

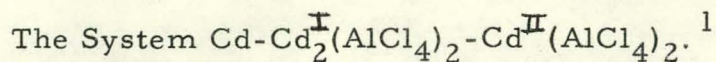
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Stabilization of the Cadmium(I) Oxidation State.



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Abstract--The effects of added salts on the degree of solubility of cadmium metal in the molten cadmium(II) halides are reinterpreted in terms of acid-base reactions between the added halides and a solution of Cd_2X_2 in CdX_2 . At 335°, melts containing 67, 57 and 31 mole percent Cd_2^{+2} result when CdCl_2 , CdBr_2 and CdI_2 are reduced in the presence of two moles of the respective aluminum trihalides per mole of the dihalide. The presence of stable cadmium(I) salts in the diamagnetic, white to yellow products obtained on solidification of these melts is confirmed by the $\text{Cd}-\text{Cd}_2(\text{AlCl}_4)_2-\text{Cd}(\text{AlCl}_4)_2$ phase diagram and by the isolation of $\text{Cd}_2(\text{AlCl}_4)_2$. This salt decomposes to metal and a melt containing 65% Cd_2^{+2} at 227° and disproportionates in all solvents much more basic than benzene.

In the melts the increased stability of the cadmium(I) oxidation state when X^- is replaced by the larger and less basic AlX_4^- is considered to result from the decrease in the interaction of the

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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more acidic cation, Cd^{+2} , with the anion, and, in the solid, to a related decrease in the difference in lattice energies of the salts in the two oxidation states. The contrast between the light green color of the reduced tetrachloroaluminate melts and the opacity of those containing chloride ion is discussed.

Introduction

The apparent solution of cadmium metal in molten cadmium(II) chloride, bromide or iodide was first reported in 1890 by Morse and Jones.² The black solids Cd_4Cl_7 , Cd_4Br_7 and $\text{Cd}_{12}\text{I}_{13}$ that they

(2) H. Morse and H. Jones, Am. Chem. J., 12, 488 (1890).

obtained on solidification of the metal-saturated melts were believed to be mixtures of the dihalide and the cadmous halide since an unstable CdOH was claimed to have been obtained upon washing these products with water. However, subsequent studies have shown that this phenomenon is solely one of the liquid state and that the resultant solids are indeed only mixtures of the cadmium(II) halide and finely divided metal.^{3, 4}

(3) W. Hollens and J. Spencer, J. Chem. Soc., 1062 (1934).

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

The resulting speculation regarding the nature of these and other similar melts has been considerable. The possibility of "pyrosole" formation⁵ was eliminated by the marked depression of

(5) R. Lorenz and W. Eitel, "Pyrosole", Akademische Verlagsgesellschaft, Leipzig, 1926.

the freezing point of CdCl₂ by added metal⁴ and by the absence of colloidal metal in the melt,⁶ while the nonexistence of a significant

(6) W. Eitel and B. Lange, Z. anorg. allgem. Chem., 171, 168 (1928).

concentration of mobile electrons, as with the alkali metals in their molten halides,⁷ was indicated by the gradual decrease in conduc-

(7) H. R. Bronstein and M. A. Bredig, J. Am. Chem. Soc., 80, 2077 (1958).

tivity of liquid CdCl₂ on addition of metal.⁴ However, other work has not, in general, allowed a clear and unambiguous distinction to be made between 'atomic' cadmium, a cadmium subhalide or a mixture of these as the solute. The observed diamagnetism,⁸ for

(8) J. Farquharson and E. Heymann, Trans. Farad. Soc., 31, 1004 (1935).

example, presumably ruled out CdCl but not Cd^0 or Cd_2Cl_2 . Similar conclusions have resulted from the nature of the distribution of metal between bismuth-cadmium alloys and the melt,⁹ and to the obser-

- (9) E. Heymann and E. Friedländer, Z. physik. Chem., 148, 177 (1930). See also E. Heymann, R. Martin and M. Mulcahy, J. Phys. Chem., 47, 473 (1943).

vation of a two-electron oxidation-reduction process relating the solute and the solvent.¹⁰ On the other hand, it was reported that

- (10) S. Karpachev and A. Stromberg, Zhur. Fiz. Khim., 13, 397 (1939).

distinctly better agreement with the accepted heat of fusion of CdCl_2 was found if Cd_2Cl_2 instead of Cd^0 was taken as the solute for an analysis of the freezing point depression data.^{11, 12} An unex-

- (11) K. Grjotheim, F. Grönvold and J. Krogh-Moe, J. Am. Chem. Soc., 77, 5824 (1955).

