

RECENT PROGRESS IN THE HIGH TEMPERATURE CHEMISTRY OF INORGANIC SALT SYSTEMS

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Certain processes involving the use of inorganic salts at high temperature are of ancient origin, including as they do the salt glazing of ceramic pottery. The use of molten cryolite as a solvent for alumina in the electrowinning of aluminium, is a more recent example of the founding of an industry based on chemistry in a high temperature salt system. Sodium, magnesium, the alkaline earth metals and other light metals, are commercially important elements which rely also for their production on the use of molten salts. Other well-established practices involving molten salts are found in the metallurgical industries, where for many years, they have been used in heat treating baths and for the descaling of metals.

Much of the investigational work now being carried out with molten salt systems, is directed to their use in the production of the less common metals including titanium, zirconium, thorium, beryllium, niobium and tantalum. Such metals are potentially suitable for nuclear reactors, jet engines, missiles and space vehicles.

Molten salt nuclear reactors would have important advantages over those using solid fuels, as molten salt media can be used to circulate the fuel, remove fission products and to provide good heat transfer, as well as operating at atmospheric pressure and allowing the use of high operating temperatures to promote good thermal efficiency. In such applications uranium tetrafluoride can be used in a molten mixture of fluorides, *e.g.* sodium fluoride and zirconium fluoride or the fluorides of lithium, beryllium and thorium. One of the disadvantages of using molten salts in reactors is that being excellent solvents, they tend to be corrosive towards the container materials. The production of pure uranium and plutonium for use in other types of reactors, is carried out on a large scale from salt melts.

The use of molten salts in fuel cells is a possible future development. Cheap carbonaceous fuels such as natural gas, petroleum and coke could be employed in fuel cells in which molten carbonates either free or in a porous, non-conducting medium would form the electrolyte. At present their high operating temperatures and relatively low current densities tend to mitigate against this application, but these defects are partially compensated by their very favourable power per unit volume, thus resulting in a fuel cell of compact structure. Salts may also prove valuable as fuels where reactions to produce inorganic salt vapours would provide propulsion for rockets and space vehicles.

Hitherto, water has been the most common solvent in chemical reactions. However, the wide range of solutes varying from metals to gases which will dissolve in molten salt systems, make it apparent that reactions in molten salt solvents will assume much greater importance in future. The preparation and purification of certain salts can be carried out by taking advantage of the exchange of partners involving reciprocal systems and also phase relationships pertaining to partially miscible systems.

Halides will be used here as typical examples of salts. Similar considerations apply to sulphates, nitrates and carbonates, but polymeric salts such as the silicates are beyond the scope of the present discussion. Many solid salts including sodium chloride, lead chloride and barium fluoride are known to crystallize in ionic lattices, *e.g.* sodium chloride which has the simple cubic structure with coordination number 6. On the other hand, cadmium chloride has a layer lattice structure with octahedral CdCl_6 groups linked to form infinite layers.

For systems of two or more salts, the phase diagrams often show the separation of intermediate solid phases. Phase diagrams for binary systems involving a salt such as cadmium chloride or lead chloride with an alkali-metal chloride, become more complex as the radius of the alkali-metal cation increases. This can be illustrated¹ with reference to the phase diagrams of the systems $\text{PbCl}_2 + \text{NaCl}$ (*Figure 1*), $\text{PbCl}_2 + \text{KCl}$ (*Figure 2*) and $\text{PbCl}_2 + \text{RbCl}$ (*Figure 3*). In the solid salt system $\text{PbCl}_2 + \text{NaCl}$, there is no intermediate phase, while in the system $\text{PbCl}_2 + \text{KCl}$, one congruently melting compound and one incongruently melting compound are formed. The $\text{PbCl}_2 + \text{RbCl}$ system shows three congruently melting compounds. Somewhat similar behaviour is observed in other systems, *e.g.* cadmium chloride with the alkali-metal chlorides.

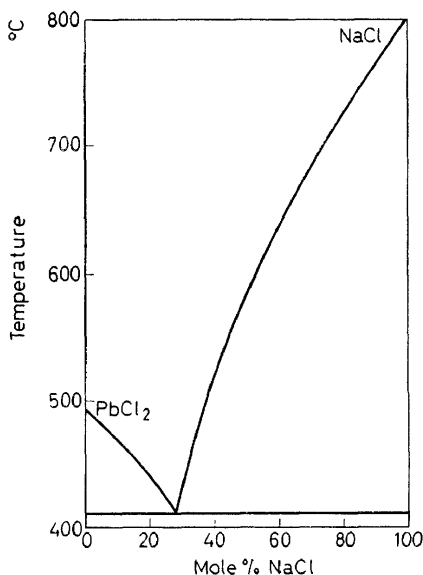


Figure 1. System $\text{PbCl}_2 + \text{NaCl}$: phase diagram

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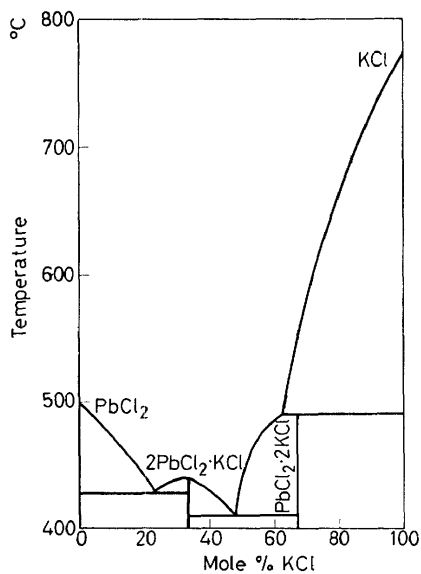


