and Derge[156] studied the electrolysis of antimony sulphide Sb_2S_3 at 635°–690° and i = 0.25–1.5 A cm^{-2} with a carbon cathode and a liquid metal anode, and attributed the low current efficiency to partial electronic conductivity. No one has confirmed this experimentally for fused chlorides.

Spooner[157] noted the depolarising action of the process

$$Pb + PbS \longrightarrow Pb_2S$$

during the electrolysis of PbS in a chloride melt.

Antipin[158-160] analysed the shape of the cathodic polarisation curves for the electrodeposition of aluminium from cryolite–alumina melts and concluded that instead of the proposed reduction reaction

$$Al^{3+} + 3\varepsilon \rightarrow Al,$$

the reduction processes at the cathode involved the formation of sub-ions:

$$2Na^{+} + \varepsilon \rightarrow Na_2^{+},$$

$$Al^{3+} + 2\varepsilon \rightarrow Al^{+},$$

$$Al^{+} + \varepsilon \rightarrow Al,$$

$$Na_2^{+} + \varepsilon \rightarrow 2Na.$$

Each of these reactions corresponds to a definite branch on the polarisation curve. Antipin also detected two branches on the polarisation curves for the electrolysis of $PbCl_2$, AgCl, and other fused chlorides, and explained these on the assumption that the primary processes involve the formation of sub-ions (Ag_2^{+}, Pb^{+}).

Sucki[162-164] studied the electrolysis of fused calcium chlorides and showed that until the electrolyte is saturated with metal, the cathodic process is

$$Ca^{2+} + 2\varepsilon \rightarrow Ca,$$

but that after saturation and at low current densities, the primary process is accompanied by the reduction

$$Ca_2^{2+} + 2\varepsilon \rightarrow 2Ca.$$

Under these conditions the reaction $2Ca^{2+} \rightarrow Ca_2^{2+}$ apparently does not occur.

According to Sucki, the following processes are possible in the electrolysis of fused KCl and NaCl

$$K^{+}(Na^{+}) + x\varepsilon \rightarrow K(Na)\ \text{(dissolved)},$$

$$K(Na)\ \text{(dissolved)} + y\varepsilon \rightarrow K(Na)\ \ (\text{where } x + y = 1),$$

and

$$K^{+}(Na^{+}) + \varepsilon \rightarrow K(Na).$$

Smirnov and Chukreev[165] established that during the anodic dissolution of beryllium in a KCl–LiCl melt, Be^{+} ions are formed in addition to Be^{2+} ions, and the ratio Be^{+}/Be^{2+} increases with decrease in current density (Table 16), accompanied by a shift of the anode potential towards more negative values. Since the dissolution of beryllium takes place without polarisation, the potential shift can be due only to a change in the $[Be^{2+}]/[Be^{+}]$ ratio in the melt, in accordance with the Nernst equation

$$\varphi = \varphi_0 + \frac{RT}{F} \ln \frac{[Be^{2+}]}{[Be^{+}]}$$

Calculation confirms this assumption.

It has been established[24,166,167] that Al^{+} ions are formed during the dissolution of aluminium in fused salts. Belyaev[167] also noted the formation of Sn^{+} during the dissolution of tin in a chloride melt. The anodic current efficiency was 120% for aluminium and 200% for tin, but decreased rapidly with increase in the anodic current density.

TABLE 16. Influence of current density on the current efficiency for the dissolution of beryllium.

i, A cm^{-2}	Current efficiency, %	Fraction	
		Be^{+}	Be^{2+}
0.004	135.5	0.357	0.643
0.005	124.0	0.242	0.758
0.05	113.5	0.137	0.863
0.4	109.5	0.095	0.905
0.5	106.5	0.065	0.935

XIII. CONCLUSION

In concluding this examination of the dissolution of metals in fused salts we must point out that despite the recent intensified interest in this question, no final solution has yet been reached. Although in many cases the phenomenon can be related to the formation of sub-compounds, under certain conditions the formation of atomic solutions is undoubtedly possible, particularly in the case of the alkali metals. Certain data obtained from the study of solutions of bismuth and alkali metals show the existence of the equilibrium

$$\text{sub-ion} \rightleftharpoons \text{dissolved atom},$$

in addition to the equilibrium

$$\text{normal ion} \rightleftharpoons \text{sub-ion}.$$

The dissolved atoms and ions also undoubtedly tend to polymerise.