- (12) A heat of fusion for CdCl_2 35% higher than that employed in ref. 11 has recently been obtained calorimetrically (L. E. Topel and L. D. Ranson, unpublished), so that this conclusion no longer appears warranted.

plained break in the decomposition potential of solutions of CdCl_2 (or SnCl_2) in NaAlCl_4 ¹³ may be due to a stepwise reduction.

(13) Y. Delimarskii, L. Berenblyum and I. Sheiko, Zhur. Fiz. Khim., 25, 398 (1951).

An interpretation of metal-metal halide solutions in general and of the effect of foreign salts on the Cd- CdCl_2 system in particular has been given by Cubicciotti¹⁴ in terms of a solution of metal atoms

(14) D. Cubicciotti, J. Am. Chem. Soc., 74, 1198 (1952).

(as ions plus electrons). In this, the larger halide ions were taken to be essentially close-packed and therefore structure determining, with the cations occupying octahedral holes in this loose, anion structure. It was then suggested that the vacant holes would be filled by the cations of the dissolved metal, with their valence electrons being transferred to a band structure in the salt. Cubicciotti noted that such a picture was in qualitative agreement with known metal solubilities, which increase with cation size and with anion-to-cation ratio in the salt. In addition, the solubility of cadmium in CdCl_2 was found to decrease most rapidly on addition of KCl and least rapidly with CeCl_3 , in agreement with their anticipated

effects on the number of cation vacancies. Although 1:2 salts would not be expected to disturb the model structure as markedly, the somewhat greater effect of the more electropositive ions (Ca^{+2} > Mg^{+2} > Mn^{+2}) on the solubility was attributed to an increase in the energy of the electron bands within the salt. No supporting conductivity data are available.

Arguments have also been advanced for a general, but perhaps not universal, interpretation of solutions involving at least the post-transition metals in terms of the formation of dilute solutions of slightly-stable lower halides.¹⁵ This approach is attractive not

(15) J. D. Corbett and R. K. McMullan, ibid., 78, 2906 (1956).

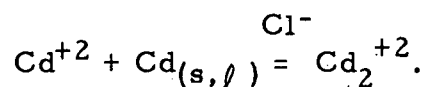
only intuitively but also from the thereby-understandable variations in metal solubility with change in halide or metal ion and from the occurrence of a parallel, and presumably similar, reduction of the same salts in the gas phase.¹⁶ In the present paper, the acid-

(16) J. D. Corbett, S. v. Winbush and F. C. Albers, ibid., 79, 3020 (1957).

base reactions expected on the addition of extraneous salts to the metal-lower halide-normal halide equilibrium are discussed and applied to the isolation of stable cadmium(I) salts.

Results and Discussion

The consequences of the addition of halide salts to the Cd-CdCl₂ system are also understandable in terms of the equilibrium



Introduction of basic salts such as KCl would shift the equilibrium toward Cd⁺² by virtue of the stronger interaction of the chloride ion with the more acidic or polarizing Cd⁺² ion.^{11, 16} According to the data of Cubicciotti,¹⁴ the fraction of Cd⁺² apparently reduced at 740° in the presence of one mole KCl per mole of CdCl₂ is only about 15% of that observed in the binary system. Indeed, it was the similar behavior of the Cd-CdCl₂ and the Hg-Hg₂Cl₂-HgCl₂ systems on the addition of alkali metal chlorides that von Hevesy and Löwenstein¹⁷ considered indicative of the formation of Cd₂Cl₂ in

(17) G. von Hevesy and E. Löwenstein, Z. anorg. allgem. Chem., 187, 266 (1930).

the former melt. The addition of large amounts of such halides has, in fact, been employed to reduce undesirable metal solubility in technological applications of molten salts.¹⁸

(18) P. M. Gruzensky, J. Electrochem. Soc., 103, 171 (1956).