Figure 2. System $\text{PbCl}_2 + \text{KCl}$: phase diagram

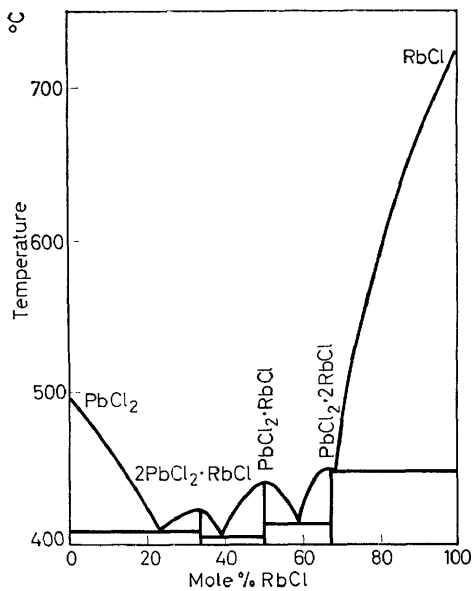


Figure 3. System $\text{PbCl}_2 + \text{RbCl}$: phase diagram

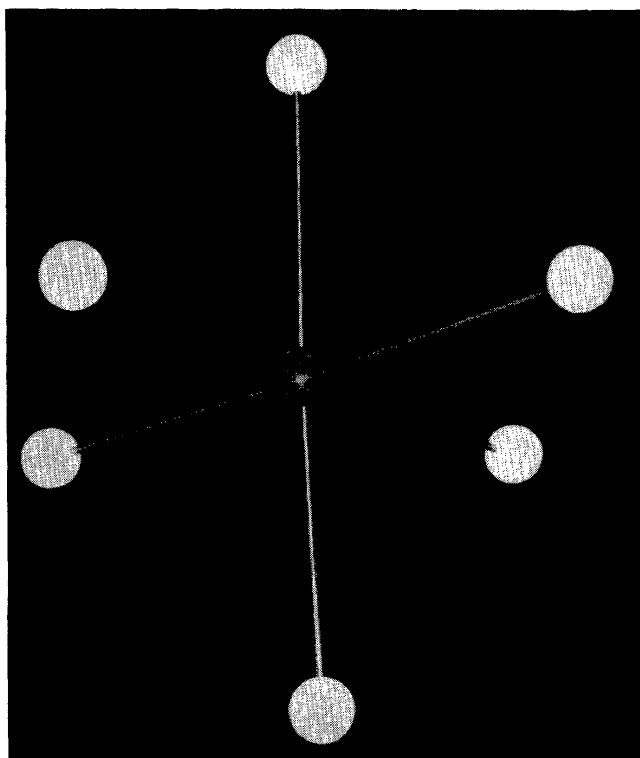


Figure 4. CdCl₄²⁻: structural unit

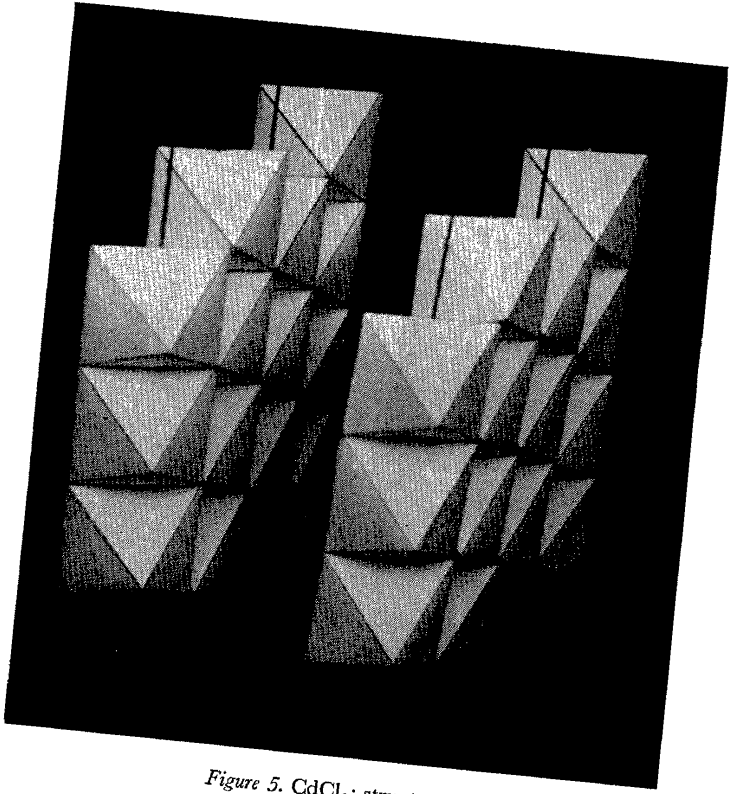


Figure 5. CdCl₂: structure

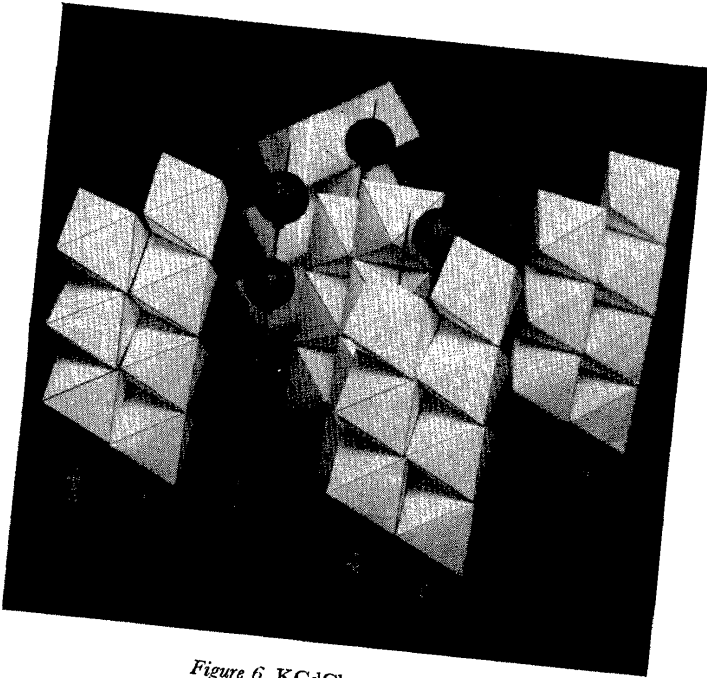


Figure 6. KCdCl₃: structure

The structure of intermediate phases as determined by X-ray crystallographic studies² can be illustrated with reference to systems containing cadmium chloride, of which the octahedrally coordinated CdCl_6^{4-} structural unit is shown in *Figure 4*. Solid cadmium chloride is built up of such octahedra linked in infinite sheets, each octahedron sharing three edges with other octahedra as illustrated in *Figure 5*. (In *Figures 5* and *6*, the CdCl_6^{4-} octahedra are shown as solid bodies).

Figure 6 shows the structure of the double salt KCdCl_3 which is obtainable from cadmium chloride and potassium chloride either from the melt or from aqueous solution. In this case the octahedra are arranged in double strings (shown for clarity at a greater separation than actual). In the structure of K_4CdCl_6 the CdCl_6^{4-} octahedra are separated by potassium ions in positions of 8-fold coordination. The CdCl_6^{4-} units in these structures are tightly bound groups which are predominantly covalent in character. Similarly, PbCl_6^{4-} octahedral groups are found in the $\text{PbCl}_2 + \text{KCl}$ system with potassium ions again in positions of 8-fold coordination.

