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SPECTROPHOTOMETRIC STUDY OF THE
REDUCTION OF MELTS CONTAINING Cd(II)
SALTS.**

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SPECTROPHOTOMETRIC STUDY OF THE REDUCTION
OF MELTS CONTAINING Cd(II) SALTS

by

Richard David Barnes

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Iowa State University
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1965

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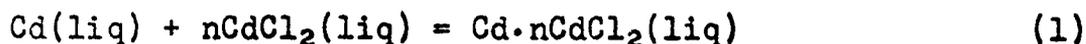
INTRODUCTION

The study of the interaction of metals with their molten salts dates back to the isolation by Morse and Jones (1) of black solids of gross composition Cd_4Cl_7 , Cd_4Br_7 and $Cd_{12}I_{23}$ from reaction of excess metal with the fused dihalide. Studies of electrolysis of some fused salts also revealed apparent violation of Faraday's laws (2,3) which was explained by dissolution of the electrolyzed metal in the melt. Since these original observations of the general phenomenon of the solution of metals in their molten salts, many workers have concerned themselves with identification of the metal species present in the melt.

The Cd-CdCl₂ system seems to have become something of a model system on which the most extensive work has been done. This is perhaps a result of the easily obtainable temperatures involved, the stability of glass as a container, and the high metal solubility. The first suggestion of the mode of dissolution was that the metal was present as a colloid in the salt ("pyrosol"), the most obvious reason being that on cooling, the solid was found to be a mixture of very finely divided metal and the normal salt. This theory was set forth in some detail by Lorenz and Eitel (4). The work of Aten (5, 6), although apparently ignored or discounted by these workers, has survived the test of time remarkably well with only small refinements. He studied the phase diagram of the

Cd-CdCl₂ system and found a marked depression of the melting point of CdCl₂ on addition of cadmium, indicating formation of a true solution. He found no evidence for the formation of a stable reduced compound in the melt or in the solid. This was corroborated for the melt by Eitel and Lange (7) who examined CdCl₂ containing Cd on an ultramicroscope stage and found no particles down to colloidal size in the melt. Hollens and Spencer (8) confirmed that the quenched solids are a physical mixture of CdCl₂ and Cd, the particle size of the latter being determined by the rate of quenching. Little more has been heard about the "pyrosol" theory.

Work then turned to differentiation between three likely mechanisms for the reaction of cadmium with CdCl₂:



Reaction 2 has been pretty well discredited by magnetic susceptibility measurements on both the reduced liquids and solids. A CdCl species would be paramagnetic whereas Cd, Cd₂Cl₂ and CdCl₂ would all be diamagnetic. Hollens and Spencer (8) found the "reduced" solid Cd₄Cl₇ to be diamagnetic, and Farquharson and Heymann (9) examined both the reduced solid and liquid and found them diamagnetic. This, then, reduces the likely possibilities to two: solvated metal

atoms and (solvated) Cd_2^{2+} ions.

Unfortunately unambiguous methods for distinguishing between these two species are few and far between. There is increasing evidence, however, favoring the reduced species Cd_2Cl_2 . von Hevesy and Lowenstein (10) concluded that this reduced species was present from the similarity of behavior of Cd- CdCl_2 and Hg- HgCl_2 melts on addition of alkali metal halides. Added MX decreases the metal solubility of Cd in CdCl_2 and, in a parallel manner, results in decomposition of Hg_2Cl_2 (decreased solubility of Hg in HgCl_2). Grjotheim et al. (11) analyzed the freezing point depression of CdCl_2 by Cd and found the best agreement with the then-accepted heat of fusion of CdCl_2 using Cd_2Cl_2 as the solute model. Subsequently Topol and Ransom (12) obtained a calorimetric heat of fusion some 35 percent higher than that used by Grjotheim, casting some doubt on his conclusions. In an e.m.f. study of the Cd- CdCl_2 system Topol (13) found Nernst $n = 2$, which would apply equally well to solvated cadmium atoms and to Cd_2Cl_2 , but not to CdCl. Okada et al. (14) found the same result from similar e.m.f. studies but noted in a parallel polarographic study that the polarograms obtained could be better explained in terms of Cd_2Cl_2 than solvated cadmium atoms.

Attention has turned recently to a detailed consideration of the effect of added salts on the properties and

constitution of these reduced systems. Already mentioned was the decrease in cadmium solubility in CdCl_2 on addition of alkali metal chloride found by von Hevesy and Lowenstein. Cubicciotti (15) made a systematic study of the solubility of cadmium in CdCl_2 mixed with a number of other salts. For the series KCl , CaCl_2 , CeCl_3 the cadmium solubility decreased fastest with KCl and slowest with CeCl_3 . For the series CaCl_2 , MgCl_2 , MnCl_2 the solubility was least with CaCl_2 and increased through the series. Cubicciotti has explained these effects with a model involving close-packed chloride ions with metal ions situated in the octahedral holes. He postulated that the dissolved metal entered this "lattice" with metal ions going into the holes and electrons into a conduction band. Thus 1:1 salts added to the melt greatly reduced the number of vacancies for the dissolving metal, lowering the solubility more than a 1:3 salt which leaves more cation vacancies. For added divalent salts the most electropositive metal decreased the solubility most because it raised the energy of the conduction band. There have been no conductivity studies on these salt systems to check this, but the conductivity of Cd-CdCl_2 melts is found to decrease slightly on addition of cadmium (5, 6). Grjotheim et al. (11) have noted that actually the amount of cadmium dissolved in CdCl_2 mixed with other divalent metal chlorides is nearly proportional to the amount of CdCl_2 in the melt, the added salts

serving mostly to dilute the CdCl_2 . In fact, CeCl_3 actually enhances the solubility of Cd with respect to the amount of CdCl_2 present, while KCl does indeed repress it.

Corbett, Burkhard and Druding (16) have advanced an interpretation of these phenomena in terms of acid-base theory and its effect on the equilibrium



They suggest that Cd^{2+} , a rather polarizing cation, is stabilized by Cl^- , a rather polarizable anion, relative to the much less polarizing Cd_2^{2+} . Addition of the chloride of a less polarizing cation than Cd^{2+} (the chloride base KCl, for instance) shifts the equilibrium to the left (in favor of $\text{Cd} + \text{Cd}^{2+}$). On the other hand addition of a chloride acid (CeCl_3) will in effect remove Cl^- from the Cd^{2+} and shift the equilibrium to the right, a situation which indeed obtains. Similarly, the use of a LiCl-KCl eutectic bath for the electrolysis of BiCl_3 has been shown to be feasible because of the repression of bismuth solubility (17). Corbett *et al.* (16) used AlCl_3 as a chloride acid and found not only that the solubility of cadmium in the melt increased greatly, but also that a stable, reduced solid was formed. The AlCl_3 here removed chloride ion and substituted the poorly polarizable AlCl_4^- as the anion in the system. This two-fold effect in the liquid plus the salutary effect of the larger

anion on the stability of the reduced solid (18) combined to permit isolation of the solid.

This white reduced solid was formulated as $\text{Cd}_2(\text{AlCl}_4)_2$ on the basis of chemical analysis, its diamagnetism, its discrete X-ray powder pattern (16) and spectrum (19). For the 65 percent reduced liquid at 250° and for the solid at 70° the Raman spectrum showed a line at 183 cm.^{-1} which was ascribed to the Cd_2^{2+} ion. In addition the principal lines of AlCl_4^- were seen, confirming that this is the anion in the system. It might be noted that such acid stabilization of lower oxidation states is not without precedent. Examples of such solid reduced compounds are GaAlCl_4 , "BiAlCl₄" (20) which may be $\text{Bi}_3(\text{AlCl}_4)_3$ (21) and $\text{Ga}^+(\text{GaCl}_4^-)$ (22).

From an e.m.f. study of the $\text{Cd}-\text{Cd}(\text{AlCl}_4)_2$ system in $\text{NaAlCl}_4 + \text{AlCl}_3$ Munday (23) concluded that Cd_2^{2+} ions rather than solvated metal atoms must be present. Okada *et al.* (14) observed no change in e.m.f. when either KCl or AlCl_3 was added to $\text{Cd}-\text{CdCl}_2$ melts at 600° and concluded there was no change in cadmium species with addition of these salts.

These reduced solutions have rather interesting chromatic properties. The simple metal-metal halide melts are almost all extremely highly colored. In the case of CdCl_2 the reduced melt is deep red even at low reductions and in small thicknesses. Upon addition of AlCl_3 the reduced melt becomes a pale yellow-green. It was this striking color change which suggested the present study of these systems.

This color change could arise from several causes. There could be completely different solute bands in the two extreme systems resulting either from different metal species or the changed anion environment. There could also be merely a shift of the same band caused by the change in anion. In an attempt to resolve this, the visible and UV absorption spectra of Cd-CdCl₂ and Cd-Cd(AlCl₄)₂ melts as well as those of intermediate anion composition have been obtained.