Inasmuch as the chloride ions inherent to the Cd-CdCl_2 melt to some degree stabilize Cd^{+2} in the same manner, addition of a strong chloride acid should increase the amount of reduction. Although the consequences of such an interaction have not been previously recognized, published data¹⁴ do show that the apparent fraction of Cd^{+2} reduced at 740° is increased by 41% by the addition of an equal molar amount of CeCl_3 , presumably as a result of greater interaction or association of the Cl^- with the more polarizing Ce^{+3} . At this point the use of the more appropriate aluminum trihalides is suggested and the results are very striking. With AlX_4^- as the anion ($\text{CdX}_2:\text{AlX}_3 = 1:2$) not only is the amount of reduction greatly increased but a stable cadmium(I) tetrahaloaluminate is also obtained.

In Table I the percentage reductions of Cd^{+2} that result under these conditions in the liquid chloride, bromide and iodide systems at 335° are compared with those calculated from the most complete data on the binary systems at the monotectic temperature ($\text{CdX}_{2(s)}\text{-solution-Cd}_{(l)}$).¹⁹ For this purpose it is again assumed that the

(19) S. Yosim, private communication. A large temperature coefficient is found in the binary systems, the percent reductions being 33, 38 and 29%, respectively, at 900° .

solubility in the binary systems can be entirely attributed to Cd_2^{+2} , although, as already noted, there is no conclusive evidence either for or against this assignment. The increase in the amount of

Table I.

Percent Reduction of Cd^{+2} by $\text{Cd}_{(l)}$ in the Melts CdX_2 and $\text{CdX}_2 \cdot 2\text{AlX}_3$

Halide	Cd-CdX ₂ ¹⁹ Monotectic		Cd-Cd(AlX ₄) ₂ 335°
	T°C	%	%
CdCl ₂	534°	15.5	67.0
CdBr ₂	540°	15.9	57.4
CdI ₂	385°	2.4	31.2

reduction found when the anion is changed from X^- to AlX_4^- is, of course, the net result of the opposing acidities of AlX_3 and Cd^{+2} toward X^- . Although insufficient data are available to consider this quantitatively, the change is particularly noteworthy with the iodides, where cadmium(II)-iodide complexes are known to be relatively stable.¹⁶

In contrast to the black Cd-CdX₂ mixtures that result when the binary melts are solidified, the solids obtained from the present systems are white, white and yellow, respectively, give unique powder patterns, and produce clouds of metal when added to water. In order to further verify the presence of a stable

cadmium(I) tetrahaloaluminate in these products, the phase diagram for the chloride system shown in Fig. 1 has been obtained. The formulation of the mixture $\text{CdCl}_2 \cdot 2\text{AlCl}_3$ as a compound, presumably $\text{Cd}^{++}(\text{AlCl}_4^-)_2$, is supported not only by the diagram but also by powder pattern data. The separation of a new phase on reduction is clearly shown by the presence of a eutectic at about 31% reduction and 185° . At the peritectic temperature of $226 \pm 1^\circ$ this reduced phase is in equilibrium with solid metal and the 65% reduced liquid. The limiting reduction of the melt increases slowly to 68-69% at the melting point of cadmium (319°) and thereafter decreases slightly. The dependence of the reduction limit at 335° on the ratio of AlCl_3 to CdCl_2 in the initial melt is shown in Fig. 2. Although this aspect was not investigated as thoroughly when it became apparent that excess AlCl_3 did not give greater than about 80% Cd_2^{+2} , the presence of solid CdCl_2 below a ratio of about 1.5 and the break in amount of reduction at a ratio of 2.0 support the assumption that AlCl_4^- is the principal anion in the system.²⁰

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- (20) The principal frequencies of the AlCl_4^- ion (H. Gerding and H. Houtgraaf, Rec. trav. chim., 72, 21 (1953)) as well as that of Cd_2^{+2} have also been observed in a study of the Raman spectra of the reduced chloride melt at 260° . J. D. Corbett, unpublished.

