anol and dried at 100–110°. A yield of 70% of the theoretical amount was obtained. The light-purple microscopic crystals were found to melt at 205°.

Anal. Calcd. for $C_{13}H_{14}F_6O_2N_2Cu$: C, 38.29; H, 3.46; N, 6.87; Cu, 15.58. Found: C, 39.00; H, 3.80; N, 7.10; Cu, 14.91.

Bis-*p*-bromobenzoylacetonepropylenediiminocopper(II).—The general procedure was followed with acetone as the solvent. The reaction mixture was refluxed for approximately 20 hours. The product, which was recrystallized from acetone, was in the form of brown microscopic crystals which melted at 205.5–207.0°. The compound is fairly soluble in acetone, but only slightly soluble in alcohol and benzene. A 42% yield was obtained.

Anal. Calcd. for $C_{23}H_{22}O_2N_2Br_2Cu$: C, 47.48; H, 3.81; N, 4.82; Cu, 10.92. Found: C, 47.59; H, 3.71; N, 4.20; Cu, 10.72.

Metal Analyses.—All metal analyses were made in the following manner. The sample was placed in a sealed tube with concentrated HNO_3 and heated in a Carius furnace until completely oxidized. After it had cooled, the tube was opened and the contents were diluted with water and made alkaline with ammonia. The metal was titrated with a solution of disodium salt of ethylenediaminetetraacetic acid, with murexide as the indicator, according to the procedure described by Schwarzenbach.[13]

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(13) G. Schwarzenbach, "Die Komplexometrische Titration," Ferdinand Enke, Stuttgart, 1955.

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[CONTRIBUTION FROM THE INSTITUTE OF SILICATE SCIENCE, NORWEGIAN INSTITUTE OF TECHNOLOGY, INSTITUTE OF CHEMISTRY, UNIVERSITY OF OSLO; INSTITUTE OF THEORETICAL CHEMISTRY, NORWEGIAN INSTITUTE OF TECHNOLOGY]

The Solution of Cadmium in Liquid Cadmium Chloride

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The melting point depression of cadmium in cadmium chloride has been measured. From the results it is inferred that cadmium probably forms Cd_2^{++} ions on dissolving in liquid cadmium chloride. Related experimental data are discussed and found to support this view. It seems that also in other cases the formation of metal–metal bonds might be responsible for the solubility of a metal in its halides.

Introduction

The solubility of metals in their liquid halides has been subject of much discussion, but the nature of the solutions seems not to be settled yet. Much experimental work is still needed to throw light upon the valence states in question. Unfortunately, large experimental difficulties are encountered in several of the most interesting and technically important systems, as that of aluminum and cryolite.[1] Some systems, like the Cd–$CdCl_2$ system, are easier to deal with, however, and data from these systems might provide a clue to the general problem. Many authors have therefore studied the solution of Cd in $CdCl_2$, but no definite conclusions as to the nature of the solution have been agreed upon.[2–6]

The cadmium chloride rich part of the Cd–$CdCl_2$ phase diagram for the system Cd–$CdCl_2$ has been investigated by Aten,[2] Hedger and Terrey,[7] and Urazow and Karnaukhov[8] by thermal analysis.

Accurate measurements in this region of the phase diagram can be shown to give strong evidence about the nature of the solution. To get sufficiently accurate data, the liquidus curve has been redetermined by the present authors from 0 to 9.4 mole % metallic cadmium. It will be shown that the experimental data provide support to the view that Cd_2^{++} ions are present in the liquid. This view is also confirmed by other experimental data.

Experimental

Cadmium chloride of C.P. grade was heated with NH_4Cl and melted in a stream of argon gas before use. The argon was a pure grade commercial preparation from tank origin, purified by passing over copper at 500°, over cupric oxide at 300°, and dried by passing through a calcium chloride, ascarite and phosphorus pentoxide train. A laboratory reagent cadmium metal from "British Drug House" was used.