Beer's law is often used to distinguish whether there is more than one solute species present in a solution. Deviations become very large when there is more than one species derived from a common source. It will be used here in its customary form,

$$A = \epsilon bM \quad (5)$$

where A is absorbance ($= \log_{10} I_0/I$), M is the concentration of the chromophore expressed in moles per liter, b is the path length in centimeters, and ϵ is the molar absorptivity (or molar extinction coefficient). Thus a plot of A versus M should yield a straight line of slope ϵb if Beer's law is obeyed. Modest deviations from this straight line would be indicative of physical or chemical interaction of the solute with other solutes or the solvent.

There have been two reports of spectra of molten Cd-CdCl₂. Using a Perkin-Elmer Model 13 spectrophotometer and 8 mm. Pyrex tubing for a cell, Greenberg (24) obtained

the spectrum of a 5 mole percent solution of Cd in CdCl_2 . At 575° he found a strong band at 4550\AA and a smaller shoulder at about 4000\AA . At higher temperature (593°) the main band broadened, then split again (618°) with maxima at 4500 and 5500\AA . In contrast, Bookless and Egan (25) observed a single band at about 3400\AA in a $50\ \mu$ layer of saturated (15 mole percent) reduced melt at 575° . There has been no previous spectral work on the tetrachloroaluminate melts.

An interesting and perhaps related phenomenon in aqueous solution is the intense non-additive "interaction absorption" which occurs in solutions containing two oxidation states of certain metals in the presence of chloride. This has been found for Sb(III) and Sb(V) (26, 27), Cu(I) and Cu(II) (28), Fe(II) and Fe(III) (29), and Sn(II) and Sn(IV) (30). The absorption of all these solutions is markedly greater than would be predicted from application of Beer's law to the individual absorptions. The authors ascribe this increased absorption to a binuclear chloro complex containing one atom of each of the two oxidation states of the metal. Supporting this is the observation that the absorbance is proportional to the product of the concentrations of the two species and increases with the chloride concentration. The interaction absorption appears only in chloride solutions and is virtually nil for iron in aqueous perchlorate. They propose

that the two metal atoms in the dimer are bridged by chloride(s) and that the absorption arises from an electron exchange between the metal atoms through the chloride(s). The absence of this phenomenon with water ligands (presumably perchlorate does not coordinate) has a parallel in chromium systems in which bridged species are known. There a chloride bridge is more effective than water in promoting electron exchange in redox reactions. Corbett et al. (16) and Nachtrieb (31) have remarked on the possibility of similar effects in these aqueous systems and in the molten metal-metal halide systems.

EXPERIMENTAL

Materials

Aluminum trichloride

Commercially available anhydrous AlCl_3 reportedly contains between 0.0004 and 0.005 percent Fe, present as yellow FeCl_3 . Vacuum sublimation at 120° failed to remove the yellow color which would obviously interfere with the spectral studies. Following a suggestion by Morrey (32), sublimation under 20 mm. of dry helium at 160° effected a very clean separation. The helium was admitted through a trap cooled with liquid nitrogen which also served to trap any HCl produced. Batches of about 60 g. of AlCl_3 were sublimed in a two chamber Pyrex tube. The sublimate formed a solid plug just outside the furnace and extended back into the furnace. The sublimate was sealed off from the residue and the vacuum line, and the salt stored in this evacuated condition until ready for use. At that time the glass could be easily broken away from the plug of salt. After sublimation, the salt was handled only in an argon-filled dry box or in an argon-flushed polyethylene glove bag.

Some AlCl_3 was prepared by reaction of dry HCl (prepared by dropping concentrated H_2SO_4 on KCl and dried by bubbling through concentrated H_2SO_4) on Al shot at 340° with a small amount of helium mixed as a carrier. The re-

sulting salt was then sublimed in vacuo and under helium as described above.

Cadmium (II) chloride

Cadmium chloride (Baker Analyzed) was treated with Cl_2 (Matheson) at 500° and sublimed in vacuo at that temperature through a coarse frit, the sublimate forming as a solid crystalline mass. It was stored in evacuated ampoules and handled only in an inert atmosphere.

Cadmium (II) tetrachloroaluminate

The salt was prepared simply by fusing together AlCl_3 and CdCl_2 in molar ratio 2:1 in vacuo. As the melt usually was rather dark colored, it was digested (32) at $425-450^\circ$ for 2-4 days. A voluminous (but rather light-weight) black mass (carbon?) coagulated to leave a clear melt. This was gravity filtered through a medium frit which separated the two chambers of the digestion tube. After cooling there remained a clear colorless liquid in amount ranging up to 1 ml. in a 50 g. preparation. This liquid was not identified but was theorized as being a light chlorocarbon. It was incompletely removed from contact with the salt by cooling the end of the tube containing the residue in liquid nitrogen while sealing off the end containing the salt.

Because of evidence (see under Impurities, below) of an oxidizing impurity in the melts, the salt and a small piece

of cadmium were put in a tube similar to the digestion tube but having a small coarse frit just before the stopcock leading to the vacuum line. After evacuation argon was admitted to a pressure of 30 cm. through a trap cooled by Dry Ice and the tube heated to 350° for several hours until the metal dissolved in the melt to form a dilute reduced solution. A sufficient length of tubing extended beyond the furnace so that AlCl_3 condensed before reaching the small frit. A small amount of chlorine gas was then admitted to oxidize all the cadmium. All gases were trapped or pumped out and the salt frozen and sealed off below the small frit. The salt was then redigested for about a day, filtered, and stored in small ampoules containing about 4 g. each.

Non-stoichiometric salts

For salts with molar ratios $\text{AlCl}_3/\text{CdCl}_2 < 2$, the appropriate quantities of the two salts were reacted together as before. Down to a ratio of 1.5 the same procedure was used as for the stoichiometric salt. For the salt with ratio 1:1 the metal was added to the salts when they were mixed. Following digestion the salt was transferred to a tube to which a small amount of Cl_2 was subsequently admitted to oxidize all the cadmium. The salt was then remelted in the chlorine atmosphere and excess chlorine trapped out in a finger and sealed off. The salt was then stored in 4-5 g. lots in evacuated ampoules.

Reduced melts

Weighed pieces of cadmium (up to about 3 mg.) were added to known weights (4-5 g.) of the unreduced salt in the optical cell to produce the desired reduction. The cadmium was weighed to ± 0.01 mg.

Cadmium

Cadmium used in preparing reduced melts was obtained from A. D. Mackay, Inc. with a purity of 99.999 percent. It was sublimed once under vacuum after it became badly oxidized during the course of another investigation. Just prior to use it was cleaned and brought to the desired weight by treatment with 4N HNO_3 .

Apparatus

Cells and spacers

The optical cells were precision cells of US22-240 silica obtained from Pyrocell Mfg., Inc. with a silica-to-Pyrex graded seal fused to the top of the cell. The short ($<100 \mu$) path lengths were obtained by the use of precision silica inserts (also from Pyrocell). The inside dimensions of the cells were measured with an indicating hole gage, the outside dimensions of the inserts by an indicating micrometer and a travelling microscope.

Spectrophotometer and furnace block

A Cary Model 12 (Serial 15) recording spectrophotometer was used throughout this study. The only modifications came in the sample compartment. The standard sample compartment was replaced by a water-cooled one with an overall increase of $\frac{3}{8}$ inch in the direction of the light path. This was adjudged to be unimportant as far as focusing the light beam on the photocells was concerned.

The standard cell holder was replaced in the sample compartment by a furnace block-cell holder pictured in Figure 1. Made of type 304 stainless steel, it had provisions for holding two cells at a time. Two horizontal rectangular holes permitted passage of the light beam. Heating was provided by six 120 volt, 250 watt Chromlox C-208 cartridge heaters. The four corner heaters were connected in parallel to a Variac; the two center heaters, also wired in parallel, were connected to a Celectray controller. Two thermocouples located between the cell compartments and extending about to the middle of the light path measured the temperature. One was used for the controller, the other for independent temperature monitoring with a Leeds and Northrup potentiometer. Temperature fluctuation was about $\pm 2^{\circ}$ in the furnace block and an estimated $\pm 0.5^{\circ}$ in the sample.