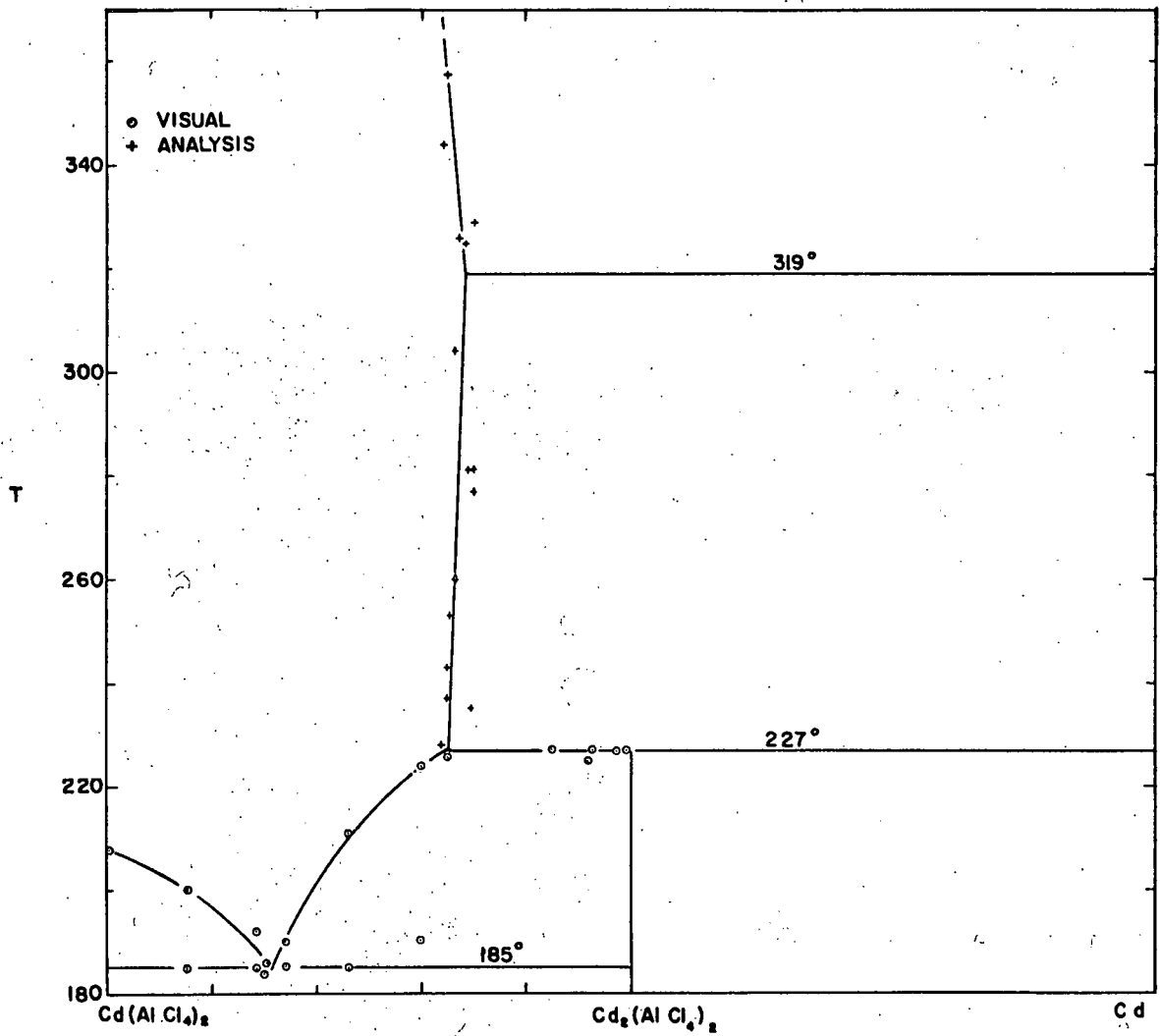


Fig. 1. The system $\text{Cd}(\text{AlCl}_4)_2 - \text{Cd}_2(\text{AlCl}_4)_2 - \text{Cd}$.