The heats of formation of solid salt mixtures at 25°, have been determined recently³ and are shown in *Figure 7* for the $\text{CdCl}_2 + \text{PbCl}_2$, $\text{CdCl}_2 + \text{KCl}$,

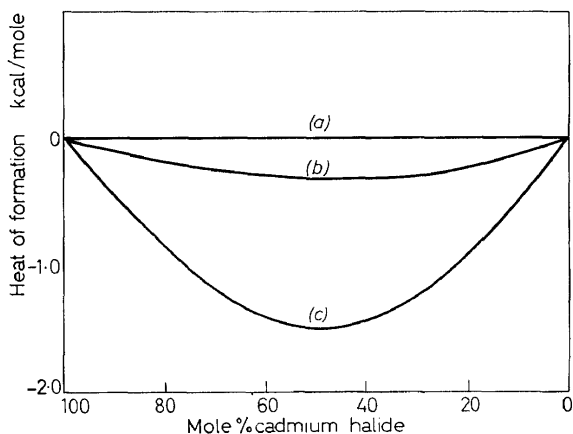


Figure 7. Heat of formation of solid at 25°
(a) $\text{CdCl}_2 + \text{PbCl}_2$ (b) $\text{CdI}_2 + \text{KI}$ (c) $\text{CdCl}_2 + \text{KCl}$

and $\text{CdI}_2 + \text{KI}$ systems. For systems whose phase diagrams show the separation of intermediate solid phases, heat is evolved in the formation of the solid mixtures from their constituent salts at 25°, but in systems such as $\text{CdCl}_2 + \text{PbCl}_2$ in which no intermediate compound is formed, there is no heat change on mixing. For the systems $\text{CdCl}_2 + \text{KCl}$ and $\text{PbCl}_2 + \text{KCl}$ in each of which there is one congruently melting compound, the minimum in the heat of formation curve coincides with the composition of the respective compound. Hence the formation of the solid mixture corresponding to the congruent compound of the phase diagram, involves stronger interionic forces in the case of the $\text{CdCl}_2 + \text{KCl}$ and $\text{PbCl}_2 + \text{KCl}$ systems, than in the $\text{CdCl}_2 + \text{PbCl}_2$ system.

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The melting of a salt such as an alkali-metal chloride has been shown to result in only relatively small structural changes as far as the first and second coordination shells are concerned. Harris, Wood and Ritter⁴, Danilov and Krasnitskii⁵, Zarzycki⁶ and Levy *et al.*⁷ have investigated the structure of molten salts by X-ray or neutron diffraction. During melting of the alkali-metal chlorides, the coordination number for nearest neighbours (unlike ions) usually decreases from 6 to about 4. The cation-anion distance also decreases slightly, but on the other hand, cation-cation and anion-anion distances increase slightly. This is illustrated in *Table 1* for several salts.

Table 1. Interionic distance and coordination number for some molten and solid salts by X-ray diffraction⁷

Salt	Liquid			Solid at <i>m.p.</i>		
	Cation-anion distance (Å)	Coordination number cation-anion	Cation-cation or anion-anion distance (Å)	Cation-anion distance (Å)	Coordination number cation-anion	Cation-cation or anion-anion distance (Å)
LiCl	2.47	4.0	3.85	2.66	6	3.76
CsCl	3.53	4.6	4.87	3.57	6	5.05
LiI	2.85	5.6	4.45	3.12	6	4.41
NaI	3.15	4.0	4.80	3.35	6	4.74

The most far reaching structural change on melting is the complete loss of long range order. Investigations show also that the molar volume increases on melting by about 25 per cent for alkali chlorides⁸. In order to account for the results of X-ray and molar volume measurements it is necessary to conclude that short range order in the liquid is much the same as in the solid but that extra free volume, probably in the form of vacant "lattice sites" or widely dispersed "holes", is introduced into the structure.

Apart from X-ray evidence, the determination of electrical conductance offers conclusive evidence for the predominantly ionic structure of molten salts, these being, in general, excellent conductors of electricity. As an example, potassium chloride at 800° has a specific conductance which is some 22 times greater than its normal aqueous solution at 20°. For lithium chloride, its equivalent conductance is 180.8 ohm⁻¹ cm² at 710° compared with 115.0 ohm⁻¹ cm² for its infinitely dilute aqueous solution at 25°; for sodium chloride, its equivalent conductance is 152.5 ohm⁻¹ cm² at 908° compared with 126.5 ohm⁻¹ cm² for its infinitely dilute solution at 25°. These results and a comparison of the molar refractivities of molten salts with their aqueous solutions at infinite dilution (see *Table 2*) show that such high temperature liquids are composed mainly of ions, although from the close proximity of such ions, it is clear that strong forces of interaction must exist between them.

The classic experiments of Faraday, who showed that his laws of electrolysis apply to molten salts, proved that the conduction process is ionic for these liquids. Apart from ions and holes as units of structure, molten salts

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Table 2. Molar refractivity of some alkali chlorides⁹

Salt	Molar refractivity R_{0c}	
	Molten state	Aqueous solution at infinite dilution (25°)
LiCl	8.20 (at 650°)	8.76
NaCl	9.48 (at 850°)	9.27
KCl	11.60 (at 800°)	11.30

may also contain ion-associated entities such as “ion-pairs” and “complex ions”; the latter are particularly important in mixtures of molten salts.

The melting of inorganic salts leads in most cases to the formation of highly conducting ionic melts as in the case of the alkali-metal chlorides. In some cases, however, a viscous, poorly conducting liquid results on melting, as shown in *Figure 8* for zinc chloride¹⁰. This salt, which is typical of the zinc

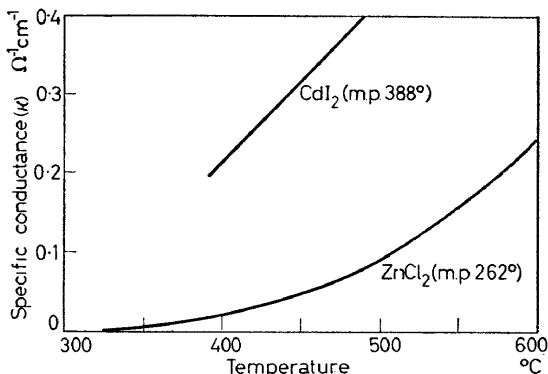


Figure 8. Specific conductance (κ) of molten CdI_2 and $ZnCl_2$

halides in respect of conductance, is almost a non-conductor near its melting point but it has a reasonably high conductance at higher temperatures. This behaviour contrasts with that of cadmium iodide¹⁰ although both salts have a layer structure in the solid state. In the case of cadmium iodide the netted structure must be destroyed on melting, while in the case of zinc chloride a free ionic structure is only achieved at higher temperatures when its thermal energy is sufficient to break up the network. The relatively high melting points of most salts ensure that their thermal energy is too great to allow much of the solid structure beyond the second coordination shell to exist in the melt, except within a few degrees of the melting point.