As originally constructed there was a large vertical thermal gradient in the furnace block. This gradient was reduced to $5-10^{\circ}$ by means of an auxiliary heater consisting of

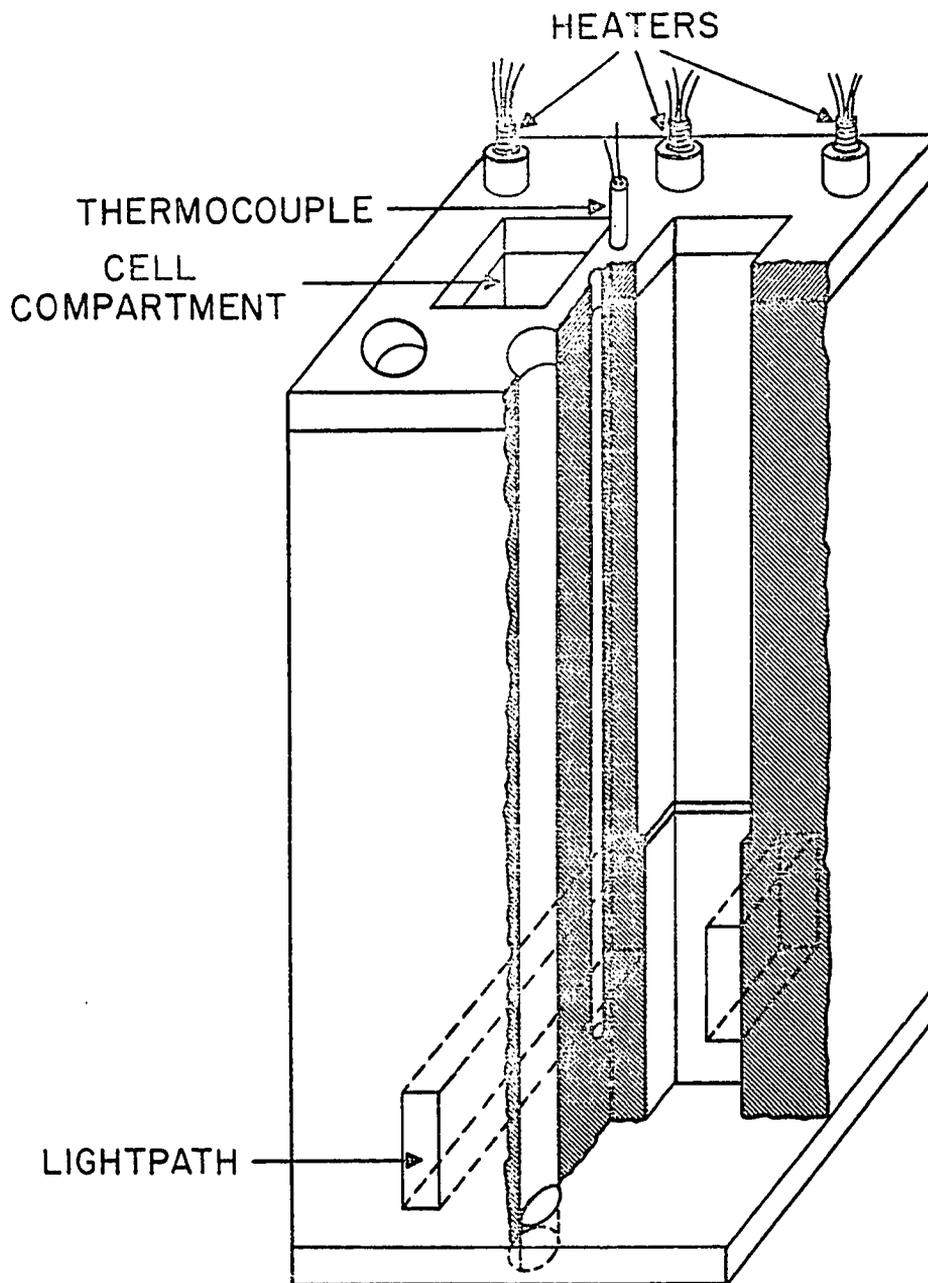


Figure 1. Furnace block-cell holder

a 2-1/2 inch length of Chromel A wire in serpentine shape inserted below the furnace block (see Figure 2). This auxiliary heater and lead-in wires were insulated from the block by asbestos sheet. Once outside the furnace block the Chromel lead-in was soldered to platinum wire leading to the external power connections and thence to a Variac.

The block and auxiliary heater together were surrounded on four sides and the bottom by asbestos sheet and 3 mil. platinum foil, both of which had holes cut for the light paths. The foil served to reduce power consumption of the cartridge heaters by almost a factor of two and also helped reduce the temperature gradient slightly. Outside the platinum was 1/4 inch thick zirconia insulation. Atop the block was a piece of 3/8 inch thick Lavite with holes to admit the cells, thermocouples, and heaters. Stainless steel caps cut down convective heat loss from the top of the cell compartments. This entire assembly was housed in a close-fitting, water-cooled, copper jacket which was mounted on a sliding brass plate. The jacket had holes for the light path and externally mounted quartz windows. Electrical and water connections were provided through a light-tight, aluminum, sample compartment extension topped by the sample compartment lid. Pre-set stops permitted accurate aligning of the furnace block in the light path.

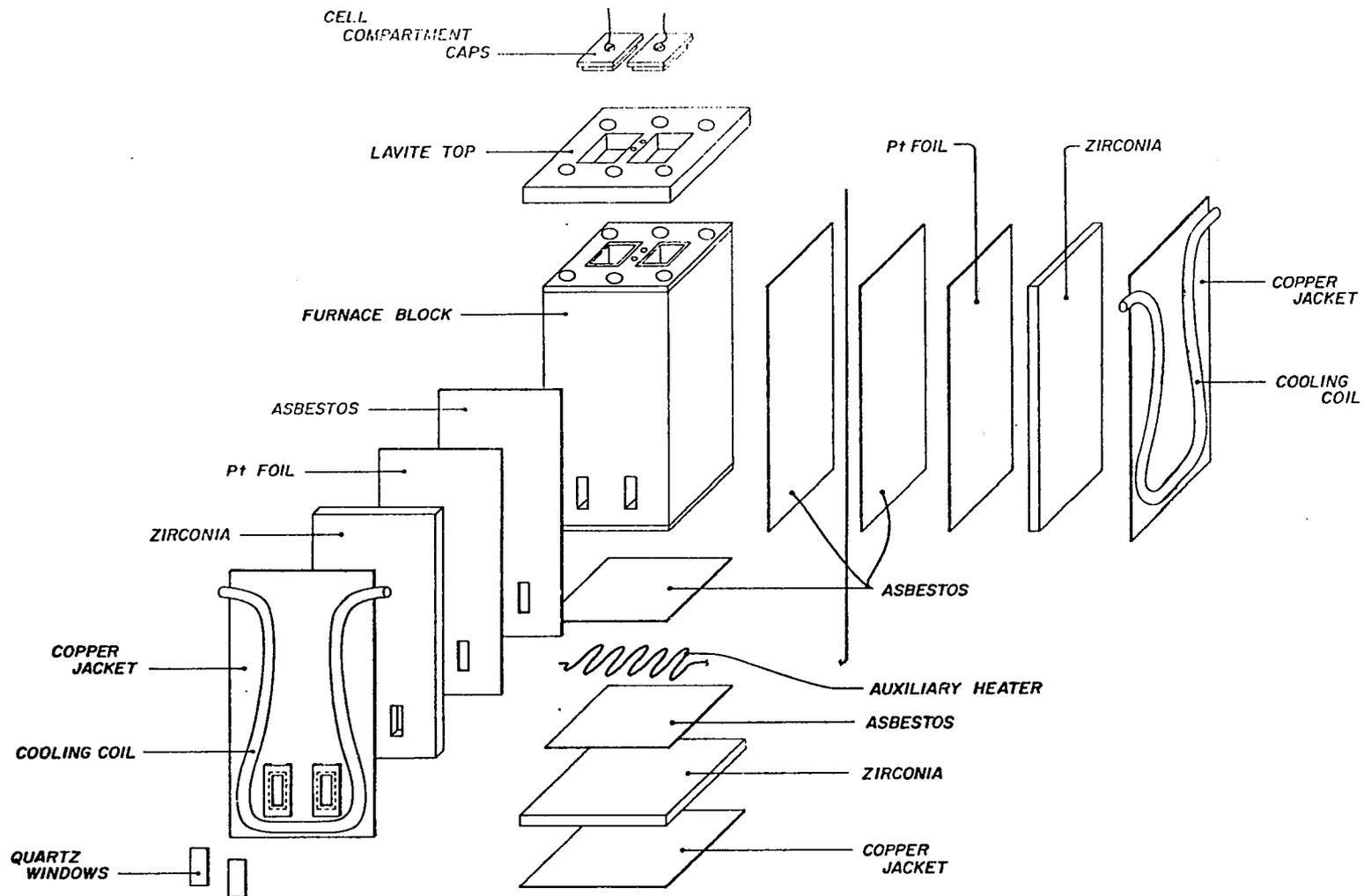


Figure 2. Assembly of furnace block and associated components

Procedure

Density measurements

For each batch of salt a small sample was used for density determination and analysis. To determine the density, the salt was melted in the ampoule and the level of the melt marked. The tube was weighed and cracked open. The pieces were quickly put in another tube and roughly evacuated. Water was admitted to dissolve the sample, the solution then being transferred to a volumetric flask for analysis. The pieces of glass from the ampoule were recovered and weighed, the difference between this and the earlier weight being the weight of salt (after buoyancy correction). The end of the tube that had held the molten salt was filled to the mark with water, the volume determined, and the density thereby calculated.

Analytical

The analytical procedure used for the determination of cadmium and aluminum is based on that of Fritz et al. (33). Cadmium was determined in the presence of aluminum by masking the latter with fluoride and then titrating with EDTA at pH 6.5 with Naphthyl Azoxine S (NAS) as indicator. Aluminum was obtained by difference from total metal (Cd + Al) determination. For this, an aliquot was allowed to stand at pH 1.5 for several hours, then excess EDTA added and the solution let stand several more hours. The solution was then

back titrated at pH 6.4 with a standard $\text{Cu}(\text{NO}_3)_2$ solution using NAS indicator. Chloride was determined gravimetrically as AgCl by standard procedures.

