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SPECTROPHOTOMETRIC STUDY OF THE GASEOUS EQUILIBRIUM OF CADMIUM AND CADMIUM(II) CHLORIDE

by

Buddy Leroy Bruner

A Dissertation Submitted to the
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INTRODUCTION

The cadmium-cadmium(II) chloride system was first investigated in 1890 by Morse and Jones (1), who upon cooling the solution obtained a black solid which they characterized as Cd_4Cl_7. The solution of cadmium in its chloride has since received considerable attention from investigators concerned with the nature of the solute species. However, in spite of repeated efforts the nature of the solute species remains somewhat ambiguous, and the system as a whole is still not well characterized.

The black solids originally reported by Morse and Jones have long since been shown to be simple mixtures of cadmium(II) chloride and finely divided metal (2). Furthermore, no new compound appears in the phase diagram (3), an apparently quantitative decomposition taking place on solidification of the melt. The inability to isolate a stable reduced compound, contrasted with the sizable solubility of the metal in the chloride (up to 33 mole % at 900°), has encouraged a number of studies intended to reveal the nature of the solute species. Aten (4), on the basis of his determination of the phase diagram and his study of the conductivity of the $Cd\text{-}CdCl_2$ solution suggested in 1910 that the Cd^+ ion was the solute species. Later observations of the diamagnetism of the melts (5) served to modify this proposal to the dimeric Cd_2^{2+} and this ion in some degree of solvation is the generally accepted species today.

Unfortunately the supporting evidence for the choice of solute is mostly inconclusive. The possibility of a "pyrosol" formation (6) appears extremely small considering the pronounced freezing point depression (57° and 13.7 mole % Cd at the monotectic point) and the absence of colloidal metal in the melt (7). However the choice between a subhalide species (8) and metal atoms dissolved as ions plus electrons (9, 10) is not clearly defined. To date most investigations have not involved direct physical measurements of the solute, but rather thermodynamic measurements on the solutions. Thus the nature of the solute must subsequently be indirectly inferred. For example, the EMF studies by Topol (11) on dilute solution (0.03 to 0.3 mole %) of Cd in $CdCl_2$ yielded an apparent value of 2.0 for the Nernst n at 578°. This value could correspond to the existence of a Cd_2^{2+} solute, but it is equally consistent with Cd°. In a series of conductivity and self-diffusion measurements on the Cd-$CdCl_2$ solutions, Angell and Tomlinson (12) noted the absence of any actual electronic conductance and found the coefficient of diffusion for the solute to be less than that of Cd^{2+}. Nachtrieb's measurements of the diamagnetic susceptibility (13) also failed to reveal a true metallic solute, but neither set of experiments permits unequivocal distinction between the subhalide and "metallic" models. The most conclusive evidence has resulted from the investigation of Herzog and Klemm (14). They studied the migration of the boundary between $CdCl_2$ and the darkly-colored solution of metal and found the mobility of Cd^{2+} (the solvent cation) to be only 8.2% greater than that of the solute species. This small difference implies that the solute is charged, and thus is strongly suggestive of a Cd_2^{2+} solute.

A great deal of support for a subhalide in the Cd-$CdCl_2$ system probably derives from comparison with chemically similar systems. It is well known, for instance, that mercury exhibits a dimeric +1 valence state, both as the solid subhalide (Hg_2Cl_2) and as the solvated ion (Hg_2^{2+}). Cadmium and the cadmium(II) tetrachloroaluminate salt form an even more closely related system. Corbett, Burkhard, and Druding (15) have not only shown that the metal solubility is significantly greater in this more acidic solvent - a predictable fact if one assumes the solution proceeds via the formation of a subhalide solute - but have also isolated a stable subhalide $Cd_2(AlCl_4)_2$. Corbett (16) has also studied the Raman spectra of the molten solution with resultant direct verification of the existence of the Cd_2^{2+} solute.