For mixtures of inorganic salts, X-ray structure investigations and heat of formation experiments lead to the conclusion that complex entities, which will be termed “complex ions”, may exist in the solid. As with pure salts, the structures of molten salt mixtures are related to the structures of the solid mixtures from which they are formed. It must be emphasized however that the correct basis of comparison is between the melt and its corresponding

solid at the melting point, not with the solid at room temperature. An indication of the considerable structural changes which take place in the $\text{CdCl}_2 + \text{KCl}$ system on heating, is shown in *Figure 9* for the molar heat capacity isotherms of the solid mixtures at different temperatures (Barton and Bloom¹¹). The maximum in the heat capacity isotherms at about 65 mole per cent potassium chloride becomes more pronounced with increase of temperature, showing that structural changes are occurring in this region of composition.

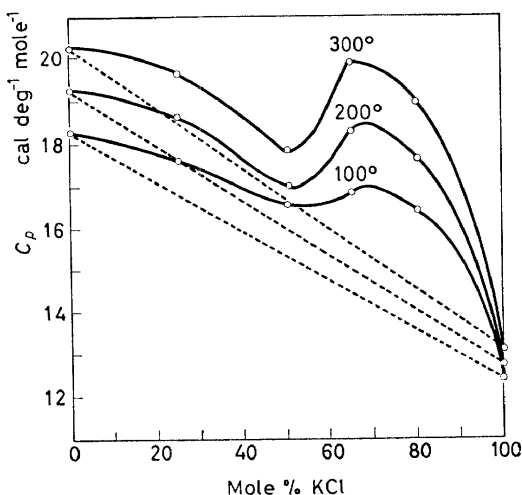


Figure 9. System $\text{CdCl}_2 + \text{KCl}$: heat capacity isotherms

Theories of the structure of molten salt mixtures have been built up from change of physical properties with composition. The properties which have been particularly useful in this respect include electrical conductance, molar volume and heat of formation as well as thermodynamic properties. Simple systems, such as $\text{CdCl}_2 + \text{PbCl}_2$ for which the phase diagram shows no intermediate compound, have isotherms of physical properties which vary in a more-or-less linear manner with composition.

When comparing the electrical conductances of molten salt systems, equivalent conductance will be used (rather than specific or molar conductance) as this quantity refers always to the conductance with one gram-equivalent of electrolyte between the electrodes. Hence its deviations from additivity will relate directly to the removal of conducting ions as complexes, or will reflect correctly the effect of change of electrical forces on the mobility of the constituent ions. The system $\text{NaNO}_2 + \text{NaNO}_3$ is one of the few systems reported¹² to have a linear relation between equivalent conductance and molar composition. In other systems the conductances of the mixtures deviate by varying amounts from the additive values *e.g.*, in the case of $\text{PbCl}_2 + \text{NaCl}$ system by up to 18 per cent. Except for a few systems, the measured equivalent conductance of the mixtures is less than the result predicted from simple additivity. Harrap and Heymann¹³ showed that the

deviation from additivity increases as the difference between the equivalent conductance of the pure components of the mixture increases. Yaffe and Van Artsdalen¹⁴ gave an explanation of this phenomenon in terms of the change of interionic electrical forces involved in replacing ions in the quasi-semi-lattice of one salt with those of another salt.

Many investigators have related very large deviations from additivity to the formation of complex ions in the mixtures—thus Bloom and Heymann¹⁵ postulated the existence of complex ions in the systems $\text{PbCl}_2 + \text{KCl}$ and $\text{CdCl}_2 + \text{KCl}$ on the basis of minima in their isotherms of equivalent conductance. Shallow minima have been reported¹⁴ in a few systems such as $\text{LiCl} + \text{KCl}$, in which complex ions are not likely to exist, but this system has a large difference between the conductances of the component salts and large deviations from additivity would be expected because of the marked change in electrical forces on adding one salt to the other.

The equivalent conductances¹⁶ of molten mixtures of $\text{PbCl}_2 +$ alkali-metal chloride are shown in *Figure 10*. For the system $\text{PbCl}_2 + \text{NaCl}$ the

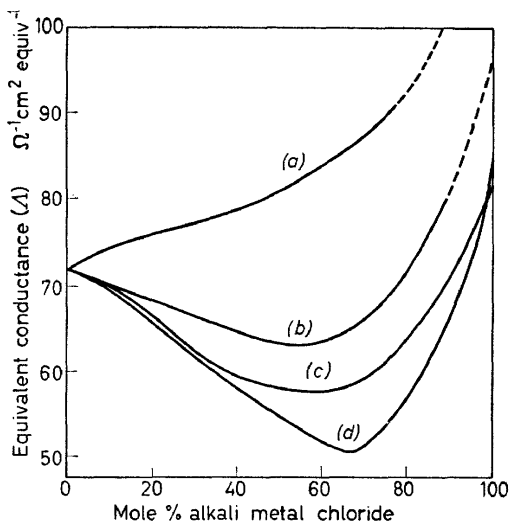


Figure 10. Isotherms of equivalent conductance of molten salt systems at 720°

- (a) $\text{PbCl}_2 + \text{NaCl}$ (b) $\text{PbCl}_2 + \text{KCl}$
 (c) $\text{PbCl}_2 + \text{RbCl}$ (d) $\text{PbCl}_2 + \text{CsCl}$

deviations from additivity could possibly be caused by the change of electrical forces on mixing two salts of very different conductance. However, for the systems $\text{PbCl}_2 + \text{MCl}$, where $\text{M} = \text{K}, \text{Rb}$ or Cs , the percentage deviation from additivity becomes larger as the radius of the alkali-metal cation increases. This effect, which is seen in *Figure 11*, is contrary to the generalization of Harrap and Heymann¹³ and cannot, therefore, be accounted for solely by the changing electrical forces on adding one component of the mixture to the other.