The primary crystallization temperatures were measured with a Pt–Pt 10% Rh thermocouple connected to a precision potentiometer and a mirror galvanometer from Tinsley and Co. Ltd. The e.m.f. could be read with an accuracy of ±0.0005 mv. The couple was mounted in an alumina tube having two bores, the tube being sealed with fused alumina cement at one end. As the melting point of alumina is considerably higher than that of platinum this sealing of the end had to be done with considerable care. The more commonly used external thermocouple sheath would, however, considerably reduce the rate of heat transfer from the surroundings to the hot junction, and hence make the temperature measurements less reliable than the present ones. The thermocouple was standardized by determining the e.m.f.'s at the melting point of aluminum and silver, and plotting the deviations from the standard reference table of Bureau of Standards Research Paper 530.[9] The furnace was of the ordinary electrically heated vertical type. The nickel-chromium heating wire was wound on a "Pythagoras" (Trade Mark, Porzellan-Manufaktur, W. Haldenwanger, Berlin, Germany) tube and covered with alundum cement. The space between the heating element and the outside wall was filled with silogel powder. The windings were bifilar, and more closely spaced toward the ends of the furnace, to compensate for the extra loss of heat there. A voltage stabilizer was used for the heating current. The furnace tube was internally heat insulated toward the bottom with a porous magnesia firebrick and toward the top by a similar, but more porous firebrick with appropriate holes for the thermocouple, a seeding tube and a mechanical device for stirring the melt. The poorer heat insulation of the top firebrick around the thermocouple caused the first

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(1) K. Grjotheim, *Allumino*, **21**, 679 (1953).

(2) A. H. W. Aten, *Z. physik. Chem.*, **73**, 578 (1910).

(3) R. Lorenz and W. Eitel, "Pyrosole," Akademischer Verlagsgesellschaft, Leipzig, 1926.

(4) G. v. Hevesy and E. Løwenstein, *Z. anorg. allgem. Chem.*, **187**, 266 (1930).

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(6) D. Cubicciotti, *J. Metals*, 1106 (1953).

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(8) G. G. Urazow and A. S. Karnaukhov, *Doklady Akad. Nauk. U.S.S.R.*, **96**, 535 (1954).

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TABLE I

EXPERIMENTAL DATA ON THE $CdCl_2$ SIDE OF THE SYSTEM Cd–$CdCl_2$

No.	Weight, g. Metallic Cd	Weight, g. $CdCl_2$	Obsd. Beginning solidification, °C.	Obsd. Eutectic temp., °C.	$\frac{1}{T} \times 10^3$ °K.	Calcd. as a soln. of Cd_2^{2+} ions $N_{Cd^{++}}$	Calcd. as a soln. of Cd_2^{2+} ions $-\log N_{Cd^{++}}$	Calcd. as atomic soln. of Cd $N^*_{Cd^{++}}$	Calcd. as atomic soln. of Cd $-\log N^*_{Cd^{++}}$
1	0	160.28	570.8		1.1847	1	0	1	0
2	0	162.44	570.6		1.1851	1	0	1	0
3	3.6746	165.285	563.8		1.1947	0.9637	0.0161	0.9650	0.0155
4	7.8107	156.235	551.8		1.2121	.9185	.0369	.9246	.0341
5	5.3060	142.964	557.2	524.6	1.2042	.9394	.0272	.9431	.0254
6	11.1430	175.960	545.5	525.0	1.2215	.8967	.0474	.9063	.0427

crystallization to start at the end of the thermocouple protection tube.

The crucible with auxiliaries was made of pure graphite. Mixtures of the metal and the salt (total weight between 160 and 190 g.) were made by weighing the components. The graphite crucible containing the mixture was placed in the furnace and a slow stream of purified argon was passed through it. The temperature was raised to about 600° and held there for approximately 15 min. The furnace was then allowed to cool at a fixed rate of 0.8°/min. Supercooling was prevented by stirring and repeating seeding with small crystals of cadmium chloride. The e.m.f. was observed every 30 seconds, and the e.m.f. corresponding to the initial crystallization of cadmium chloride determined. For two compositions also the eutectic temperature was noted as a second hold in the cooling curve.

Results

The observed temperatures of beginning and eutectic crystallization in the cadmium–cadmium chloride system are given in Table I and Fig. 1. No perceptible solid solution was observed, neither by the thermal analysis, nor from X-ray powder photographs taken of quenched samples. Hence the heat of fusion of cadmium chloride, ΔH_f, can be approximately determined from the freezing point depression, if it is assumed that the deviation from ideal solution is small ($\gamma \approx 1$).

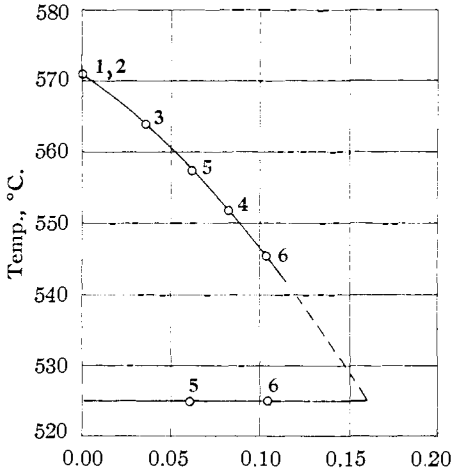

Fig. 1.—The $CdCl_2$-rich part of the $CdCl_2$–Cd phase diagram.