Spectra

The cell and insert to be used in a given run were carefully rinsed with distilled water and flamed out. The insert was put in the cell and a 19/38 standard taper joint attached to the cell. The cell was then cleaned with aqua regia, dried, and baked out under vacuum for at least six hours at 450° . The spectrum of the empty, evacuated cell and insert was run at 300 or 450° from $2200\text{-}4000\text{\AA}$ using the hydrogen source and $3400\text{-}10,000\text{\AA}$ using the tungsten source. The cell was then loaded with unreduced salt from one of the small ampoules, evacuated, and sealed off above the graded seal. The cell was heated about 50° above the melting point of the salt and transferred quickly to the furnace block. Spectra were usually run at several temperatures. At each temperature the sample was allowed to equilibrate in the furnace block for one hour before the spectrum was run. Upon completion of a run the cell was removed, and the salt and insert tipped to the seal-off end to prevent cracking the cell during cooling. After the cell had cooled, it was cracked open at the seal-off, washed out and prepared for another run. For reduced runs a small weighed piece of

cadmium metal was put in the cell at the same time as the salt. A complete series of runs consisted of one unreduced run and several reduced runs with various concentrations of added metal. All spectra were run vs. air.

RESULTS AND DISCUSSION

Impurities

Attempted preparation of salts of adequate spectroscopic purity represented a major part of this research. Mention has been made in the Experimental section of the need to digest the salts to remove a black impurity. The melts were dark, seemingly no matter how elaborate the precautions taken in purifying the component salts. The duration of the digestion varied a good deal with temperature, taking only one to two days at $> 450^{\circ}$ but four days or more at $< 425^{\circ}$. These high temperatures were approached with some trepidation at first, bearing in mind the very high vapor pressure of AlCl_3 . However, if the AlCl_3 was allowed to react with the CdCl_2 at about 225° the procedure was entirely safe. The composition of the black coagulum is as yet unknown, but is probably carbon¹. Upon cooling the melt a small amount of a clear colorless liquid remained, partly trapped in and partly free of the salt. Some of this liquid was isolated after partial fractionation from HCl . Rough measurements showed a melting point of about -67° and a vapor pressure of 190 mm. at 20° . An IR spectrum was run on a

¹Munday, T. F. Ames, Iowa. Probable composition of black digestion product. Private communication, 1964.

small sample, but because of its volatility the sample evaporated before the run was complete, rendering the spectrum inconclusive. The melting point and vapor pressure data are suggestive of CHCl_3 , but this is by no means definite.

Occasionally a reduced melt would be prepared that would give only the spectrum of the unreduced salt. Evidently there had been an oxidizing impurity present, not necessarily in large quantity, for only 0.5 - 2 mg. of cadmium had been added to those salts. In those samples giving spectra typical of the reduced samples, the actual amount of reduction may then have been lower than calculated because of only partial oxidation by the impurity.

In order to try to eliminate this uncertainty a small bit of "sacrificial" cadmium was added to the bulk salt to form a dilute reduced solution, thereby (hopefully) voiding the salt of the impurity. Chlorine was then added to oxidize the cadmium to the +2 state and the excess chlorine removed. Even this, however, proved not completely satisfactory as will be noted later in the discussion of reduced melts. Very late in this investigation a clear 1:1 melt was prepared using AlCl_3 prepared as described and CdCl_2 which was first vacuum sublimed through a frit, then melted and filtered through another frit. There was no black impurity requiring digestion and no colorless liquid remaining after cooling. This suggests these two impurities are related, as had been supposed.

Treatment of Data

The data were obtained as graphs of absorbance versus wavelength on a chart with an absorbance range of 0 - 3.4. The high end of the scale thus corresponds to a transmission of < 0.1 percent. At these high absorbances, of course, the signal to noise ratio becomes very small, so absorbances were generally kept < 2.7.

The absorbance of a given empty cell and insert combination was measured and subtracted from the absorbance of subsequent unreduced and reduced melts. The absorbance of an unreduced melt of given composition was subtracted from the absorbances of reduced melts using that salt. This subtraction was accomplished manually by tabulating absorbance at eight equidistant points per 100\AA . The spectra resulting from reduction (reduced minus unreduced) were plotted as absorbance versus wavelength, from which such characteristics of the band as position and absorbance at the maximum and the half width were measured. As the solute band was always poorly resolved on the low wavelength side, the half width was determined by doubling the width from λ_{max} to the high wavelength side.

Since the zero of absorbance could not be assigned a fixed position on the spectrophotometer chart, it was determined for each spectrum individually. In particular, the spectra of the melts reached lower absorbances on the chart

than did the empty cells, probably resulting from different reflectances of the vacuum-silica and melt-silica interfaces. Since the index of refraction of the unreduced and reduced melts probably does not vary appreciably, the above subtraction of spectra would still be valid. Such cell corrections were commonly < 0.10 absorbance units. To determine the zero for melts (whose absorbances were frequently finite at 4000\AA , the upper limit of the UV range on the instrument) the further drop above 4000\AA was added to the UV tail. Only for CdCl_2 melts did this "splicing" involve more than about 0.05 absorbance units. There was no further absorbance out to $10,000\text{\AA}$ in any of the melts studied, supporting the method of determining the zero.

Spectra of Unreduced Melts

The spectra of the unreduced salts can be considered to separate the region studied into two rather distinct parts - one of complete absorption and one of essentially zero absorption. The dividing line is very steep, the percent transmission falling as much as two powers of ten in 100\AA . This is clearly just the foot of a very intense band customarily assigned to a charge transfer process.

In molten salts, as in aqueous solution, a charge transfer band always appears, most usually in the UV or far UV. Occasionally it is near enough to the visible region that

the absorption of the tail of this band gives rise to a colored solution or melt. With absorptivities in the tens or hundreds of thousands, these must be allowed transitions.

In the systems under study here, the edge of the band appears in the UV, but shifts toward the red (lower energy) with increasing temperature and toward the blue (higher energy) with increasing AlCl_3 content. Pure molten CdCl_2 is yellow, reflecting the proximity of the edge to the visible, whereas $\text{Cd}(\text{AlCl}_4)_2$ is colorless. The wavelength at which the absorbance equals 1.0 for the unreduced melts studied here is given in Table 1, corrected to a common path length of 0.01 cm. Several of the spectra are shown in Figure 3.

Table 1. Properties of cadmium (II) melts

Run no.	Al/Cd ^a	Temp.	λ for $A = 1.0^b$
63	1.99	300°C.	2570Å
		400°C.	2690Å
37	1.54	300°C.	2585Å
		400°C.	2693Å
60	0.92	550°C.	3071Å
55	0.00 ^c	600°C.	3470Å

^aMolar ratio $\text{AlCl}_3/\text{CdCl}_2$.

^bCorrected to path length of 0.01 cm.

^cPure CdCl_2 .