The formation of progressively deeper conductance minima from potassium chloride to caesium chloride in the $\text{PbCl}_2 + \text{MCl}$ systems, can best

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be explained by the formation of complex ions in such systems. This effect results in the removal of mobile simple ionic conducting species from the melt and thus leads to conductance minima. Conductance results indicate that the formation of complex ions becomes increasingly important as the size of the alkali-metal cation increases.

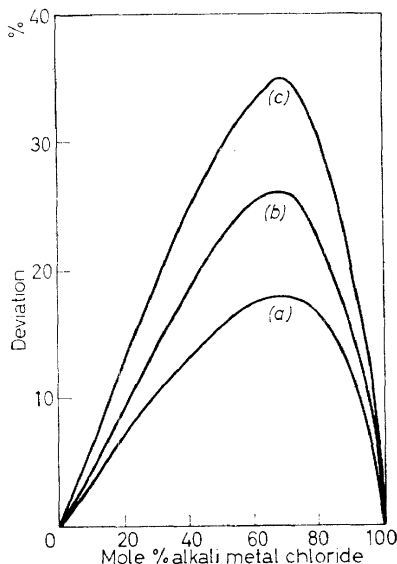


Figure 11. Percentage deviation of equivalent conductance at 720°

- (a) $\text{PbCl}_2 + \text{NaCl}$ system
- (b) $\text{PbCl}_2 + \text{KCl}$, and $\text{PbCl}_2 + \text{RbCl}$ systems
- (c) $\text{PbCl}_2 + \text{CsCl}$ system

Other evidence for complex ion formation comes from molar volume determinations¹⁶ as shown in Figure 12 for the $\text{PbCl}_2 + \text{MCl}$ systems where $\text{M} = \text{Na}, \text{K}, \text{Rb}$ or Cs . For simple systems in which there is no complex formation, molar volume is a simple additive function of composition. The increasingly large positive deviations from additivity in the molar volume isotherms from Na to Cs, could result from the greater tendency to form complex ions in these systems as the size of the alkali-metal cation increases. Complexes such as the octahedral PbCl_6^{4-} , would pack less economically in the liquid than the simple ions which are produced by the melting of the pure salts, leading thus to an increased volume on mixing.

Attempts to establish the detailed structures of complex ions in molten salt mixtures have not been altogether successful. The maximum deviation from additivity in the conductance isotherms, varies with temperature and with the alkali-metal cation present. Possible formulae for complex ions in the $\text{PbCl}_2 + \text{MCl}$ and $\text{CdCl}_2 + \text{MCl}$ systems are PbCl_3^- , PbCl_4^{2-} , PbCl_6^{4-} and CdCl_3^- , CdCl_4^{2-} , CdCl_6^{4-} , respectively.

On investigating the Raman spectrum of $\text{CdCl}_2 + \text{KCl}$ mixtures, Bues¹⁷ obtained a strong Raman line at 259 cm^{-1} which was attributed to the

complex ion, CdCl_3^- . On the other hand, Bredig and Van Artsdalen¹⁸ were of the opinion that the CdCl_2^- complex ion would better account for the Raman line. A further possibility is the CdCl_6^{4-} complex ion which, in octahedral configuration, would be expected to have a strong highly polarized Raman line and two weak lines (not observed by Bues owing to a high incidence of background noise). Assuming that the building up of octahedral complex ions began as potassium chloride, rubidium chloride or caesium chloride were added to cadmium chloride, these would reach a

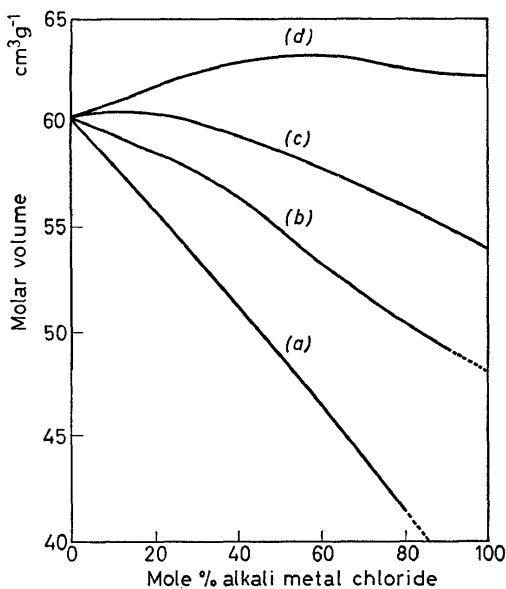


Figure 12. Molar volume at 720°
 (a) $\text{PbCl}_2 + \text{NaCl}$ (b) $\text{PbCl}_2 + \text{KCl}$ (c) $\text{PbCl}_2 + \text{RbCl}$ (d) $\text{PbCl}_2 + \text{CsCl}$

maximum concentration at 80 mole per cent alkali-metal chloride when the stoichiometric composition is M_4CdCl_6 . At compositions less rich in MCl than 80 mole per cent, it is possible that CdCl_3^- , CdCl_2^- and CdCl_3^- , could be built up successively or that equilibria between CdCl_6^{4-} and the simple ionic species would result.

The ultimate tendency to form CdCl_6^{4-} or PbCl_6^{4-} is indicated by the change of specific conductance of mixtures of molten salts as the temperature of crystallization approaches¹⁵. In Figure 13 the specific conductance of the mixtures, 50 mole per cent $\text{NaCl} + \text{PbCl}_2$ and 79.6 mole per cent $\text{KCl} + \text{CdCl}_2$ are shown as a function of temperature. The mixture of lead chloride and sodium chloride shows the normal relation between conductance and temperature, *i.e.* an almost linear dependence over a temperature interval of more than 100°. This is preserved to within a few degrees of its crystallization temperature. The cadmium chloride and potassium chloride mixture, however, shows strong curvature in the range 30–40° above the temperature at which crystals are first deposited from the melt and this very striking decrease of conductance with decrease of temperature indicates

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that in the vicinity of the stoichiometric composition of K_4CdCl_6 , ions of very low mobility are present. As the temperature decreases, such ions are able to form an array which is almost characteristic of the solid lattice. The same type of behaviour is observed also in the $PbCl_2 + KCl$ system at compositions in the vicinity of 80 mole per cent potassium chloride.