Under these circumstances the following expression is valid

$$\ln N_{Cd^{++}} = -\frac{\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_f}\right)$$

where $N_{Cd^{++}}$ is the cation mole fraction of Cd^{++} in the mixture, T_f and T are the liquidus temperatures of pure cadmium chloride and of the mixture respectively.

The heat of fusion deduced from this expression by plotting $\ln N_{Cd^{++}}$ as a function of $1/T$ will depend upon the structure model chosen for the solution. When the heat of fusion is known, a means of distinguishing different cases is provided.

If the cadmium metal dissolves according to the reaction

$$Cd(metal) + Cd^{++} = Cd_2^{++}$$

the cation fraction is given by

$$N_{Cd^{++}} = \frac{n_{CdCl_2} - n_{Cd}}{n_{CdCl_2}}$$

where n_{Cd} and n_{CdCl_2} are the molar amounts of cadmium and cadmium chloride in the mixture. Plotting $\ln N_{Cd^{++}}$ as a function of $1/T$ gives a nearly straight line as shown in Fig. 2, corresponding to a heat of fusion of 5.4 ± 0.3 kcal./mole.

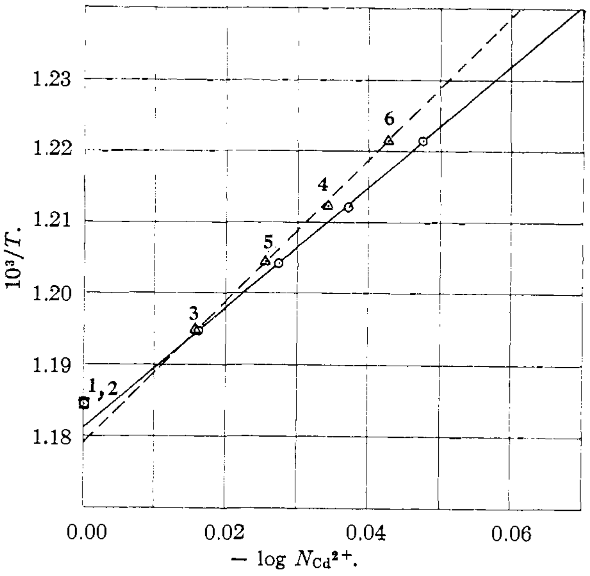

Fig. 2.—The logarithm of the mole fraction of cadmium chloride as a function of the inverse absolute temperature: ⊙, ionic solution of Cd_2^{2+} and Cd^{2+}; △, "atomic" solution; □, pure $CdCl_2$.

If the cadmium metal atoms are assumed to dissolve under formation of a true solution in the sense of the model of Cubicciotti,[6] electrons from the dissolved metal are transferred from the metal to bands belonging to the salt system as a whole. The dissolved cadmium atoms are assumed to occupy cation positions in the liquid lattice. Hence in this case the cation fraction $N_{Cd^{++}}$ can be expressed by the expression

$$N^*_{Cd^{++}} = \frac{n_{CdCl_2}}{n_{CdCl_2} + n_{Cd}}$$

From a plot of ln $N^*_{\mathrm{Cd^{++}}}$ (see Fig. 2) against $1/T$, a heat of fusion of 4.6 ± 0.3 kcal./mole is found.

A third possibility, the solution of metallic cadmium by the reaction

$$\mathrm{Cd(metal)} + \mathrm{Cd^{++}} = 2\mathrm{Cd^{+}}$$

gives a cation fraction

$$N^{+}_{\mathrm{Cd^{++}}} = \frac{n_{\mathrm{CdCl_2}} - n_{\mathrm{Cd}}}{n_{\mathrm{CdCl_2}} + n_{\mathrm{Cd}}}$$

corresponding to a heat of fusion of 10.4 kcal./mole.