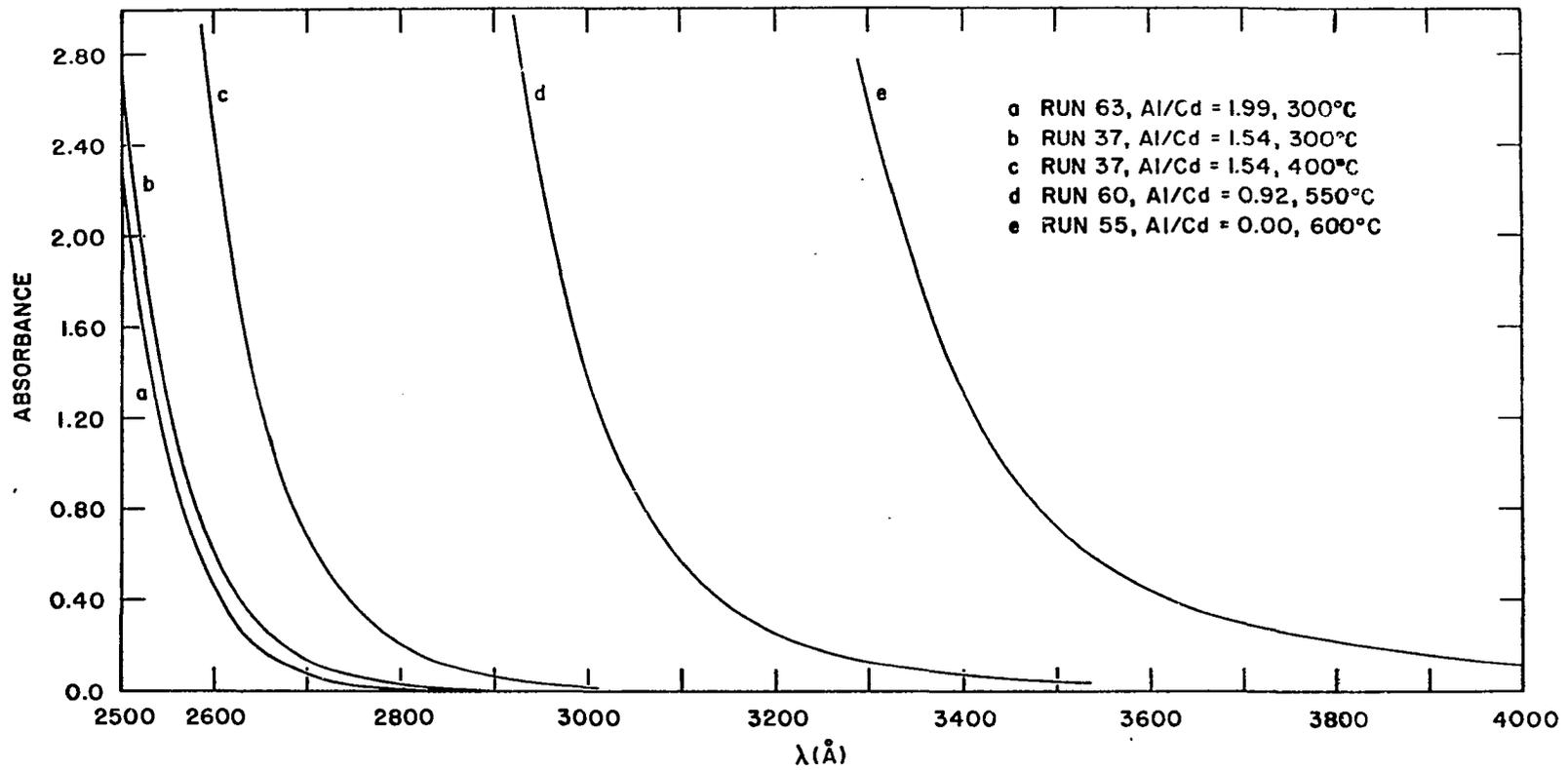
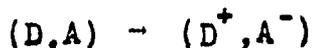


Figure 3. Spectra of cadmium (II) melts

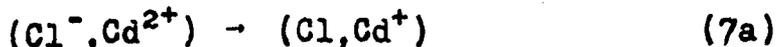
The process causing this intense absorption is assigned as a charge transfer process involving electron transfer from the anion to the cation. After Murrell (34), this can be represented as



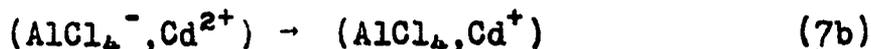
where D and A are the electron donor and acceptor respectively. As an approximation, the energy difference between these two states can be given by

$$\Delta E = I_D + E_A + C \quad (6)$$

where I_D is the ionization energy of the donor, E_A the electron affinity of the acceptor and C the mutual electrostatic energy of D^+ and A^- relative to D and A. In these systems such a transfer might be



and



with energy

$$\Delta E = I_{X^-} - I_{2Cd} + C \quad (8)$$

Here the electron affinity of Cd^{2+} is the negative of its second ionization potential, I_2 . Equations 7 picture the reactions as they would occur in the gas phase. Transfer of the reactions to the melt complicates evaluation of the energy terms, in particular the coulombic term. There one would have to pick a structural model for each system, a

procedure which would be somewhat arbitrary and rather unrealistic. Looking at the situation qualitatively, however, reveals the essential trend in energetics. Recognizing the non-spontaneity of the reaction, ΔE will be positive in each case. The electron affinity of Cd^{2+} , being common to both reactions, can be ignored for these qualitative comparisons. Ionization of AlCl_4^- is expected to be more difficult than for Cl^- . In part, the polarity of the Al-Cl bond will render the chlorines less negative than in chloride, raising the ionization energy. The ionization energy of Cl^- is 3.8 ev.; it is not known for AlCl_4^- , but for the electronically similar CCl_4 it is 11.5 ev. (35). Correction for the electrostatic contribution reduces the value for CCl_4 to about 5.8 ev. Thus the change in ionization potential acts to shift the charge transfer to lower energy for Cl^- , Cd^{2+} .

The determining factor will be the change in the coulombic term with the change in anion. An increase in anion size usually causes a red shift because of expansion of the "lattice" with resultant loss of coulomb energy. Thus on going from CdCl_2 to CdI_2 the color darkens and molten CdI_2 is black. (The lower ionization energy of I^- helps here, too.) Similarly solid $\text{Cd}(\text{AlI}_4)_2$ is yellow whereas $\text{Cd}(\text{AlCl}_4)_2$ is colorless. There is an additional effect at work here - covalency. It would be expected that there

would be greater covalent character with Cl^- than AlCl_4^- melts. Raman spectra show that in molten NaAlCl_4 the anion is tetrahedral (36). The same Raman lines were found by Corbett (19) in a molten $\text{Cd}_2(\text{AlCl}_4)_2$ - $\text{Cd}(\text{AlCl}_4)_2$ mixture, suggesting that there is no distortion from tetrahedral symmetry of the AlCl_4^- . There has also been speculation about possible complex ion formation in molten CdCl_2 (37). Covalency will decrease the coulombic energy loss in Cl^- melts relative to AlCl_4^- and will increase the loss with increasing $\text{AlCl}_3/\text{CdCl}_2$. The overall effect is to increase the charge transfer energy in $\text{Cd}(\text{AlCl}_4)_2$ relative to CdCl_2 and decrease this energy for CdCl_2 at intervening compositions.

Assignment of the band to a d-p transition in the Cd^{2+} ion seems less likely because the 5p orbitals lie some 16.5 ev. above the 4d's in the gaseous ion. Although considerable stabilization of the 5p's can be expected on putting the ion in an anion environment, the required stabilization seems too high when compared to what such a change of environment does Cu^+ and Ag^+ .¹ The temperature effect on these bands is entirely normal and is caused by the increased thermal energies of the atoms.

¹McClure, D. S. Electronic spectra of molecules and ions in crystals. In Seitz, F. and Turnbull, D., eds. Solid state physics. Vol. 9. pp. 521-523. New York, N. Y. Academic Press. 1959.

Spectra of Reduced Melts

After correction of the spectra for solvent absorption the reduced melts show a strong absorption band, generally at slightly lower energy than the solvent absorption edge. This band is characteristic of only those melts to which cadmium metal was added, leaving no doubt that the band is related to the reduction. There was no other absorption out to $10,000\text{\AA}$. This band, like the solvent band, exhibits a blue shift with increasing AlCl_3 content and a red shift with increasing temperature. The position of the band (along with certain other of its properties to be discussed shortly) is given in Table 2; representative spectra are shown in Figure 4. This band is seen to be less sensitive to anion and to temperature than the edge of the unreduced (solvent) melts. Consequently, in Cd-CdCl_2 melts the anticipated solute band lies buried beneath the solvent absorption. This will be dealt with subsequently in more detail. The molar absorptivity of the band (ϵ) decreases with decreasing AlCl_3 content and with increasing temperature. This latter effect is accompanied by a broadening of the band as measured by the half width δ (the width of the band where $\epsilon = 1/2\epsilon_{\text{max}}$). The quantity $\delta\epsilon_{\text{max}}/2$ (Table 2) is proportional to the integrated cross section of the transition assuming a Gaussian form for the absorbance curve, and is seen to remain fairly constant as a function of temperature for a given run.

Table 2. Properties of absorption bands caused by reduction

Run no.	Al/Cd ^a	M (moles/l) ^b	b (cm.)	Temp.	λ_{\max}	A max	$\delta/2(\times 10^{-3} \text{ cm.}^{-1})$	$\epsilon_{\max}/2(\times 10^{-7})$
65	1.99	0.00639	0.0088	300°C.	2909Å	1.81	2.77	8.92
				400°C.	2937Å	1.50	3.18	8.49
66		0.00399		300°C.	2914Å	1.06	2.83	8.55
				400°C.	2930Å	0.97	3.19	8.77
68		0.00826		300°C.	2912Å	2.77	2.79	10.70
				400°C.	2936Å	2.41	3.05	10.10
38	1.54	0.00447	0.0075	300°C.	2915Å	0.68	2.87	5.77
				400°C.	2930Å	0.59	3.27	5.76
39		0.00868		300°C.	2920Å	1.98	2.80	8.48
				400°C.	2945Å	1.80	3.09	8.56
40		0.01178		300°C.	2918Å	2.55	2.86	8.27
				400°C.	2942Å	2.31	3.14	8.20
59	0.92	0.00668	0.0073	550°C.	3125Å	0.65	3.22	4.31
62		0.00943		550°C.	3125Å	0.82	3.06	3.64
64		0.01600		550°C.	3106Å	1.71	3.17	4.63
58	0.00	0.01080	0.0088	600°C.		1.10 ^c		

^aMolar ratio AlCl₃/CdCl₂.

^bMoles per liter of added Cd.

^cMaximum A before band is swamped by solvent-corresponds to a minimum value of $\epsilon = 11,600$.