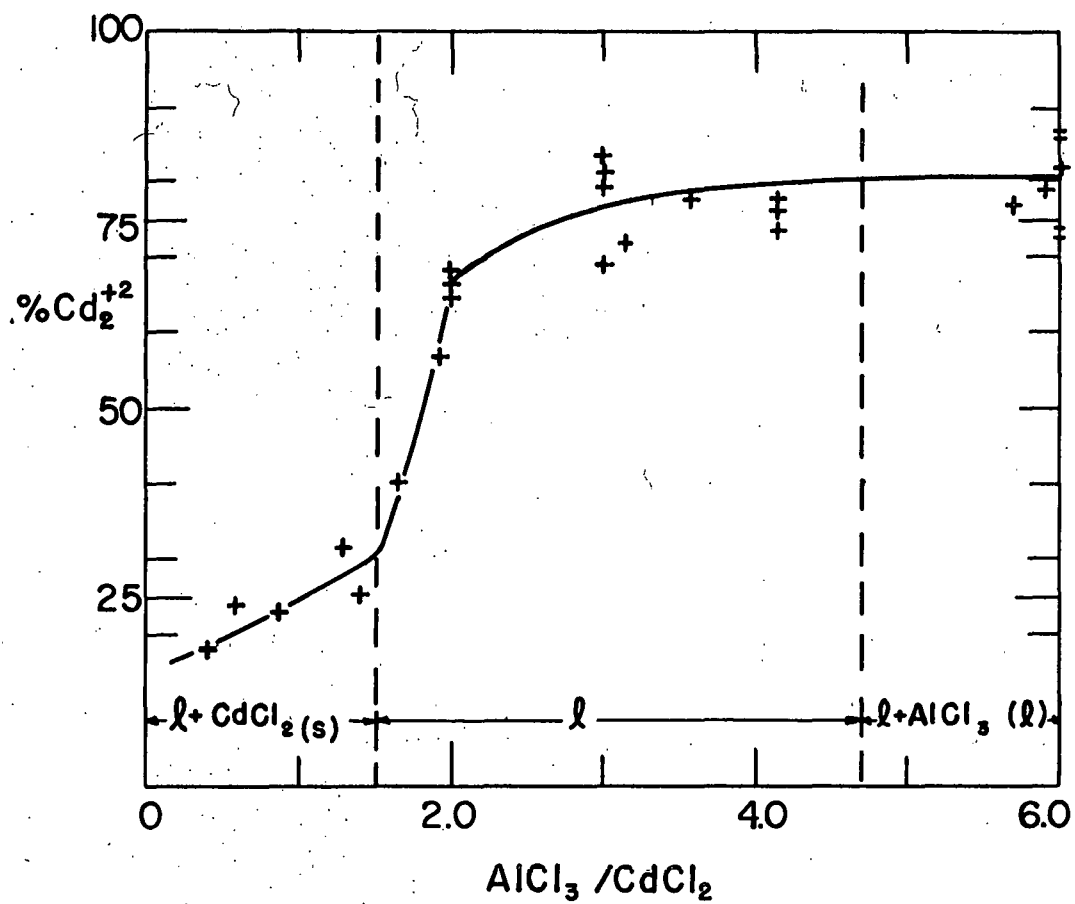


Fig. 2. The percent reduction of Cd^{+2} to Cd_2^{+2} at 335° as a function of the ratio of AlCl_3 to CdCl_2 in the initial salt.

Identification of the new phase that separates from the reduced chloride melts as $\text{Cd}_2(\text{AlCl}_4)_2$ has been confirmed by the isolation and analysis of this diamagnetic salt. Although in principle complete reduction of the liquid phase by excess, solid cadmium metal should result below 226° , in practice the reaction is slow, and an 80 to 90% conversion is the best that has been obtained; such an enriched mixture deposits fibrous cadmium metal as it melts at 227° . No suitable solvent for the separation of the two cadmium tetrachloroaluminates has been found. Though benzene dissolves the mixture to a small extent so that some separation might be expected, ²¹ $\text{Cd}(\text{AlCl}_4)_2$ is actually somewhat more soluble than

(21) R. K. McMullan, private communication.

