

rium atoms and if one assumes that D_2 and D_3 amount to a total of 2%, then a total of 11% of the molecules have undergone process b. This value is very close to the percentage racemization, 10.3. One could assume, then, that process b inherently causes racemization.

Similar considerations apply to run D at 263°. About 3.3% of the molecules underwent process b, the fraction racemized was 3.2%. In run F at 345°, the % of molecules which underwent process b, about 16%, somewhat exceeds the fraction racemized, 10.8%. As will be seen in comparing

runs D, E and F, the ratio of the rates of processes b and a increases with temperature. It is even probable that the slight loss in rotation at 200°, run C, is occasioned by process b.⁵⁷

(57) Within the sensitivity limits of this particular mass spectral recording, 0.2% of a species at the parent peak, there were no species more multiply exchanged than those shown in run C, Table II. However, examination of the amyl carbonium ion peaks, which are twenty-fold more intense, disclosed the presence of more multiply exchanged species with a distribution rather as in run D. Analysis using these peaks gave values for D_1 , D_2 and D_3 reasonably consistent with those obtained using the parent peaks and gave the sum of D_1 to D_{11} as 2.0% which is not far from the degree of racemization, 1.8%.

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The Cadmium-Cadmium Halide Systems¹

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The solubility of cadmium in CdCl_2 , in CdBr_2 and in CdI_2 to about 1000° was determined by thermal analysis and decantation techniques. The monotectics for the systems were found to be 13.7 mole % Cd at 537° in CdCl_2 , 14.1% at 536° in CdBr_2 and 2.5% at 383° in CdI_2 . The solubility of the metal was greatest in the bromide, slightly less in the chloride and least in the iodide. The solubilities of the salts in the metal were found to be about 0.05 mole % at 320°. Cryoscopic analyses of the salt-rich liquidus curves yield a cryoscopic number of one and suggest the species, Cd_2X_4 or Cd_3X_6 , in the solvents CdCl_2 and CdBr_2 .

Introduction

The solubility of cadmium in cadmium chloride has been studied by many investigators.²⁻⁹ The metal has also been shown to be soluble in its bromide³ and iodide^{3,10} although very few measurements have been made in these systems. In the present work measurements of the Cd-CdCl₂ immiscibility curve have been repeated and extended over a larger temperature range. The solubility of the chloride in the metal near its melting point has also been determined. In addition the Cd-CdBr₂ and Cd-CdI₂ phase diagrams have been investigated in order to afford a comparison between the systems.

Experimental

Materials.—Reagent grade CdCl_2 was dried by heating the salt in an atmosphere of dry HCl; the molten salt was then cooled in argon. The CdCl_2 thus treated had a melting point of 569°.

CdBr_2 and CdI_2 were synthesized from the elements¹⁰ in a sealed tube. The melting points of the bromide and iodide were 568° and 388°, respectively.

Mallinckrodt's reagent grade cadmium, with an assayed purity of 99.9%, was employed throughout. Before use, the metal was filtered through quartz wool *in vacuo* to remove any oxide present.

Apparatus and Procedure.—In all the measurements Vycor or fused silica tubing was used. The liquidus curves in the CdBr_2 and CdI_2 systems were determined by the usual freezing point method.¹¹ The two-phase liquid regions of these systems were studied by decantation techniques¹² and by differential thermal analysis. In the differential thermal analyses the sample and an aluminum oxide or pure cadmium halide standard were enclosed in a large nickel block; this assembly was heated to a given temperature in a rocking furnace. The furnace was allowed to cool slowly with or without rocking, and the temperature of the sample as well as the difference in temperature between the sample and standard were measured with chromel-alumel thermocouples inserted into wells in the containers. The differential voltage was magnified 200-fold by a Leeds and Northrup stabilized d. c. microvolt amplifier and recorded along with the sample temperature on a Leeds and Northrup Speedo-max x-y recorder. The sample temperature could also be read directly and accurately by switching to a Rubicon potentiometer.

Results and Discussion

The solubility of cadmium in its chloride, bromide and iodide is shown in Fig. 1. The results for the Cd-CdCl₂ system are in good agreement with those of other investigators,²⁻⁶ especially at temperatures below 700°. For the Cd-CdBr₂ system the one solubility reported in the literature,³ 14.0 mole % Cd at 600°, obtained by quenching, is somewhat less than the 16.2% found in this study. Two studies have yielded widely different values for the solubility of Cd in its iodide; v. Hevesy and Löwenstein³ reported 6.1 mole % at 600°, whereas Corbett, *et al.*,¹⁰ found 1.5 mole % at the same temperature and 0.6% at 410°.