The heat of fusion of cadmium chloride is given as 5.3 kcal./mole in the critical compilation by Kelley.[10] This excludes that cadmium is dissolved according to the latter reaction scheme, implying the formation of $\mathrm{Cd^+}$ ions. The experimental results are in best agreement with the first model, indicating the presence of $\mathrm{Cd_2^{++}}$ ions in the melt. By assuming a deviation from ideality, however, the result can also be reconciled with Cubicciotti's model. The observed melting point of cadmium chloride, 570.8°, is somewhat higher than the value 568° commonly given in the literature.[2,7,8,10] By extrapolating from the depression as in Fig. 2, still larger values are deduced, the discrepancy being smallest with the $\mathrm{Cd_2^{++}}$ model. Here a melting point of 573.0° is found. The cause of these observations may be a dissociation of pure cadmium chloride, according to the scheme

$$2\mathrm{Cd^{++}} + 4\mathrm{Cl^-} = \mathrm{Cd_2^{++}} + 2\mathrm{Cl^-} + \mathrm{Cl_2}$$

A smell of chlorine above a melt of cadmium chloride can be detected. In agreement with this explanation a lowering of the melting point of pure cadmium chloride, which had been kept molten for some time, was observed.

Discussion of Other Experimental Data

Aten[2] has measured the electric conductivity of melts of cadmium chloride containing various amounts of dissolved cadmium metal. He finds a decrease in conductivity with increasing amounts of metal dissolved, from which he deduces that the dissolved metal contributes little, if any, to the current transport.

Even a relatively small mobility of the $\mathrm{Cd_2^{++}}$ ion will give a significant contribution to the electrical conductivity. It can be shown, however, that the dissolved metal atoms really participate in the current transport. For this purpose the following experiment was carried out, which utilizes the intense color of the solution of the cadmium in cadmium chloride. A vitreous silica tube, containing a porous plug made of alundum cement, served as connection between two vessels containing platinum electrodes. The whole system was kept above the melting point of cadmium chloride. The plug was soaked with pure cadmium chloride in advance, and served as partition between the vessels which both contained the strongly colored saturated solution of cadmium in cadmium chloride. When an electrical field was applied, the color front was seen to enter the plug and move rapidly toward the cathode. This indicates that the color associated with the dissolved metal is connected with positively charged particles.

Experiments with electrolysis of saturated solutions of cadmium in cadmium chloride give a current efficiency exceeding 100% if only $\mathrm{Cd^{++}}$ cations are considered in the transport process.[11] The result can be explained by assuming the formation of $\mathrm{Cd_2^{++}}$ ions in the melt, but it is not so easily understood in terms of the hypothesis by Cubicciotti[6] (arsenic electronic bands may cause a loss in current yield).

The formation of perceptible amounts of $\mathrm{Cd^+}$ ions in the melt is not only contradicted by our thermal data, but also by the magnetic measurements of Farquharson and Heymann.[5] The $\mathrm{Cd^+}$ ion should be expected to be paramagnetic. The diamagnetic melt of cadmium chloride, however, remains diamagnetic on dissolving cadmium in the melt. The present authors have confirmed this result by measuring the magnetic susceptibility of the solution at 720° by the method of Gouy. The magnetic measurements are compatible both with the formation of solvated cadmium atoms or $\mathrm{Cd_2^{++}}$ ions. From the previous considerations the latter assumption is seen to be most likely.

On examining mixtures of cadmium chloride with other divalent halides[12] one finds that the amount of cadmium going in solution is roughly proportional to the amount of cadmium chloride in the solution. The effect of the other chlorides is thus merely to dilute the cadmium chloride.[13]

In mixtures containing trivalent cerium chloride it was found, however, that each mole of cadmium chloride is capable of dissolving a larger amount of cadmium than the amount which can be dissolved by pure cadmium chloride. In mixtures with potassium chloride the opposite effect is seen.

The equilibrium

$$\mathrm{Cd^{++}} + \mathrm{Cd} = \mathrm{Cd_2^{++}}$$

is thus shifted to the right by trivalent $\mathrm{Ce^{+++}}$ cations and to the left by monovalent $\mathrm{K^+}$ cations. Divalent ions like $\mathrm{Ca^{++}}$, $\mathrm{Mg^{++}}$ and partly $\mathrm{Zn^{++}}$ is seen to have less influence on the equilibrium.

As the reaction is a cation reaction, the equilibrium is strongly dependent on the anionic environment, and to a smaller extent dependent on other cations.

The influence of foreign cations on the $\mathrm{Cd_2^{++}}$ ion will therefore be more indirect. A major factor determining the stability of the $\mathrm{Cd_2^{++}}$ ion is perhaps the polarizability of the surrounding anions. The more polarizable these ions are, the less stable is the $\mathrm{Cd_2^{++}}$ ion. The strong contrapolarizing effect of the trivalent cerium ions thus stabilizes the metal–metal bond in cadmium, whereas potassium chloride delivers easily polarizable chloride ions, that weaken the metal–metal bond. The small effect of calcium ions on the equilibrium finds its explanation in that the contrapolarizing power of this ion and the $\mathrm{Cd^{++}}$ ion are about equal.