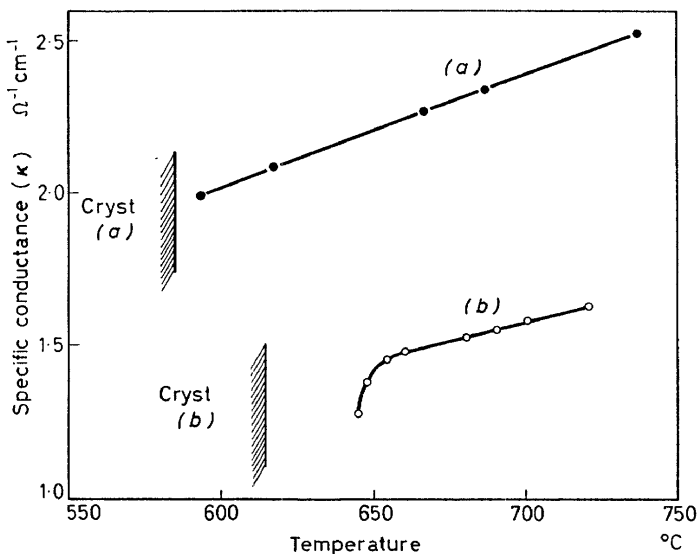


Figure 13. Specific conductance near crystallization point

- (a) 50 mole % NaCl + 50 mole % $PbCl_2$
 (b) 79.6 mole % KCl + 20.4 mole % $CdCl_2$

The effect of different alkali-metal cations in binary systems with cadmium or lead chloride is very marked. The lithium ion and to a lesser extent the sodium ion, owing to their high charge density, will tend to compete strongly with the cadmium or lead ions for chloride ions, thus making it impossible for ions such as Cd^{2+} and Pb^{2+} to build up their coordination complex shells. The tendency to build up complexes will be less inhibited as the alkali-metal cation becomes larger and its charge density becomes less, thus leading to the family of curves shown in *Figures 10 and 11*. The stability of complexes in systems $PbCl_2$ and MCl or $CdCl_2$ and MCl where MCl is an alkali-metal chloride, thus becomes greater as the size of the alkali-metal cation increases.

Other properties which reflect the formation of complex ions in molten salt systems, are thermodynamic activity¹⁹ and heat of mixing³. Activity isotherms are shown in *Figure 14* for the $CdCl_2 + PbCl_2$ and $CdCl_2 + KCl$ systems, respectively. In the $CdCl_2 + PbCl_2$ system, the activity of cadmium chloride is a little greater than the ideal value. However, when cadmium chloride is diluted by potassium chloride, the activity of cadmium chloride decreases almost to zero when the composition approaches 80 mole per cent of potassium chloride. Similarly in *Figure 15*, the heat evolved on mixing³ to

form one mole of mixture for the systems $\text{PbCl}_2 + \text{KCl}$ at 750° , $\text{CdCl}_2 + \text{NaCl}$ at 700° , $\text{CdCl}_2 + \text{KCl}$ at 700° and $\text{CdI}_2 + \text{KI}$ at 700° is seen to become greatest in the composition range 50 to 70 mole per cent alkali metal halide, giving further weight to the possibility that exothermic complexes exist in these systems. (In the case of the systems involving potassium chloride or sodium chloride below the melting point, the results pertain to the hypothetical liquid potassium chloride or sodium chloride, respectively.) These

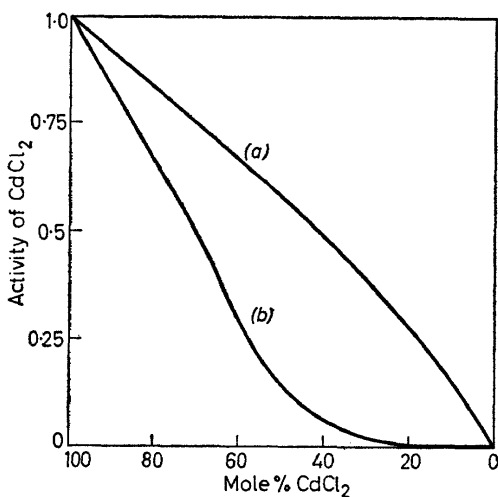


Figure 14. Activity of CdCl_2
Systems (a) $\text{CdCl}_2 + \text{PbCl}_2$ at 700° (b) $\text{CdCl}_2 + \text{KCl}$ at 900°

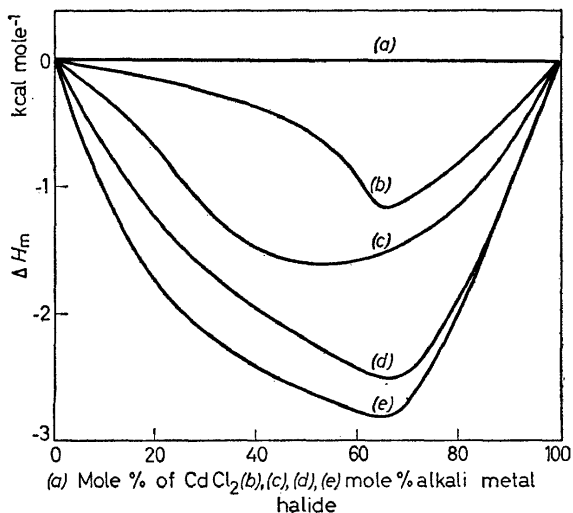


Figure 15. Heat of mixing of molten salts
(a) System $\text{CdCl}_2 + \text{PbCl}_2$ at 600° (b) System $\text{PbCl}_2 + \text{KCl}$ at 750°
(c) System $\text{CdCl}_2 + \text{NaCl}$ at 700° (d) System $\text{CdI}_2 + \text{KI}$ at 700°
(e) System $\text{CdCl}_2 + \text{KCl}$ at 700°

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heats of mixing are in contrast to the $\text{CdCl}_2 + \text{PbCl}_2$ system for which the heat of mixing is zero at 600° .

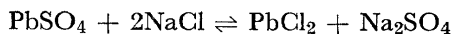
The methods described above for molten salt systems are similar to those used in aqueous solution chemistry to establish the presence of complex ions. Many other methods have also been used in both cases, *e.g.* ultra-violet spectra, coefficient of diffusion, infrared spectra and others. Although it cannot be stated that the compositions of the complex ions found in molten salt systems have been established uniquely, it is probable from the considerable weight of evidence accumulated, that complex ions do in fact exist in many systems.

Molten salt systems in which there is good evidence²⁰ for the formation of complex ions are shown in *Table 3*.