(11) S. W. Mayer, S. J. Yosim and L. E. Topol, *J. Phys. Chem.*, **64**, 238 (1960).

(12) S. J. Yosim, A. J. Darnell, W. G. Gehman and S. W. Mayer, *ibid.*, **63**, 230 (1959).

(1) This work was supported by the Research Division of the Atomic Energy Commission. It was presented in part before the Division of Inorganic and Physical Chemistry at the National Meeting of the A.C.S. in New York, September, 1957.

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

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

(4) E. Heymann and E. Friedlander, *Z. physik. Chem.*, **A148**, 177 (1930).

(5) R. E. Hedger and H. Terrey, *Trans. Faraday Soc.*, **32**, 1614 (1936).

(6) E. Heymann, R. J. L. Martin and M. F. R. Mulcahy, *J. Phys. Chem.*, **47**, 473 (1943).

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

(8) G. G. Urazov and A. S. Karnaukov, *Doklady Akad. Nauk S.S.S.R.*, **96**, 535 (1954).

(9) K. Grjotheim, F. Grönvold and J. Krogh-Moe, *THIS JOURNAL*, **77**, 5825 (1955).

(10) J. D. Corbett, S. von Winbush and F. C. Albers, *ibid.*, **79**, 3020 (1957).

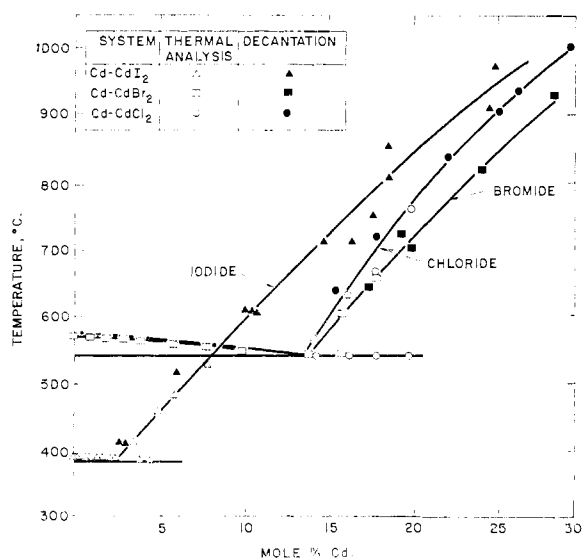


Fig. 1.—Cadmium-cadmium halide systems.

These solubilities, determined by quenching, are all less than those measured in this investigation (10.6% and 3.5% at 600° and 410°, respectively). It is difficult to explain the exceedingly low values found by Corbett, *et al.* Their reduction of free volume above the melt to 5%, in an attempt to minimize vaporization or distillation of the metal, could result in inadequate mixing and produce this effect. In the present investigation several Cd-CdI₂ mixtures were run with free volumes varying from 10 to 50%, and all of these samples, after being equilibrated, yielded virtually identical results by differential thermal analysis. Further evidence in favor of the solubility results found in this investigation is that the monotectic composition, 2.5 mole % Cd, is consistent with both freezing point measurements on the liquidus and with differential thermal analysis results in the two-phase liquid region. Extrapolation of Corbett's solubilities to the monotectic temperature would yield a composition of about 0.5%.

From Fig. 1, it is seen that the solubility of cadmium metal in its molten halides is greatest in the bromide and least in the iodide. The monotectics were found to be 13.7 mole % Cd at 537° for CdCl₂, 14.1% at 536° for CdBr₂ and 2.5% at 383° for CdI₂. The solubility of the salts in cadmium metal was calculated to be about 0.05 mole % at 320°. This value was obtained by measuring the maximum freezing point depression of Cd, 0.9°, and substituting this and the heat of fusion of Cd, 1.46 kcal.,¹³ into the Raoult-van't Hoff expression. (Ideal behavior of the solvent and dissociation of the solute into two foreign particles were assumed.¹¹) Other investigators in a visual study have reported that Cd dissolves less than 0.05 mole % CdCl₂¹⁴ at 1000° and in an exploratory experiment found less than 1 mole % CdI₂ in Cd at the same temperature. Thus the solubility of these Cd salts in Cd metal appears

(13) K. K. Kelley, U. S. Bur. Mines Bull. 393 (1936).