The occurrence of vapor phase transport is also a common observation among systems in which the metal exhibits an appreciable solubility in the fused salt. In this case both salt and metal are transported from a heated zone and deposited together on a cold wall even when one of the two components has a negligible vapor pressure. The existence of a stable, gaseous subhalide which disproportionates on condensation has been commonly postulated to explain the mechanism of such transport. While no one apparently has actually observed transport of $CdCl_2$ by the more volatile metal and while the stable subhalide in the companion Hg-$HgCl_2$ system is said to "sublime" as the disproportionation products (at least above 250°) (17, 18), there is a moderately positive indication for the existence of a stable, gaseous subhalide of $CdCl_2$ under equilibrium conditions. Tarasenkov and Skulkova (19) found $CdCl_2$ to be significantly less volatile in a Cl_2 stream than in a N_2 stream, as would be expected if the disproportionation, $2\ CdCl_2 = \frac{2}{x}(CdCl)_x + Cl_2$, were appreciable.

In the final consideration, the liquid phase of the Cd-$CdCl_2$ system has been extensively studied and although the solute is generally felt to be Cd_2^{2+} most of the evidence is indirect. More direct evidence is difficult to obtain. Raman measurements in the visible are prevented by the deep red-black coloration of the solution and must await the possible disclosure of a "window" elsewhere while Smith (20) has characterized the electronic spectra as "uninteresting". NMR measurements of either the 111 or 113 isotopes of Cd require a considerably enriched sample for optimum resolution not to mention the modifications necessary to operate at high temperatures.

The gas phase, however, has had very little investigation and a number of interesting questions remain to be answered in this area. There has been no direct determination of the species present in the gas phase even though information concerning the existence of a stable gas phase subhalide would be particularly interesting. Presuming such a subhalide exists there are at present only rough thermodynamic estimates of its equilibrium with gaseous Cd and $CdCl_2$ or with the Cd-$CdCl_2$ solution.

The thesis problem described herein was thus originally selected with the intent: (1) To determine the nature of the gas phase species above a solution of Cd in $CdCl_2$, particularly to determine if a subhalide exists and, if so, to fix the degree of polymerization, and (2) to evaluate the equilibrium constant for the interaction of the gas phase species. Both aspects of the problem were to be attacked by a study of the electronic spectra of the vapor phase since in principle each (of the two or more) species present could thus be simultaneously and independently identified and its equilibrium concentration determined. It should be noted that one of the major complications for studies of the gas phase of the Cd-$CdCl_2$ system is the fact that above 500° both the metal and the salt are present in appreciable concentration. Few methods are capable of distinguishing among the species present while permitting simultaneous and quantitative measurements on such a multicomponent system. The use of the visible and UV spectra rather than the mass and infra-red spectra was favored as being somewhat more likely to yield unambiguous answers. (A less subtle consideration was the immediate availability of either a small Hilger spectrograph or a DU spectrophotometer.) Experimentally, the measurement of absorption spectra permits accurate determinations with the sample at a selected temperature. The use of either emission or discharge spectra would provide a means of identification and quantitative analysis, but would not permit the introduction of the sample temperature as a variable. (Temperature in these cases is a function of the arc or discharge characteristics.)

The feasibility of identification and quantitative analysis of cadmium vapor has been conclusively established by Walsh and others (21) in their work with atomic absorption spectra, employing both the 2288 Å and 3261 Å resonance lines. The identification of $CdCl_2$ presents some difficulties although the absorption spectra of the vapor has been studied by Evans (22), Deb (23), and Oeser (24). The vapor is said to exhibit a broad, structureless continuum near 2000 Å which extends toward the red with increasing temperature. Identification would thus require a careful examination, particularly if any overlap occurs. Quantitative measurements would likewise require care, but should be possible by a careful calibration of the band edge. Pearse and Gaydon (25) and Herzberg (26) both list spectral systems attributed to the subhalide, CdCl. In particular, Walter and Barratt (27) and Oeser (24) are cited as observing sharp absorption bands at 3072 and 3181 Å in a $CdCl_2$ discharge tube. Thus in principle the presence of the subhalide could be verified by the observation of these transitions which do not overlap with either the metal lines nor the $CdCl_2$ continuum. A quantitative determination would, however, require a calibration of at least one of these lines. The simplest means of calibration for this or any additional species would be by measurements on an all gas phase system of known initial stoichiometry. (Direct calibration by decomposition of $CdCl_2$ would probably not be possible in this case due to the high thermal stability of the dichloride.)