$\text{Cd}_2(\text{AlCl}_4)_2$ and, in addition, disproportionation of the latter in the residue takes place if the extraction is excessive, probably due to loss of AlCl_3 . However, if the limiting mixture is simply refluxed with benzene for two to three weeks, flat plates and sheets of $\text{Cd}_2(\text{AlCl}_4)_2$ can be hand-picked from the mixture. (Further reduction to about 94% Cd(I) can be accomplished simultaneously by the addition of a large excess of metal.) Although with a normal amount of patience, the yield is small,

their identity is corroborated by disproportionation at 226-227° and by analysis. For the latter, Cd: 39.6₂, 39.5₄%; Al: --, 9.7%; Cl: 49.59, 49.97%; Cl/Cd: 3.96₉, 4.00₇; for Cd₂(AlCl₄)₂: 39.97, 9.59, 50.43%, 4.00; for Cd(AlCl₄)₂: 24.98, 11.99, 63.03%, 8.00, respectively. (The crystals were neither washed with benzene nor subjected to evacuation to remove surface salts or occluded benzene.) There is no evidence for a benzene complex of the salt, such as is found with the analogous mercury compound.²¹

Although the previous discussion of the acid-base interactions in the melt accounts for the increased reduction of CdCl₂ in the presence of AlCl₃, stability in the solid state does not necessarily follow. Reduction beyond the Cd(II)-Cd(I) eutectic is, of course, required, and even though this in theory can be described in terms of well-known physical laws, an alternate discussion in terms of lattice energies and their dependence on the anion is illuminating. The enthalpy of the decomposition $\text{Cd}_2\text{Y}_2 \longrightarrow \text{CdY}_2 + \text{Cd}$ can be completely represented as the sum of the difference between the second and first ionization potentials of the metal atom, the energy of the condensation $\text{Cd}_{(g)} \longrightarrow \text{Cd}_{(s)}$, and the difference in the experimental lattice (or solvation) energies ($U_{\text{Cd}_2\text{Y}_2} - U_{\text{CdY}_2}$), + RT. Of these, only the lattice energy difference is subject to

adjustment in condensed systems and this by a choice of Y^- . As discussed by Van Arkel,²² the effect of an increase in halide size (without a change in structure) in a series of halides of a given element

(22) A. Van Arkel, Research, 2, 307 (1949).

is to decrease the difference in lattice energies of two different states.²³ From a qualitative viewpoint the replacement of a given X^-

(23) This, of course, expresses the well-known result that low oxidation states are frequently the most stable as the iodides, although not with mercury and apparently cadmium.¹⁶

by the larger AlX_4^- can therefore be considered to reduce further the difference in lattice energies of the two states and hence the tendency of the lower to disproportionate. The combined concept of acid stabilization is thus one of lessening the relative stability of the higher oxidation state both in solution and in the solid. Another example of this effect is the formation of $Ga^+(GaCl_4^-)$ in the $Ga-GaCl_3$ system; here the parent "salt" itself functions as the acid.²⁴

(24) R. K. McMullan and J. D. Corbett, J. Am. Chem. Soc., 80, 4761 (1958).

It is now apparent why the cadmium(I) state has not been detected here-to-fore, since decomposition results with all the common, basic solvents such as H_2O , NH_3 , DMF, ethers and molten LiCl-KCl due to strong solvation of the Cd^{+2} ion. In fact, all solvents much more basic than benzene, such as xylene, CH_3CN and THF, have been found to promote disproportionation. No reducing reaction other than that due to the product metal has been observed.