(14) S. J. Yosim and E. B. Luchsinger, *Ann. N. Y. Acad. Sci.*, **79**, 1079 (1960).

to be quite small in the temperature range of 320 to 1000°.

An estimate of the heats of solution, $\Delta\bar{H}_2$, of Cd may be made¹⁵ since one of the immiscible phases in these systems is essentially pure metal. With the assumption of regular solution behavior as a first approximation, $\Delta\bar{H}_2$'s of 3–4 kcal./mole for Cd in the chloride and bromide systems and about 7 kcal./mole in the iodide were computed. If it is assumed that Cd goes into solution by subhalide formation (see below) and regular solution behavior is followed, the data yield values for the ΔH^0 of reaction 1 below of about 6 kcal./mole for the chloride and bromide melts and approximately 8 kcal./mole for the iodide system. These values for $\Delta\bar{H}_2$ and ΔH^0 are all positive.

The nature of the solution of cadmium in its halides is of great interest. Several possibilities are: (1) solution as metal atoms, dimers or polymers, (2) solution by reaction with the solvent to form a subhalide species, (CdX)_n, where *n* is an integer, and (3) a combination of the above. Magnetic susceptibility measurements¹⁶ have shown that solutions of Cd in CdCl₂ at temperatures up to 800° are diamagnetic. This appears to eliminate the existence of the subhalide, CdCl, but not (CdCl)_{2n} or metal atoms or polymers. Grjotheim, *et al.*,⁹ on the basis of both the motion of the dark metal solution boundary in an electric field and a cryoscopic study, concluded that Cd dissolves in the chloride by formation of Cd₂Cl₂. However, the heat of fusion of CdCl₂ used by Grjotheim, *et al.*, has been shown to be in error,¹⁷ and a re-analysis of their data with the new value (7.22 kcal./mole) leads to the results shown in Fig. 2.

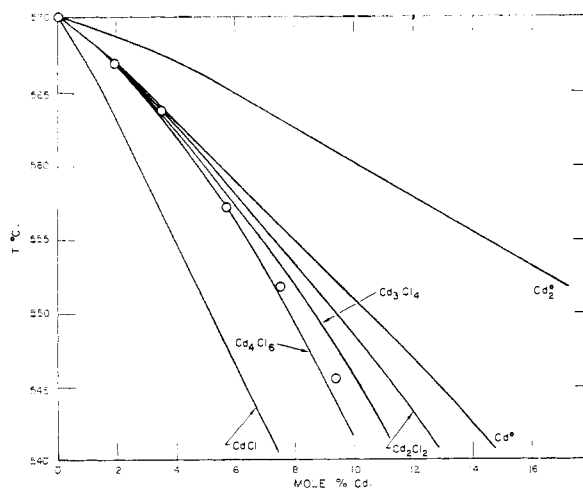


Fig. 2.—Comparison of experimental freezing points of CdCl₂ with those calculated for various cadmium species.

The data, which still yields a cryoscopic number of one as was found by Grjotheim, now are consistent with the species, Cd₄Cl₆ or Cd₃Cl₄. Examples of species which have these stoichiometric formulas are Cd₂Cl₂ strongly associated with 1 or

(15) See A. T. Williamson, *Trans. Faraday Soc.*, **40**, 421 (1944).

(16) J. Farquharson and E. Heymann, *ibid.*, **311**, 1004 (1935).

(17) L. E. Topol and L. D. Ransom, *J. Phys. Chem.*, **64**, 1339 (1960).