MATERIALS

For the accurate, unambiguous, and quantitative spectral measurements desirable in this study it was necessary to use chemicals in a state of high purity. The resulting products, though not extremely sensitive to reaction with moisture and oxygen, were transferred either under vacuum or in an argon-filled dry box with entry through an evacuable lock.

Cadmium Metal

Commercial high purity cadmium metal (A. D. MacKay 99.999%) was fused under vacuum, cooled, and the resulting surface impurities (primarily oxide) dissolved in dilute HNO_3. This operation was repeated until no surface deposits were evident upon fusion. Buttons of this product were then twice distilled at 415° under dynamic vacuum (approximately 10^{-7} Torr) in a Pyrex tube that had been degassed at 500°. The cadmium was subsequently distilled directly into a cell for measurement or into a slender finger which was then sealed off for storage.

Cadmium(II) Chloride

High purity cadmium(II) chloride was obtained from William J. Burkhard who had prepared it by direct chlorination of the metal (15). This product was chlorinated in a segmented Vycor tube at 500° and then sublimed twice at 550° under dynamic vacuum. The chlorination was effected by equilibration of the heated salt with the chlorine vapor above the liquid (Mathison) condensed in a trap at -80°. The purified sample was then directly sublimed into a cell for measurement or into a slender finger for storage.

APPARATUS

Spectrophotometer

A Beckman model DU spectrophotometer equipped with photomultiplier and hydrogen light source and modified for measurements of high temperature samples was employed. The choice of a spectrophotometer was particularly indicated since this type of instrument measures the absorption intensity directly (the absorption intensity being directly proportional to the concentration of the absorbing species).

The photomultiplier was a selected 1P28 tube coupled with a photomultiplier power supply built by the author. The power supply was constructed to conform to the circuit diagram of the Beckman model 4300 power supply except that two 300 volt "B" batteries were substituted for the six 90 and one 45 volt batteries specified. The hydrogen discharge lamp was a Beckman 8333 model powered by the Company's model B power supply.

The DU itself was modified to reduce the effects of furnace radiation on the detector at high sample temperatures. Absorption measurements are normally made by passing a light beam through the monochrometer, M (Fig. 1), then through the sample and/or reference and thence to the detector, D. However, for measurements above 500° thermal radiation from the furnace immediately preceding the detector in the light path increases the noise level many fold and at long wave