The color of molten $CdCl_2$ containing small amounts of dissolved metal is usually described as dark red, and this appears essentially black with one mole percent added metal. In contrast, the acidic melts described here are very much lighter, particularly for the bromide and chloride. In 1 cm thickness, the melts in equilibrium with metal at 250° are an olive green with $AlBr_4^-$ and a pale green to yellow-green with $AlCl_4^-$, the green hue becoming more intense with increasing temperature or decreasing $AlCl_3$ content. An attractive explanation of this remarkable change can be derived from a seemingly analogous behavior of certain aqueous systems, where an intense interaction absorption is observed with solutions containing two oxidation states of elements such as iron, tin,

antimony or copper.²⁵ A weak association between complex ions of the two states by means of a halide bridge appears to be a well-established prerequisite to a strong, electronic exchange interaction between the two states, and groups such as water are much less effective as the electron "bridge". In the present systems, substitution of the larger and less polarizable AlCl_4^- for Cl^- in a $\text{Cd}_2^{+2}-\text{Cd}^{+2}$ melt drastically reduces (or removes from the visible region) what appears to be a similar absorption. Analogous changes occur when Lewis acids are added to other ionic, metal-metal halide melts that are normally opaque.²⁶ It is interesting to note

(25) N. Davidson et al., ibid., 73, 1946 (1951) and previous papers referred to therein.

(26) J. D. Corbett and N. Swanson, unpublished research.

that melts in which the parent salt is molecular or strongly complexed, such as AlI_3 ,²⁷ SbCl_3 , ZnCl_2 ,¹⁶ and GaCl_4^- ,²⁴ do not

(27) J. D. Corbett and S. v. Winbush, J. Am. Chem. Soc., 77, 3964 (1955).

become visibly colored on partial reduction by the respective metals.

Experimental

Materials— CdCl_2 was prepared by chlorination of the metal (A. D. MacKay, 99.999%) or by treatment of reagent grade CdCl_2 (Bakers Analyzed, anhydrous) with dry HCl (Matheson) in Vycor apparatus. In the latter method, the HCl , dried with a -80° trap, was passed over the salt as the temperature was gradually raised to 600° and then held there for several hours. A small amount of Cl_2 was then added to the HCl to oxidize deleterious organic impurities. On completion of either reaction the CdCl_2 was sublimed twice into further segments of the apparatus under high vacuum and the final portion sealed off.

CdBr_2 was prepared by reaction of the elements in a sealed, V-shaped Vycor apparatus. The bromine (A. D. MacKay, $<0.02\%$ Cl), frozen in one arm of the vessel during the initial evacuation, was kept at 30 mm pressure while the metal was heated to 610° and was then warmed to room temperature after the reaction had started. On completion the arm containing the Br_2 was cooled to -196° , and sealed off, and the salt sublimed once. CdI_2 was similarly prepared from the elements and sublimed once in the sealed apparatus. AlCl_3 (Baker) was sublimed twice in vacuum at 180° , the last fraction being discarded each time, and was

then sealed off evacuated.

Reductions— In order to obtain the clearest melts and the whitest reduced solids considerable care is necessary in the preparation and handling of the salts. The sublimed starting materials were handled in a dry box filled with Ar that had been dried by cooling to -80° and which continuously circulated through a Linde molecular sieve. Weighings were performed within the box to 0.02 g or externally on an analytical balance using lightly-greased weighing bottles that were returned to the box for transfer of the contents. Brown colors in the (chloride) melts and the quenched solids are due to oxide impurities, presumably CdO, while small amounts of black material suspended in the melt or a light grey coloration of the reduced solid are attributed to adventitious traces of carbonaceous impurities or to metals more noble than cadmium (Fe, Cu, Ag) in the starting materials. A slight deposition of Cd is sometimes noted when reduced melts are rapidly solidified, and this is frequently observed on remelting these solids. The metal redissolves in the melt and is probably due to unavoidable decomposition of $\text{Cd}_2(\text{AlCl}_4)_2$ that accumulates locally in the melt in excess of the equilibrium amount. With care, pure white solids and clear green chloride melts can be obtained.

Two procedures have been used for the melt reductions. For small, single samples the most convenient is the reaction of weighed amounts of CdX_2 and Al (A. D. MacKay, 99.99%). For example, with the stoichiometry $4 \text{CdX}_2 + 2 \text{Al} \rightarrow \text{Cd}(\text{AlX}_4)_2 + 3 \text{Cd}$, the additional weight loss of the Cd thus produced gives a direct measure of the per cent reduction in the melt of 1:2 composition. The apparatus containing the weighed components is evacuated, flamed and sealed off and the relatively mild reaction initiated with a hand torch.