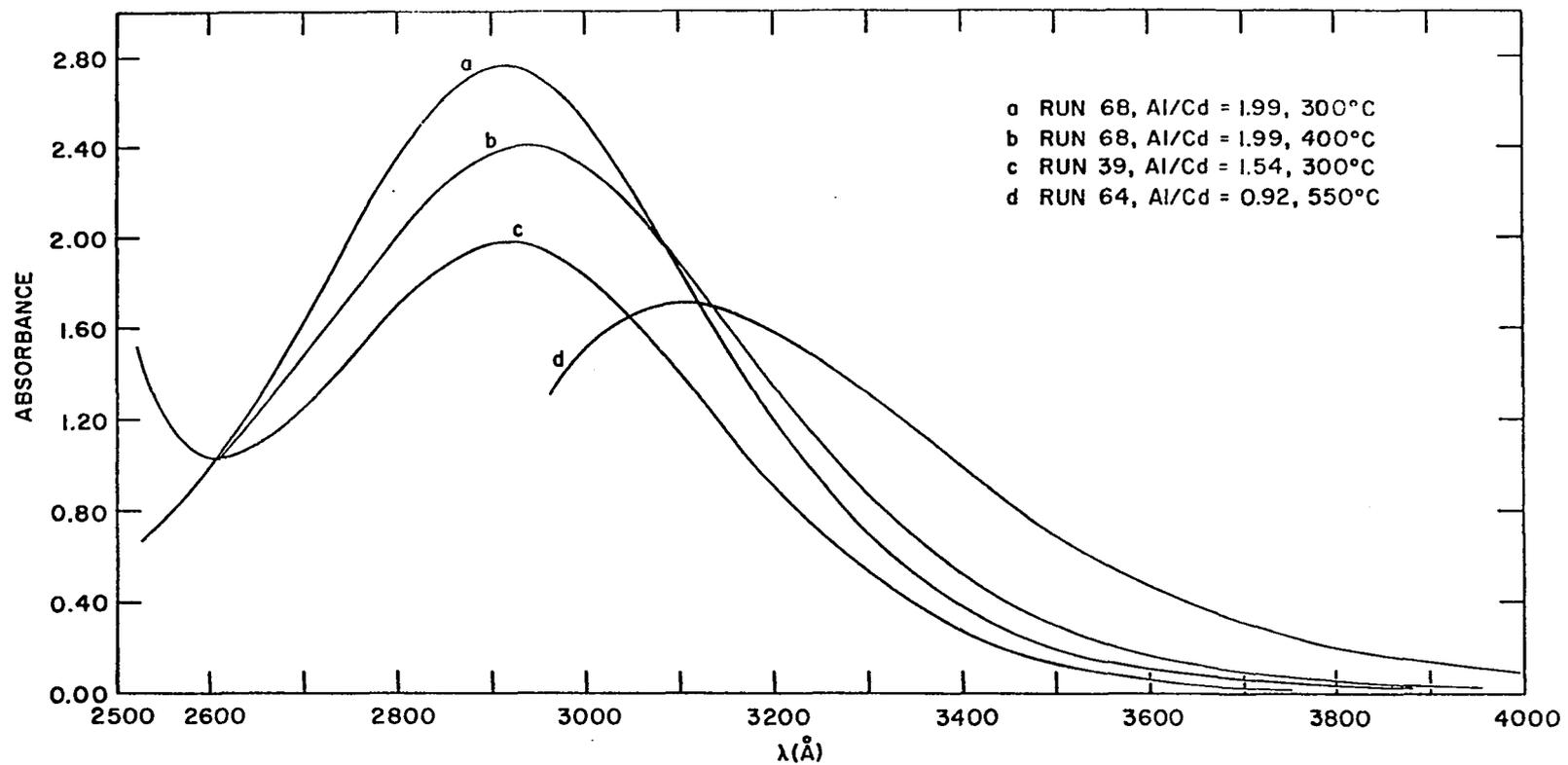


Figure 4. Spectra of reduced cadmium (II) melts

The constancy of δ for all runs at a given temperature indicates that there is no shoulder on the long wavelength side of the band. There is no indication of any new band "growing in" as the anion is changed. A Gaussian analysis of one of the curves (Figure 5) shows only very small deviations (of the order of experimental errors) on the long wavelength side of the band. The possibility of another band at higher energy will be discussed later. It thus appears that the shift of the band with changing anion composition is a true shift of the same band, rather than the disappearance of one band and the appearance of a new one.

For runs with the same anion composition but different amounts of reduction, plots of absorbance (A) versus concentration (M), Figure 6, are found to obey Beer's law to within about 10 percent. As there is no trend in the deviations, these are indicative only of the reliability of ϵ . Data for Cd-CdCl₂ are missing because of inability to resolve from the solvent edge any band similar to that for other reduced melts. The failure of these Beer's law plots to go through the origin indicates that the calculated concentrations of light-absorbing species are all too high. In obtaining these concentrations it has been assumed that all the cadmium metal has reacted with the solvent to produce a single light-absorbing species. All the metal apparently reacted in some way for there were no visible sign of unreacted metal in