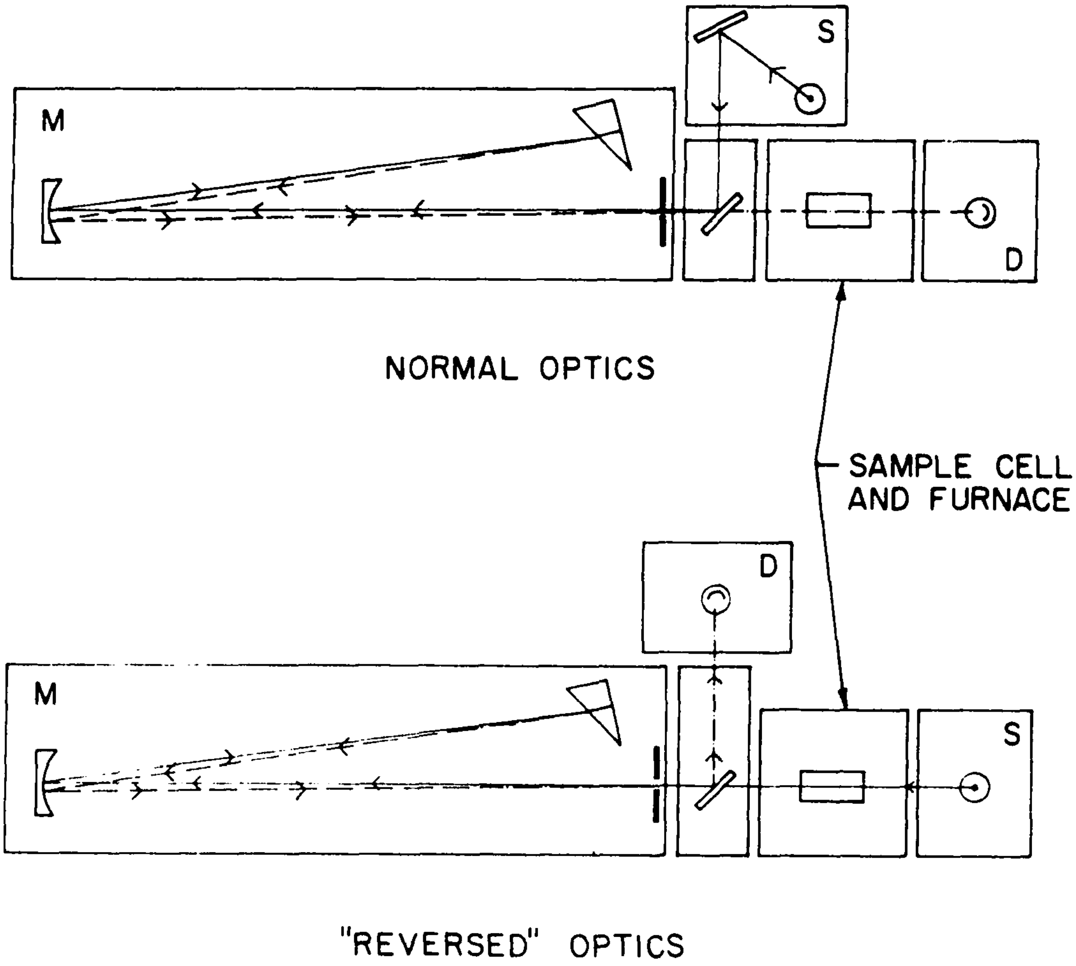

Fig. 1. Optical schematic for DU spectrophotometer

lengths swamps the sample signal. Measurements then require the detection of a small difference in large signals exhibiting substantial fluctuations. It is most helpful under these conditions to exchange the positions of the sample and monochrometer (termed "reversing the optics") so that the major portion of radiation from the furnace is "diverted" by the monochrometer and is not allowed to reach the phototube (28, 29). Note that while it would in principle be possible to accomplish the same end with selected narrow band pass filters, this latter method is prohibitively inconvenient for measurements covering any appreciable portion of the instrument's optical range (2000-20,000 Å).

The DU lends itself very readily to reversal of the optics as a consequence of its modular construction and single beam design. The reversal was accomplished by placing the detector on the cell compartment mounting block in place of the source, S, which was then relocated on the sample compartment. The new placement of the detector required modification of the cell compartment mounting block to accept the detector and to clear the new sample compartment. This modification was accomplished in a manner quite similar to that of Gruen and McBeth (30), and is illustrated in Fig. 2a. The light source housing and the mounting of the lamp itself were also modified (Fig. 2b). The condensing mirror was removed and a hole was cut in the housing wall so that the