Table 3. Systems in which complex ions are formed²⁰

<i>System</i>	<i>Method of investigation</i>	<i>Complex ions postulated</i>
$\text{KCl} + \text{CdCl}_2$	Conductance, molar volume, Raman spectra, e.m.f., vapour pressure, cryoscopy	$\text{CdCl}_{\frac{1}{3}}^-$ $\text{CdCl}_{\frac{2}{3}}^-$ $\text{CdCl}_{\frac{4}{5}}^-$
$\text{KCl} + \text{ZnCl}_2$	Conductance, Raman spectra, e.m.f.	$\text{ZnCl}_{\frac{1}{3}}^-$
$\text{KCl} + \text{PbCl}_2$	Conductance, molar volume, transport number, surface tension, e.m.f., vapour pressure	$\text{PbCl}_{\frac{1}{3}}^-$ $\text{PbCl}_{\frac{2}{3}}^-$ $\text{PbCl}_{\frac{4}{5}}^-$
$\text{KCl} + \text{MgCl}_2$	Conductance, molar volume	$\text{MgCl}_{\frac{1}{3}}^-$
$\text{KCl} + \text{CuCl}$	Conductance	$\text{CuCl}_{\frac{2}{3}}^-$
$\text{KF} + \text{ZrF}_4$	Vapour pressure	$\text{ZrF}_{\frac{1}{5}}^-$
$\text{KI} + \text{CdI}_2$	Conductance, molar volume	$\text{CdI}_{\frac{2}{3}}^-$
$\text{RbCl} + \text{PbCl}_2$	e.m.f., surface tension, conductance, molar volume	$\text{PbCl}_{\frac{1}{3}}^-$ $\text{PbCl}_{\frac{2}{3}}^-$ $\text{PbCl}_{\frac{4}{5}}^-$
$\text{CsCl} + \text{CoCl}_2$	u.v. absorption spectra	$\text{CoCl}_{\frac{2}{3}}^-$
$\text{CsCl} + \text{NiCl}_2$	u.v. absorption spectra	$\text{NiCl}_{\frac{2}{3}}^-$
$\text{CsCl} + \text{CuCl}_2$	u.v. absorption spectra	$\text{CuCl}_{\frac{2}{3}}^-$
$\text{CsCl} + \text{NpCl}_4$	u.v. absorption spectra	$\text{NpCl}_{\frac{2}{3}}^-$
$\text{CsCl} + \text{PbCl}_2$	Conductance, molar volume	$\text{PbCl}_{\frac{1}{3}}^-$ $\text{PbCl}_{\frac{2}{3}}^-$ $\text{PbCl}_{\frac{4}{5}}^-$
$\text{NaF} + \text{AlF}_3$	Conductance, surface tension, cryoscopy	$\text{AlF}_{\frac{3}{6}}^-$ $\text{AlF}_{\frac{1}{4}}^-$

There have, so far, been very few studies of chemical reactions involving molten salts although this field is now receiving more attention. Those involving reciprocal salt pairs are of particular interest because they can produce different salts by exchange of partners. *Figure 16* shows the thermodynamic activity of lead chloride in mixtures of $\text{PbSO}_4 + \text{NaCl}$ as determined by Bloom and Welch²¹ from vapour pressure measurements. It can be seen that in this reciprocal salt system, the interaction of lead sulphate and sodium chloride leads to the formation of lead chloride which can be distilled from the mixture



This method may in future allow a more economical preparation of certain

salts than can be achieved at present. Such products could be removed by vaporization, fractional crystallization or by separation of an immiscible phase.

Thermal decomposition reactions involving molten salts have been investigated mainly on nitrate systems. Alkali-metal nitrates are a good deal more stable than are commonly supposed and this has been demonstrated by the investigations of Freeman²². Sodium nitrate melts at 307° while

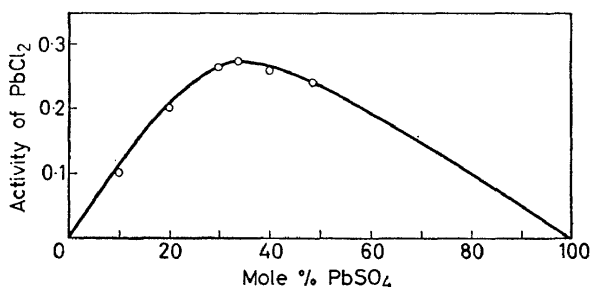
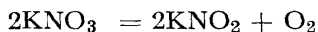


Figure 16. System $\text{PbSO}_4 + \text{NaCl}$: activity of PbCl_2 at 1003°K

potassium nitrate melts at 334°. Both salts can be heated without appreciable change in a stainless steel container until about 600° when the following reversible reactions occur.



and



The reactions are slow at 600° but go to completion in about 2 hours at 700°, the final composition of the equilibrium liquid depending on the partial pressure of oxygen. At 1 atm pressure of oxygen an equimolar mixture of nitrate and nitrite is obtained at 670° for potassium nitrate and about 730° for sodium nitrate. Smaller proportions of nitrite are obtained at lower temperatures.

At temperatures appreciably above 750° other decomposition products including nitrogen, oxides of nitrogen and alkali peroxides are obtained. In Pyrex or silica vessels the reactions are more complex as the heterogeneous decomposition then occurs, as well as reactions with the silica of the container to produce silicates. In such vessels reactions proceed at an appreciable rate as low as 550°. The end product of heating sodium nitrate in air is obtained at 900° and above—it consists of Na_2O .

The determinations by Nernst of the molecular weights of alkali-metal chlorides in an iridium apparatus based on the method of Victor Meyer, were interpreted to establish that such vapours consist of single "molecules" or more strictly ion pairs, *e.g.* Na^+Cl^- . In 1946, Brewer²³ in an important article on salt vapours stated that for the alkali-metal halides,

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“the only important gaseous species is the diatomic molecule. No polymerization has ever been observed.”

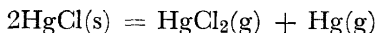
In 1953, Ochs, Cote and Kusch²⁴ found from molecular beam magnetic resonance experiments on the sodium halide vapours that these vapours are considerably associated to form dimeric species. These authors estimated that in the case of sodium chloride vapour the beam was from 25 to 75 per cent dimeric. Similar conclusions were arrived at by Friedman²⁵ who studied the ionized fragments from the vapour of lithium iodide in a mass spectrometer and found that monomers, dimers and trimers were all present. On the other hand, the vapours of cadmium and lead chlorides are mainly monomeric.