In order to conserve CdCl_2 , which is more difficult to purify than AlCl_3 , the study of the phase diagram (Fig. 1) was carried out starting with 10 g samples of $\text{Cd}(\text{AlCl}_4)_2$ that had been previously prepared in large quantities by melting the component salts in the proper proportion. As excessive supercooling obscured the liquidus points of partially reduced samples, the melting points (as well as peritectic decompositions of $\text{Cd}_2(\text{AlCl}_4)_2$) were observed visually in a melting point block. Reduction limits were established by weight loss of the metal phase upon equilibration for 8 to 40 hours (depending on sample and container size and the amount of agitation provided). The jacketed container was positioned in a vertical Marshall furnace that was slanted so as to reduce the gradient along the sample to 1° and which was controlled with a

position-proportioning controller. Samples to be equilibrated below the melting point of Cd were first held at 330° for 2 hrs. in order to speed up the approach to equilibrium with solid Cd. The equilibrium points at lower temperatures (230-260°) could be approached from either direction. The fine metal sponge cleanly separated when a melt containing larger amounts of Cd_2^{+2} was equilibrated for 24 hrs.; this metal was recovered and melted to a pellet with a minimum amount of salt. Solid buttons recovered needed only to be scraped free of salt and washed before weighing. The solubility of Al^{28} and of the salts in Cd is quite negligible. There is some indication that the higher temperatures associated with the CdCl_2 -Al reaction or prolonged equilibration of the melts in the Pyrex containers have a slightly deleterious effect on their purity.

A one-piece Soxhlet extractor was used without thimble for recrystallization of $\text{Cd}_2(\text{AlCl}_4)_2$. Benzene, dried with CaH_2 , was added to the salt therein in the dry box and the apparatus evacuated and sealed off with the benzene cooled to -80°. Magnetic susceptibilities were qualitatively observed as before. ¹⁶

(28) M. Hansen and B. Blumenthal, Metallwirtschaft, 10, 925 (1931).

Analyses— A modified form of the potentiometric EDTA titration described by Fritz et al.²⁹ was used for Cd and Al. Standard 0.05 M

(29) J. S. Fritz, M. J. Richard and S. K. Karraker, Anal. Chem., 30, 1347 (1958).

solutions of these were prepared from the pure metals, and the EDTA standardized against the Cd^{+2} . Unknown Cd^{+2} was titrated at pH 7-8 using acetylacetone to mask the Al^{+3} and pyridine as a buffer. The end point was detected potentiometrically with a pH meter equipped with a Hg electrode, the necessary Hg^{+2} ions being furnished by 1 drop of 0.01 M solution of the Hg^{+2} -EDTA complex. Aluminum was determined from a titration of Cd^{+2} plus Al^{+3} ; excess EDTA was added at pH 2 or lower and the solution allowed to stand for about 4 hrs. before back titration with Hg^{+2} at pH 8. It was also necessary for unknown solutions to stand overnight at pH 2 or less prior to the addition of EDTA in order to avoid low results due to apparent hydrolytic polymerization of the Al^{+3} . Even so, the end point was not sharp and the results were variable by $\pm 0.5\%$.

Chloride was determined gravimetrically.

X-Ray Data—Powder patterns were obtained as previously described.¹⁵

The principal distances, with relative intensities in parentheses, are, for $\text{Cd}(\text{AlCl}_4)_2$: 6.24(2), 5.97(5), 5.74(10), 4.52(3b), 3.54(2), 3.12(2), 2.86(8), 2.28₅(2), 2.21₄(6), 2.15₀(3), 1.883(7), 1.716(5), 1.692(2); for $\text{Cd}_2(\text{AlCl}_4)_2$: 10.5(4), 9.4(4), 8.8(8), 5.5₉(6), 4.47(3), 3.24(10), 2.94(5), 2.81(3), 2.25₅(3), 1.952(3b), 1.883(6).