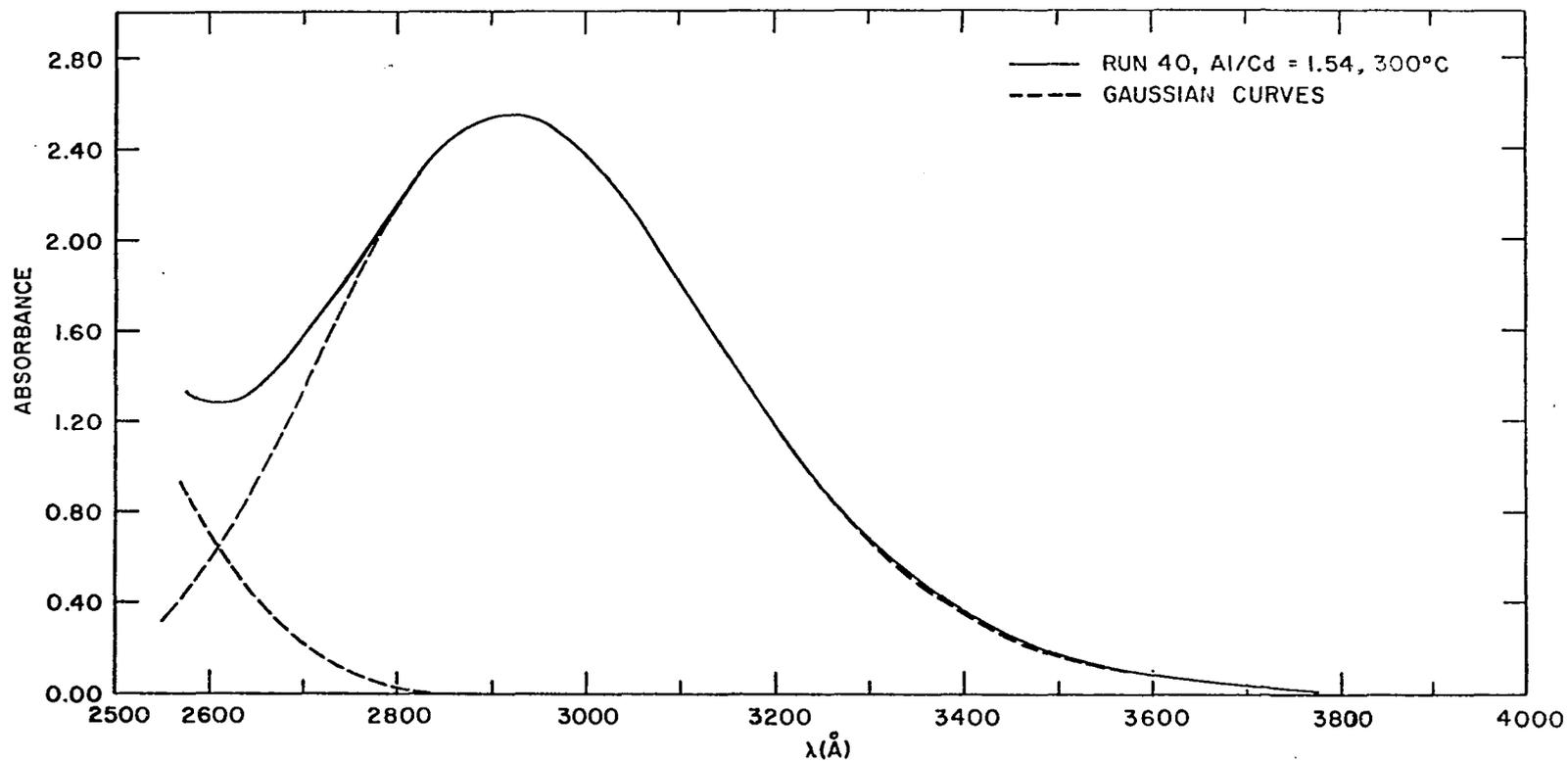


Figure 5. Gaussian analysis of a solute band

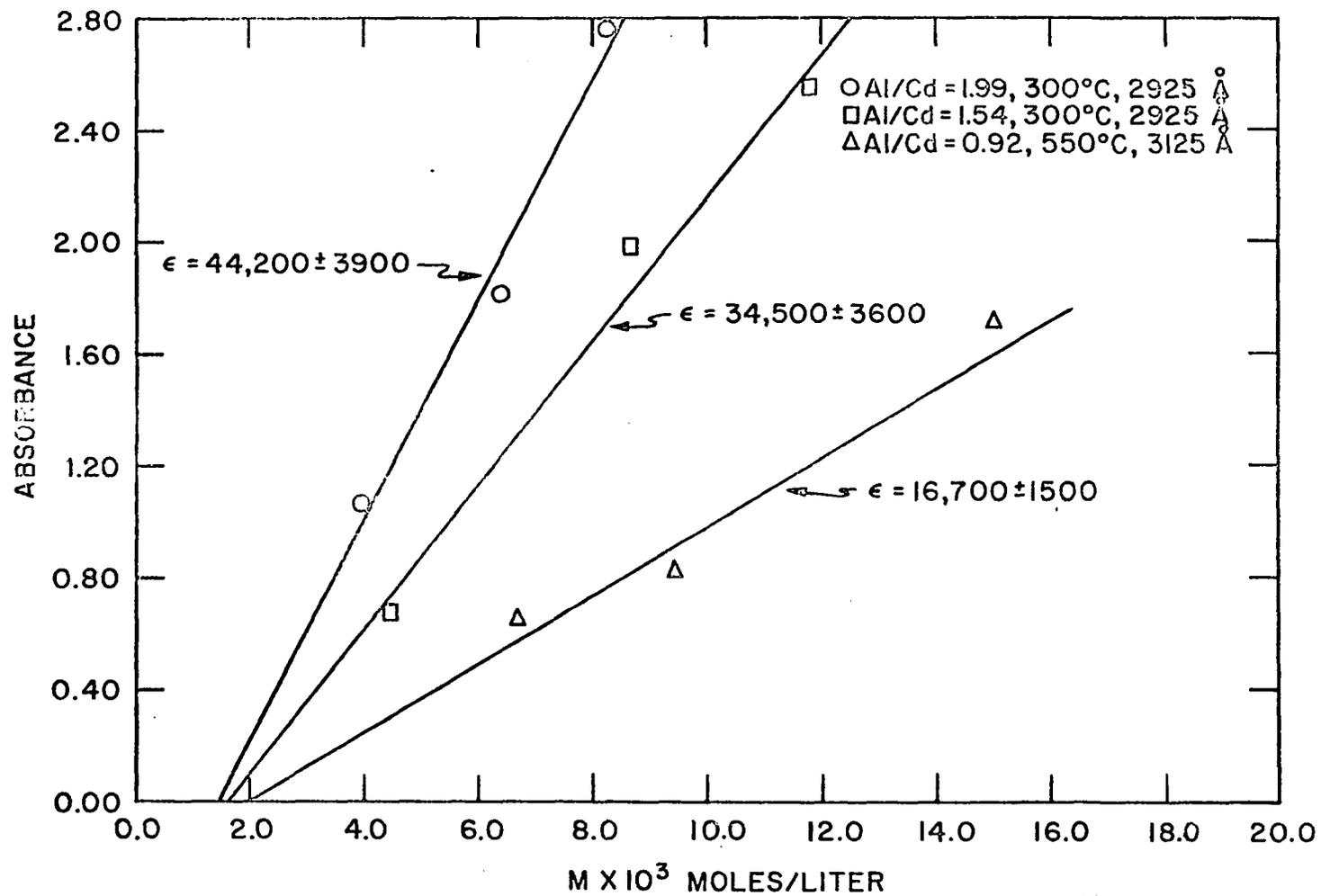


Figure 6. Beer's law plots for reduced melts

any of the melts. It might be that more than one species is formed. If this were the case, then rather drastic negative deviations from linearity should result for any concentration-dependent equilibrium. The most plausible explanation is that there remains in these salts an oxidizing impurity in remarkably constant amount from preparation to preparation. This might be explained if the source of the impurity were CdCl_2 . From Figure 6 the initial impurity level does not seem to depend on AlCl_3 content. In addition, the eventual preparation of a clear melt using filtered CdCl_2 (see Impurities) supports this. Earlier runs in which the salts were not subjected to the "sacrificial" treatment showed much larger initial impurity levels. It may be that both CdCl_2 and AlCl_3 contain troublesome impurities and that those in AlCl_3 can be removed by the "sacrificial" cadmium method whereas those in CdCl_2 cannot be. The one clear melt produced suggests that it is well to remove the CdCl_2 impurities before reaction with AlCl_3 , which may crack carbonaceous materials.

With regard to the conflicting reports of Cd- CdCl_2 spectra, this research suggests that the bands observed by Greenberg beyond $4000\overset{\circ}{\text{A}}$ may have been caused by impurities, perhaps arising from exposure of the salt to air. In one run in which the salt was open to the air for a time before the cell was sealed off, a spurious band appeared, very

poorly resolved, in the region of Greenberg's bands. This was observed in no other runs. Unfortunately the solvent (CdCl_2) tail prevented resolution of any band near 3400\AA . Shorter path lengths might have permitted this. The band position found by Bookless and Egan (25) is not inconsistent with an extrapolation of the present results, but his low molar absorptivity (~ 125) is surprising. If this absorptivity were correct, it would produce immeasurably small absorbance (~ 0.003), at the concentrations used here, when compared to that of pure CdCl_2 (~ 1.35) at 3400\AA . From the absorbance of Cd-CdCl_2 melts in this work, a minimum value of 11,600 for ϵ is obtained (see Table 2).

Models for Reduced Melts

There are several models which might be proposed to explain the spectra of these reduced melts. These are an interaction absorption process through an anion-bridged species, a charge transfer process similar to that in unreduced melts, and an internal transition between molecular orbitals of a Cd_2^{2+} species. These will be considered in turn.

First, however, any successful model must correctly explain the following observations:

1. there is a blue shift in the energy of the solvent band on going from a chloride melt to tetrachloroaluminate;
2. the solvent blue shift is faster than the

solute blue shift (that is, the energy of the solvent transition is more sensitive to anion change than the solute);

3. the intensity of the solute band increases on going from chloride to tetrachloraluminatate; and

4. both solvent and solute bands are rather insensitive to anion change until at least 1/4 of the AlCl_4^- ions have been replaced by Cl^- .

A bridged species might be analogous to the bridged species postulated for the very large interaction absorption of mixed oxidation states of metals in aqueous halide solutions. Here an anion would be interposed between a Cd^{2+} ion and a cadmium atom. The absorption would be caused by the excitation of an electron from the metal atom to Cd^{2+} through the anion bridge. The role of this anion is clearly critical. Chloride, CN^- , etc. are known to be rather effective intermediaries in interaction absorption processes and in some aqueous redox reactions while water, for instance, is poor. Similarly, the AlCl_4^- ion would be a poorer bridge and should decrease the allowedness (absorptivity) of the band. In addition, chloride, being smaller, would permit easier interaction between metal species because of the shorter metal-metal distance. Therefore an interaction absorption process would seem to require that the intensity increase with added chloride. This is what is found in the aqueous interaction absorption systems (26-30). In fact, just the opposite effect is seen here. Thus the bridged species

seems unlikely as a model for these systems.

A second possible model involves a charge transfer phenomenon similar to that invoked for spectra of unreduced melts. The difference is that here the Cd_2^{2+} ion is substituted for the simple Cd^{2+} ion as the electron acceptor. This, then, is simply a perturbation of the situation in the solvent. Processes and their energies similar to those in equations 7 and 8 will apply here with suitable changes in the cations. Consideration of the energetics in the two anion environments leads to ambiguity however. The ionization energy of AlCl_4^- will again be greater than Cl^- and the ionization energy of Cd_2^+ will be common to both anion systems in this comparison. The magnitude of the coulombic term, then, will be the deciding factor. Without complicating factors, AlCl_4^- would be expected to result in a relative red shift. Whereas in the unreduced melts covalency reverses this, the less polarizing reduced cation may not be able to. Thus the (unknown) degree of covalency in the reduced melts will determine the magnitude of the coulomb energy.

With regard to the relative shifts of solvent and solute bands with anion composition, this charge transfer model has shortcomings. Intuitively (again, energy considerations lead to no clear-cut conclusions) it seems difficult to see why the same basic process should give rise to such different

anion sensitivities. The intensity increase from chloride to tetrachloroaluminate is unexplainable by this model. There is no reason to expect any poorer overlap of the excited states of Cd_2^{2+} with the ground state of chloride than with the chlorines of the tetrachloroaluminate. The chloride is functioning only as a donor and not as a bridge as in the first model. This model also does not explain the different temperature sensitivities of the solute and solvent bands since the solvent shift to the red is some four times greater than for the solute. This charge transfer model is thus not very satisfying with respect to accounting for the experimental results.