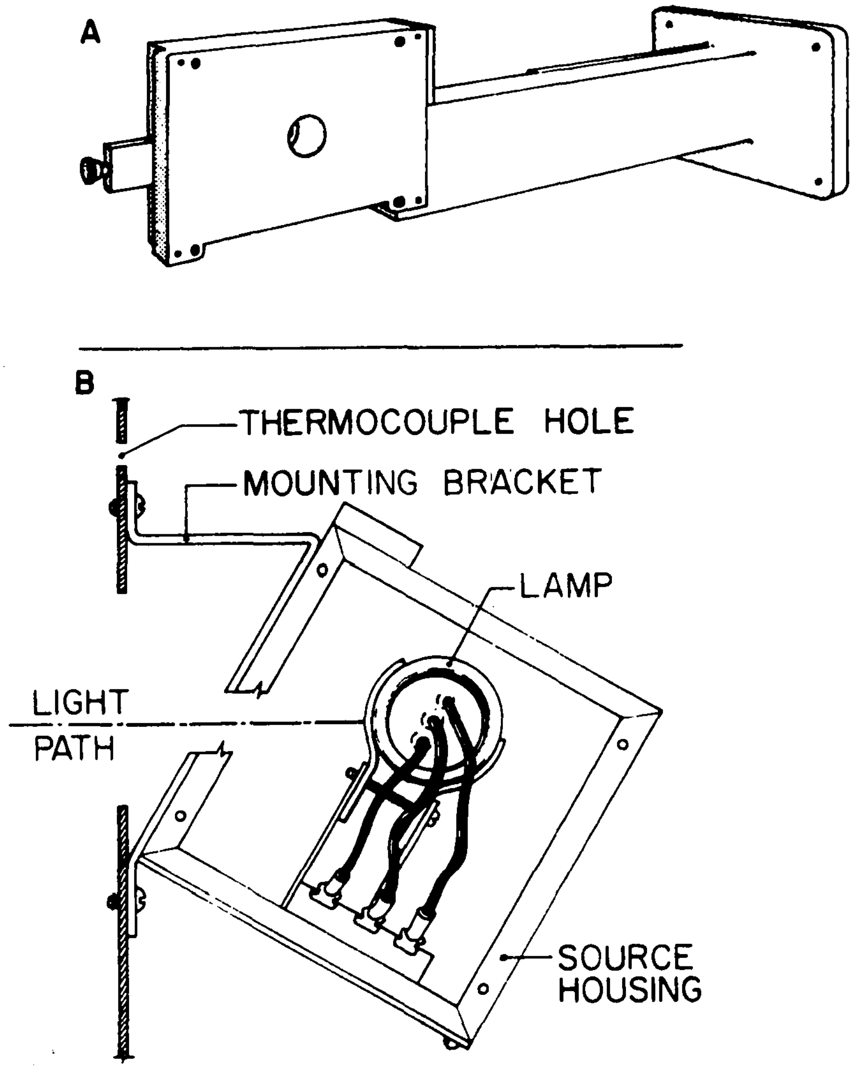

Fig. 2. Modified components:
A. Sample compartment mounting block
B. Light source and housing

light beam entered the cell compartment directly from the source rather than indirectly via the mirror. The housing was then secured to a special mounting bracket attached to the end of the cell compartment. Although it may be noted that the hydrogen lamp is mounted upside down, this position has no functional significance, rather it emerged as a convenient means for mounting the lamp within the existing housing while maintaining clearance for the thermocouple which entered the sample compartment at a point adjacent to the lamp housing.

The modifications to the light source housing were made necessary by the extreme length of the sample compartment coupled with the reversed optics. With this arrangement the path length was extended to 23 inches and the beam from the standard housing proved so divergent that satisfactory intensities could not be achieved. Two fused quartz condensing lenses (Perkin-Elmer, 35 mm diameter, 8 mm thick, and 55 mm focal length), mounted in adjustable holders at each end of the sample compartment, were therefore used to focus the beam. The lense adjacent to the source was adjusted to condense the divergent rays from the hydrogen lamp so that they assumed a parallel path through the sample. The second lense was then adjusted to bring the parallel beam to a focus on the slit.