Comparison of the properties of solutions of metals in fused salts and in solid crystals (F-centres) suggests their

close similarity. In systems containing normal metal ions and sub-ions, the excess electrons are evidently not localised on definite atoms but move freely from one to another. Dimerisation of the sub-ions hinders this process by deepening the potential box for the electron. Nevertheless, it may be assumed that electronic conductivity is shown by solutions of metals, although the conductivity should be not metallic but semiconducting in character. Thus a given solution at relatively low temperatures close to the melting point of the salt can be regarded as a system containing chiefly normal ions and sub-ions, while the same solution at high temperatures can be regarded as a solution of excess electrons; more or less prolonged localisation of the electrons on individual metal ions is possible only on dimerisation. This viewpoint explains the behaviour of a number of systems, including Bi–$BiCl_3$, Ca–$CaCl_2$, etc., which show complete miscibility at high temperatures.

A solution to the problem of the nature of fused salts is evidently to be found by treating these as special semiconducting systems, which according to Ol'shanskii, can be classified as ionic–electronic liquids.

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TECHNETIUM — ELEMENT 43

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HISTORY OF DISCOVERY

In 1871 Mendeleev predicted the existence of the element with atomic number 43, which he called "ekamanganese", and determined its position in the Periodic System[1]. However, the element remained unknown for a long time. Numerous attempts to find it in nature, based on its presumed analogy to manganese and certain platinum metals, were unsuccessful[2-13]. A typical example is the work of Ogawa[8] who claimed to have isolated a new element from molybdenite, thorianite, and certain other minerals. This "new element" had many of the properties predicted for element 43. Ogawa called it "nipponium" and described the properties of several of its compounds.

In 1925 Noddack and Tacke[12] announced the discovery, from X-ray spectroscopic data, of element 43 for which they proposed the name "masurium". The data given below show that the X-ray lines which they ascribed to element 43 approximately correspond to calculations from Moseley's relation with allowance for the screening constant.

	$K_{\alpha 1}$	$K_{\alpha 2}$	$K_{\beta 1}$
Observed wavelength, Å	0.672	0.675	0.601
Calculated wavelength, Å	0.6734	0.6779	0.6000

The relative intensity of the masurium and rhenium lines suggested identical content of both elements in the specimens studied*. From its position in the Periodic System, Noddack described some of the physical and chemical properties of masurium. He suggested that it should have an atomic weight between 98 and 99, density of 11.5, and melting point of 2300°. Its lower oxides (MaO, Ma_2O_3, MaO_2) should be yellow in colour and probably insoluble in acids. The higher oxides (MaO_3 and Ma_2O_7) should be lightly coloured and on reaction with water should yield acids analogous to manganic and permanganic.

About a year later Prandtl[13] proved Noddack's results to have been erroneous. Thus for a long time there has been no reliable experimental proof of the existence of stable isotopes of element 43, although evidence from nuclear physics suggests that such stable isotopes should exist[14].

Various nuclear reactions appear to be the only source of technetium. The element was first prepared in 1937 by Segrè and Perrier[15] by the bombardment of molybdenum nuclei with deuterons. Since this was the first preparation of an artificial element, Segrè and Perrier called it "technetium"**. Later many other nuclear reactions leading to the formation of various isotopes of this element studied.

At present nuclear fission of uranium is the principal source of technetium in relatively large quantities[17]. One of the most long-lived isotopes of technetium, ^{99}Tc, is formed in the nuclear reactor, among other products. The

* Later Noddack showed that the lines of masurium are much weaker than those of rhenium.

** From τεχνητδς "artificial" (Ed. of Translation).