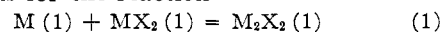
2 molecules of CdCl_2 , Cd atoms associated with 2 or 3 solvent molecules or $\text{Cd}_2(\text{CdCl}_3)_2$ and $\text{Cd}_2\text{-CdCl}_4$ ion pairs. If the two ion pairs are dissociated in the melt, then the anions must act as a common ion with the solvent to give curves approximating those depicted for Cd_4Cl_6 and Cd_3Cl_4 . Each of the above entities (with which the color is presumably associated) would be expected to migrate to the cathode in an electric field as was observed by Grjotheim.⁹ Even uncharged entities, *e.g.*, atoms or ion pairs, would behave in this manner if gravitational effects were present, since the chloride ions would be expected to carry most of the current, and the resultant increase in anolyte would cause a mass flow towards the cathode. Thus the moving boundary experiment, as described,⁹ is inconclusive. One of the limitations of the cryoscopic analysis is that the solvent is assumed to behave ideally over the whole liquidus range. Also, one mechanism is assumed to hold throughout, and it is quite possible that the dissolved metal exists as more than one species—the predominant species varying with the composition of the solution. Such a variation seems likely to occur for entities of the type, $\text{Cd}_2\text{Cl}_2 \cdot x\text{CdCl}_2$ or $\text{Cd} \cdot y\text{CdCl}_2$.

An analogous examination of the liquidus curves of the Cd– CdBr_2 and Cd– CdI_2 systems yielded results for the bromide similar to the chloride, whereas, for the iodide, no distinction could be made among the mechanisms that yield a cryoscopic number of unity because of the limited range of concentrations.

An alternative approach in interpreting the cryoscopic data is to assume solution as Cd atoms or as Cd_2X_2 and calculate the deviation of the solvent from ideality using the exact form of the Raoult-van't Hoff equation. If the cadmium dissolves monatomically, the activity coefficient of the salt (the standard state being the pure liquid) in both the chloride and bromide systems decreases to about 0.96 at the monotectic composition. Although the difference between this value and unity seems small, an error in temperature of 6°, much greater than can be accounted for experimentally, is required in order that there be no negative deviation. These negative deviations from ideality for the chloride and bromide solvents, although small, appear to be contrary to what one would usually expect for systems which exhibit an immiscibility gap. For the Cd_2X_2 case, the activity coefficient of the CdCl_2 or CdBr_2 decreases to about 0.99 at the monotectic composition; the

solvents deviate only slightly from ideality in this case, and more important, negative deviations found in "all-salt" solutions are common. (It is presumed that the subhalide has salt-like character.) Thus, solution of Cd by subhalide formation appears more consistent with experience than solution as simple atoms.

An interesting correlation is provided by a comparison of the observed solubilities with predictions of the stabilities of the Cd subhalides. In order to predict the order of stabilities the thermodynamic data^{17,18} for the mercury analogs may be used. Thus for the reaction



the ΔF^0 s at 600°K for the mercury systems are –2.0, –2.6 and –1.1 kcal. for the chloride, bromide and iodide, respectively.¹⁹ If a subhalide mechanism prevails, then the Cd solubilities would be expected to show the same trend as the stabilities of the subhalides. It is observed that this is true, *i.e.*, the bromide is the most stable mercury subhalide and also is the cadmium salt which dissolves the most Cd metal. However, this consistency with the subhalide model does not preclude the possibility of another mechanism.

Additional evidence supporting the subhalide view is the effect of acids and bases on the solubility of Cd in CdCl_2 . Bases decrease the solubility²⁰ whereas acids, presumably by stabilizing the subhalide, increase the solubility.²¹ In the latter case the acid-stabilization of a lower-valent cadmium compound has resulted in the isolation of $\text{Cd}_2(\text{AlCl}_4)_2$.²¹ However, melts of CdCl_2 containing even small amounts of Cd are black whereas the AlCl_3 – CdCl_2 –Cd solutions are reported to be light green in color.²¹ This color difference suggests that there are different Cd species in the two systems or, more probably, different relative concentrations of two or more Cd species.

The experimental data of this study, although inconclusive, as well as the observations of other investigators can be interpreted more reasonably on the basis of subhalide formation. However, the possibility of the existence of more than one species, with the predominant species varying with the amount of added metal, should not be dismissed.

(18) L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials-Thermodynamics," Ed. by L. L. Quill, McGraw-Hill Book Co., New York, N. Y., 1950.

(19) For the subhalide going to the hypothetical pure liquid, an entropy of fusion of 12 e.u. was assumed.

(20) D. Cubicciotti, *THIS JOURNAL*, **74**, 1198 (1952).

(21) J. D. Corbett, W. J. Burkhard and L. F. Druding, *ibid.*, **83**, Jan. 5 (1961).