Sample Compartment

The sample compartment for the spectrophotometer (Fig. 3) is essentially a large box, 21 inches high, 17 inches wide, and 23 inches long. The compartment was constructed with a base and mounting plate of 1/4 inch boiler plate to assure sufficient strength and rigidity to maintain alignment with the monochrometer during the repeated shifting of the heavy furnace containing the absorption cells. (The DU, as a single beam instrument, must be balanced with the reference at each wave length prior to shifting the cells for measurement of the absorption of the sample.) The mounting plate was drilled to conform to the alignment pins of the monochrometer and to accommodate the standard attachment bolts. A hole (3/4 inch diameter) was drilled for the light beam with the hole and attachment scheme being offset 5/8 inch from the center of the mounting plate so that the furnace would be centered within the sample compartment when the reference cell was in the light path. The furnace was left in this position except when measurements were being made on the sample. The size of the furnace also required that the light path be situated 11 inches above the base of the compartment; consequently, the monochrometer was supported in position with two laboratory jacks.

The mounting plate was securely positioned and attached to the base with triangular pieces of boiler plate. The base

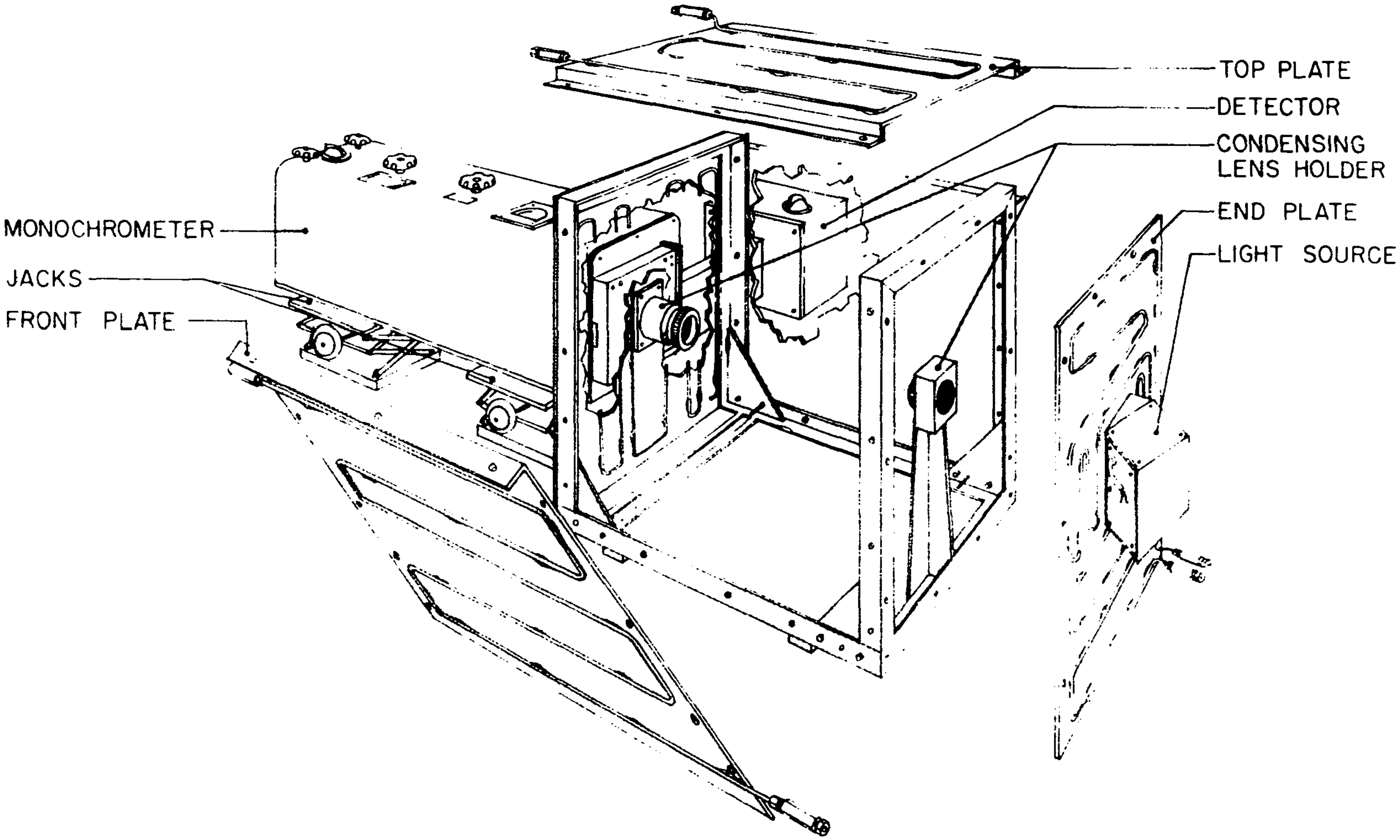

Fig. 3. Spectrophotometer and sample compartment

itself was supported by one inch steel legs. Sections of 1 1/2 inch angle iron were bolted to the base and mounting plate to provide the point of attachment for the cover plates. Three cover plates formed from 1/16 inch galvanized sheet were used on the compartment after experience demonstrated that a one-piece cover warped the box and altered the alignment when bolted into position. In practice the bolting followed a regular sequence starting with the bottom left bolt, working to the right, then up a row and again left to right until even the top cover was bolted into place. (The back cover plate was not removed and so remained bolted into place.) This procedure was designed to achieve a reproducible tension on the sample compartment from run to run although it was not shown that some alternate or haphazard scheme would actually result in a faulty alignment. Once bolted on, the cover plates were sealed at their flanges with Scotch brand electrical tape.

The front cover was appropriately slotted to clear the four (stove bolt) adjustable stops used to restrict the travel of the furnace. A slot was also provided for the shift rod of the furnace. The stops were mounted in the angle iron attached to the base. The shift rod passed through an oversized hole in the same angle iron as well as through a multiple layer of common felt which served as a light-tight "washer". The latter precaution was later found to be unnecessary. The amount of scattered light entering the monochrometer was so small that measurements made in a well-lit room without the cover plates do not differ from those made with the covers in place.