Up to this point the reduced species in this model has been assumed to be Cd_2^{2+} . Other possibilities should also be considered. The monomeric Cd^+ can be eliminated as before on the basis of the diamagnetism of the melts. Cadmium atoms, while satisfying this criterion, require either that charge be transferred from the anion to the metal, forming Cd^- (a rather unlikely species), or charge transfer from the metal to the already-negatively-charged anions. Neither of these is worth detailed consideration, nor is the likelihood of formation of higher species (Cd_3^{4+} , etc.) in view of the decreased tendency toward catenation as one goes down a group in the periodic table. Such species have also been eliminated by e.m.f. studies in NaAlCl_4 (23).

A third model regards the band observed on reduction of the melts as arising from a $\sigma - \sigma^*$ electronic transition in the Cd_2^{2+} ion. If two Cd^+ ions ($5s^1$) are brought together, molecular orbitals will be formed, the lowest of which will be $^1\Sigma_g^+$. This would be the ground state into which the two $5s$ electrons are put. The excited state will be split because of spin multiplicity into a $^3\Sigma_u^+$ and a $^1\Sigma_u^+$, of which the triplet will be lower in energy. The observed transition would be $^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$ rather than $^1\Sigma_g^+ \rightarrow ^3\Sigma_u^+$. The latter transition is spin-forbidden whereas the observed transition is allowed; the singlet-singlet transition is fully allowed. Even if the spin selection rule has been partly relaxed, the transition could not be seen at the concentrations used here unless the molar absorptivity were of the order of 10 or greater.

This model seems to be in good accord with the observed changes in band energy and intensity. The band shift with changing anion can be accommodated by noting that addition of chloride to a reduced $\text{Cd}(\text{AlCl}_4)_2$ melt will probably lengthen the Cd-Cd bond of Cd_2^{2+} , by analogy with Hg_2^{2+} . Corbett (19) has summarized and pointed out the possible similarities of these two ions. The Hg-Hg bond length in the crystal decreases steadily from 2.69\AA in Hg_2I_2 to 2.43\AA in Hg_2F_2 . Thus those anions which favor covalency are seen to exert a weakening effect on the bond. This can be explained by noting

that the metal-metal bond is not made from pure s orbitals but probably has some p character. Because it becomes energetically more favorable for the metal to use these p orbitals in formation of bonds to the halogen, the p's are withdrawn from the metal-metal bond, thus weakening it. A similar explanation can be applied to Cd_2^{2+} . Lengthening the Cd-Cd bond by withdrawal of p character will decrease the splittings between the ground and excited states because of the decreased overlap. Ultimately, as the bond lengthens, the overlap goes to zero and the splitting completely disappears, leaving two Cd^+ ions. Thus chloride decreases the energy of the absorption band, in agreement with experiment. The overrunning of the solute band by the solvent absorption is an unfortunate coincidence, as the two shifts are caused by different mechanisms. It seems logical that chloride should have a greater effect on the solvent band (charge transfer from chloride) than on the solute band (lengthening of the Cd-Cd bond). The same bond-lengthening effect, by reducing the overlap of metal orbitals, will simultaneously decrease the intensity of the absorption. Theoretical calculation of intensities is based on an integral containing the wave functions of the ground and excited states. The form of this integral leads to the result that as overlap decreases the intensity decreases also.

The fact that substantial amounts of Cl^- must be added

before much of a shift is observed seems to be a property of reciprocal salt systems.¹ The most stable ion pairs in these melts will be Cd^{2+} , Cl^- and Cd_2^{2+} , AlCl_4^- . This is in accord with the reciprocal Coulomb effect in molten salts which states that the large cation-large anion and the small cation-small anion pairs will be the most stable in a reciprocal salt system.

Some of the spectra as plotted (see Figure 4) show what may be the beginnings of a band at higher energy before the solvent cut-off obliterates it. Such a conclusion must be approached with caution. In that region the resultant spectrum as plotted is the difference between two very steeply rising curves. Any small error in wavelength either in recording the data or in measuring the curves will have a large effect on this difference. This may explain why some of the curves in Figure 4 turn up at the low wavelength end and some do not. Figure 5 shows a Gaussian analysis of one of the solute bands. The possibility of a higher energy band is particularly tantalizing from this. Such a higher transition, if real, is readily explained by this model for the molecular orbitals formed by the 5p atomic orbitals may well lie not far above the $^1\Sigma_u^+$ state.

¹For a detailed discussion of this effect with references to the original literature, see Blander, M. Thermodynamic properties of molten salt solutions. In Blander, ed. Molten salt chemistry. p. 197. New York, N.Y., Interscience Publishers, 1964.

Bruner and Corbett (38), using thermodynamic considerations and spectroscopic data, have estimated a heat of dissociation of 40 kcal. mole⁻¹ for Cd₂Cl₂ in the liquid state. This can be used to estimate the energy of a Cd₂²⁺ solute band in CdCl₂. Assuming for the moment a symmetrical splitting of the ¹Σ_g and ¹Σ_u states about the Cd⁺ 5s level, the heat of dissociation will be 1/2 the energy of the transition observed. This will be a lower limit since actually the excited state is destabilized more than the ground state is stabilized relative to the energy of the starting atomic level. This gives about 3.5 ev., which compares very well with 3.96 ev. calculated from the 3125⁰Å band (Al/Cd = 0.92) which is an upper limit because of the effect of chloride on the Cd-Cd bond discussed earlier.

A consideration of the three proposed models leads to the conclusion that the M. O. description (model 3) seems to satisfy the experimental observations most unambiguously and satisfactorily. The charge transfer mechanism (model 2), while it is not overtly in contradiction with experiment, is rather muddy. This is partly the result of inadequate theoretical development in the field of charge transfer processes in inorganic systems in general and fused salt systems in particular. It cannot be discarded entirely, for with further development the mud may settle and leave a clear solution.

Future Work

The most obvious need is for elimination (and identification) of the impurity present in these melts. The one promising preparation made late in the work can be used as a starting point in such a search. At least a quick check of these melts should be made with "pure" salts. A study of other Cd-CdX₂-Cd(AlX₄)₂ systems, the bromide particularly, might shed light on some of the ambiguous energy arguments considered in discussing the solute charge transfer model. It would be hoped that the solvents would not have shifted so as to obscure a solute band. In view of the ambiguity now existing in Pb-PbCl₂ and Pb-Pb(AlCl₄)₂ systems (23) where different solute species are evidenced in each case, a spectral study might be useful. Being unable to make successive additions of metal to the same salt is wasteful of time, salt, energy and patience. The most promising method is use of coulometric addition such as used in e.m.f. work (23). That method has proved successful for Cd(II), Pb(II) and Sn(II) tetrachloroaluminates. This would require some redesigning of the cell block to accommodate either a U-shaped tube with an optical cell at one end and the electrodes at the other or a longer straight tube. The extra effort would seem to be well worthwhile, for then one could make a complete series of runs on one salt sample. Should this prove to be impractical, a method of analyzing the reduced salt from the cell after spectra have been run would give the

actual amount of reduction. Such a method would be to measure the volume of H_2 evolved and/or the amount of base produced (for active metals) on reaction of the reduced salt with water. Both of these approaches have in common the advantage of measuring the actual amount of reduction rather than the a priori determination in this work. Extension of this work to zinc systems where preliminary gas phase work indicates a volatile $ZnCl$ species¹, probably similar to $CdCl$ (38), would seem logical.

Summary

The absorption spectra of a series of molten salts of the general type $Cd^{II}Cl_x(AlCl_4)_{2-x}$ where $0 \leq x \leq 2$ have been obtained in the visible and UV regions of the spectrum. These consist of the steeply rising tail of an intense band extending to shorter wavelengths. The absorbance of this tail is 1.0 at 2570\AA for the salt with $AlCl_3/CdCl_2 = 1.99$ at 300° and 3470\AA for pure $CdCl_2$ at 600° . For salts of intermediate composition the band is at intermediate, although not linear, positions. Absorption spectra of these same salts to which small amounts of Cd had been added were obtained at the same temperatures. These reduced melts show (in addition to the edge of the unreduced salt) a single intense band at 2900\AA ($\epsilon=44,200$) for the salt with $AlCl_3/CdCl_2$

¹Lynde, R. A., Ames, Iowa. Tentative spectroscopic identification of species in gas phase over $Zn+ZnCl_2$. Private communication. 1965.

= 1.99 at 300°, changing to 3125Å ($\epsilon=16,700$) for the salt with $\text{AlCl}_3/\text{CdCl}_2 = 0.92$ at 550°. In Cd-CdCl₂ melts the solvent cut-off overlaps the solute band, so that resolution is not possible. Both solvent and solute bands shift to the red with increasing temperature or with increasing chloride content, the solvent band shifting more rapidly in each case. The intensity of the solute band decreases with increasing temperature, but this is compensated for by a simultaneous increase in the half width of the band such that the area under the absorbance curve remains approximately constant. The intensity of the band also decreases with increasing chloride content. All these effects are accounted for by postulating for the solute absorption an electronic transition $^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$ in the Cd_2^{2+} ion. The absorption process in the unreduced melts is postulated as an electronic charge transfer process from the anion to the cation. Beer's law is found to apply approximately (within 10 percent) for the solute.

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