According to the previous discussion, the effect

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[10] K. K. Kelley, *U. S. Bur. Mines Bulletin*, Vol. **393**, 30 (1936).

[11] G. Wirths, *Z. Elektrochem.*, **43**, 486 (1937).

[12] D. Cubicciotti, THIS JOURNAL, **74**, 1198 (1952).

[13] The exception for manganese chloride and zinc chloride may be due to the reduction of these chlorides by cadmium. In computing the equilibrium constant for this reduction, Cubicciotti[12] omitted the free energy of dissolving the reduced metal in liquid cadmium. He states, however, that zinc chloride was found to be reduced by the cadmium.

of replacing the Cl^- ion with Br^- and I^- ions should be pronounced, and this is in fact the case. The solubility of cadmium is found to decrease in the series from the chloride to the iodide[4] as expected from the theory presented. The fluoride might form an exception.[14]

This interpretation finds a support in the stability of the series of mercurous halides. Mercurous iodide contains the most polarizable anion and is less stable than the chloride and bromide. In agreement with this, X-ray investigations of the mercurous halides[15] indicate that the mercury–mercury distance in the crystalline halides increases from the chloride to the iodide, corresponding to a weakening of the bond.

Discussion of Other Systems

Ehrlich and Gentsch[16] have proved the existence of a calcium monochloride. X-Ray work[17] shows that this compound has a structure with metal–metal bonds. It is therefore very likely that the formation of Me_2^{++} ions is responsible for the solution also of the even series of the second group metals in their halides. From the Ca–Ca distance the Ca radius was found to be 1.69 Å. which is in reasonable agreement with the metallic single bond radius 1.736 Å. given by Pauling,[18] and indicates the presence of strong metal–metal bonds.

An important point stressed by Heymann, Martin and Mulcahy[19] is that metals are generally soluble only in their own salts, except of course when reduction occurs. This can be explained on the basis of a metal–metal bond formation. From quantum mechanical considerations it follows that for this type of bonding the outer electron orbitals must be on approximately the same energy level if a sufficient large bonding energy shall result.

This extends the principle of metal–metal bond formation to other systems, for instance the solution of alkali metals in their halides. In this case one-electron bonds may be effective. Also here, a larger effect of foreign anions than foreign cations on the solubility of the metal may be predicted from the hypothesis of the cation reaction

$$Me + Me^+ \longrightarrow Me_2^+$$

It seems quite possible that a suitable anionic environment really stabilizes the one-electron bond.

Bredig, Johnson and Smith[20] have made measurements on the alkali metal–alkali halide systems. From their experiments they find complete miscibility at higher temperatures. Obviously, the formation of Me_2^+ ions is only the first step when passing through the whole composition range from the salt to the metallic phase, and in this connection the properties of silver sub-fluoride, Ag_2F, are very interesting. Pauling[21] points out that the substance may be considered to be intermediate between a salt and a metal. The crystal structure consists of close packed layers of atoms in the sequence F Ag Ag F Ag Ag F. The bonds between silver layers are supposed to be predominantly metallic and to cause the electric conductivity of the crystal, while bonds between silver and fluorine are of the ordinary ionic-covalent type. This compound may provide a valuable analog to the alkali metal–alkali halide system.

If the metal atoms dissolve in their salts by formation of Me_2^+ or Me_2^{2+} ions, the valence electrons are restricted mainly to the space between the cation cores to give a sufficient bonding. This does, of course, not imply that the electrons are strongly bonded. Also the restrictions on the valence electrons may decrease as the concentration of Me_2^+ ions so that conduction bands may develop.

In systems involving metals not belonging to the first or second group, reduction to lower valence states may occur. This is known to be the case for metallic thallium dissolved in a trivalent thallium salt. Also in the solution of aluminum in a cryolite melt there are some indications that Al^+ ions[1] may be formed.

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[14] L. L. Quill, "The Chemistry and Metallurgy of Miscellaneous Material," McGraw-Hill Book Co., New York, N. Y., 1950, p. 144.

[15] R. J. Havighurst, THIS JOURNAL, **48**, 2113 (1926).

[16] P. Ehrlich and L. Gentsch, *Naturwiss.*, **40**, 460 (1953).

[17] P. Ehrlich and L. Gentsch, *ibid.*, **41**, 211 (1954).

[18] L. Pauling, THIS JOURNAL, **69**, 542 (1947).

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[21] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1945, p. 421.