Accurate measurements on the dimerization of sodium chloride and potassium chloride vapours were made by Miller and Kusch²⁶ by the velocity distribution in a molecular beam, and by Barton and Bloom¹⁹ by a calculation using vapour pressure data measured by an absolute method (determination of boiling point at known pressure) and comparing the results with transpiration experiments on the same salt. At a pressure of 10^{-2} mm Hg, the degree of dimerization is about 19 per cent for potassium chloride at 625° and 62 per cent for sodium chloride at 650° . Berkowitz and Chupka²⁷ found that the lithium halides were mainly in the form of polymeric species mostly $(\text{LiX})_2$, with the monomer being a minor constituent of the vapour.

Besides the polymerization reactions observed for the alkali-metal halides, other high temperature reactions involving vapour equilibria have been reported. These are summarized by Brewer²³ and include disproportionation reactions such as



and



Vaporization by decomposition is also very common, *e.g.*



Barton and Bloom¹⁹ determined the apparent vapour pressure isotherms above mixtures of molten salts—the results are shown in *Figure 17* for the $\text{PbCl}_2 + \text{KCl}$ system, *Figure 18* for the $\text{CdCl}_2 + \text{KCl}$ system and *Figure 19* for the $\text{CdCl}_2 + \text{NaCl}$ system. Such diagrams were obtained by measuring the total vapour pressure at different compositions by means of a boiling point (absolute) method and the vapour composition by means of transpiration experiments. It was found that at 900° the apparent vapour pressure of the cadmium chloride or lead chloride shows negative deviations from Raoult's law while that of the alkali-metal chloride shows positive deviations—hence the apparent partial pressure isotherms are not in conformity with the Duhem-Margules relationship. An allowance for dimerization of the alkali-metal chloride in the vapour phase would not account for the apparent partial pressure isotherms, and the only feasible explanation is in the

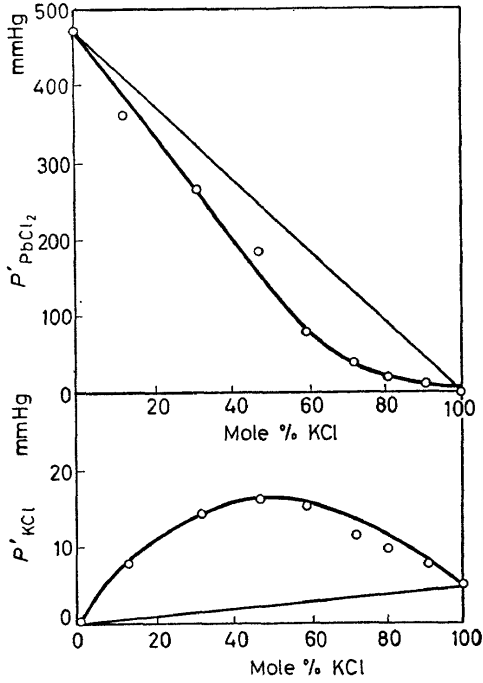


Figure 17. System $\text{PbCl}_2 + \text{KCl}$: apparent partial pressure isotherms at 900°

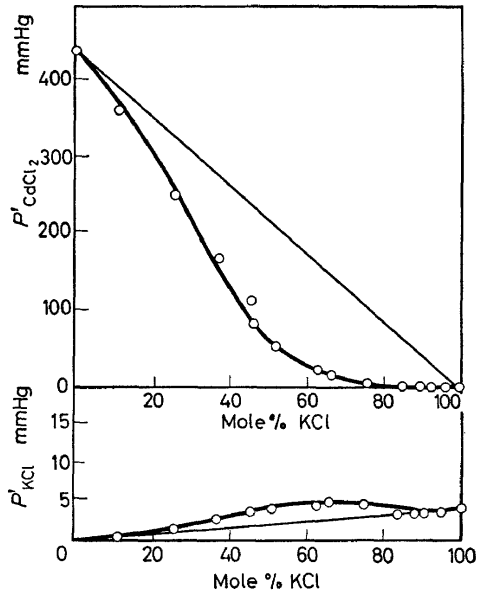


Figure 18. System $\text{CdCl}_2 + \text{KCl}$: apparent partial pressure isotherms at 900°

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formation of intermolecular compounds in the vapour between lead chloride or cadmium chloride and the alkali-metal chloride. The shape of the apparent partial pressure isotherms shows that 1:1 compounds are the most likely, since from the Gibbs-Duhem relation, the partial pressure of the equimolecular compound would be at a maximum in the vapour in equilibrium with the equimolecular mixture of the two component liquids. In

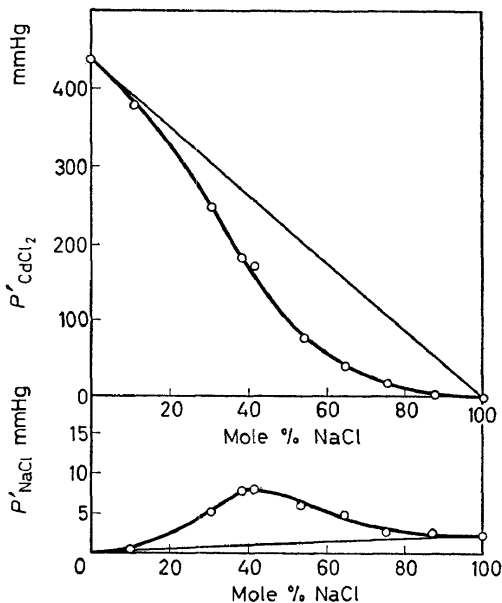


Figure 19. System $\text{CdCl}_2 + \text{NaCl}$: apparent partial pressure isotherms at 900°

fact the apparent partial pressure of the alkali-metal halide has in all these cases a maximum deviation from the ideal values at a composition approximating to 50 mole per cent, hence the compounds formed in the vapours above the three systems are $\text{PbCl}_2 \cdot \text{KCl}$, $\text{CdCl}_2 \cdot \text{KCl}$ and $\text{CdCl}_2 \cdot \text{NaCl}$, respectively. A vapour phase compound has been inferred also in the $\text{CdCl}_2 + \text{RbCl}$ system from recent vapour pressure determinations at the University of Tasmania.

This brief discussion can do no more than draw attention to some of the problems associated with the investigation of the high temperature chemistry of inorganic salt systems. It is hoped that the many investigations being carried out at present in various countries will, in the near future, lead to a better understanding of this very challenging branch of chemistry.

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