The end plate of the sample compartment was fashioned from 2 1/16 inch thick piece of sheet metal and attached to the base on a framework of angle iron much the same as was the mounting plate. Oversize holes for the attachment and rough alignment of the light source housing as well as for the adjustment of the gradient thermocouple were drilled in the plate. A large, two inch hole was punched for the light beam in order to accommodate the focusing motion of the condensing lense assembly next to the source. The sample compartment was cooled with tap water passing through 1/4 inch copper tubing soldered to the inside of the mounting plate and the outside of the covers, base, and end plate and connected with Dacron tubing when in use.

Inside the compartment a track was provided for the furnace wheels by welding two 1/8 inch thick steel strips to the base so that the furnace could only travel perpendicular to the light path. When installed, the furnace stood three inches from the ends of the compartment and traveled 1 1/4 inches during cell shifts. The adjustable, brass, condensing lense holders were also mounted on the inside of the compartment. One was mounted directly to the mounting plate, the other was welded to a stand which was bolted to the compartment base in front of the light source. Dry nitrogen gas was introduced into the compartment through a piece of 1/4 inch copper tubing soldered through a hole in the base to sweep out the oxygen and moisture in the compartment and thereby inhibit corrosion of the steel block above 500°. Thermocouples were likewise introduced through holes in the base, but in this case via short glass tubes that were waxed in place with Apiezon W. Electrical connections were provided at six standoffs mounted through another set of holes in the base. The power lines were soldered to the connectors under the compartment and the furnace lines to the connectors inside the box.

Absorption Cells

The absorption cells were matched quartz, cylindrical cells (Pyrocell US-120), 22 mm in diameter and 100 mm in length, with the windows fused in place. Each cell was originally equipped with a tube, eight mm in diameter, sealed to the "top" of the cell and positioned perpendicular to the center of the lateral axis of the cell. This open tube was used to evacuate the cell. The sample cell (Fig. 4) was further equipped with a finger (8 mm in diameter and 5 mm long) which served as the "cold" trap for the condensed phases present during the runs. This finger was placed in line with the filling tube, but on the opposite side of the

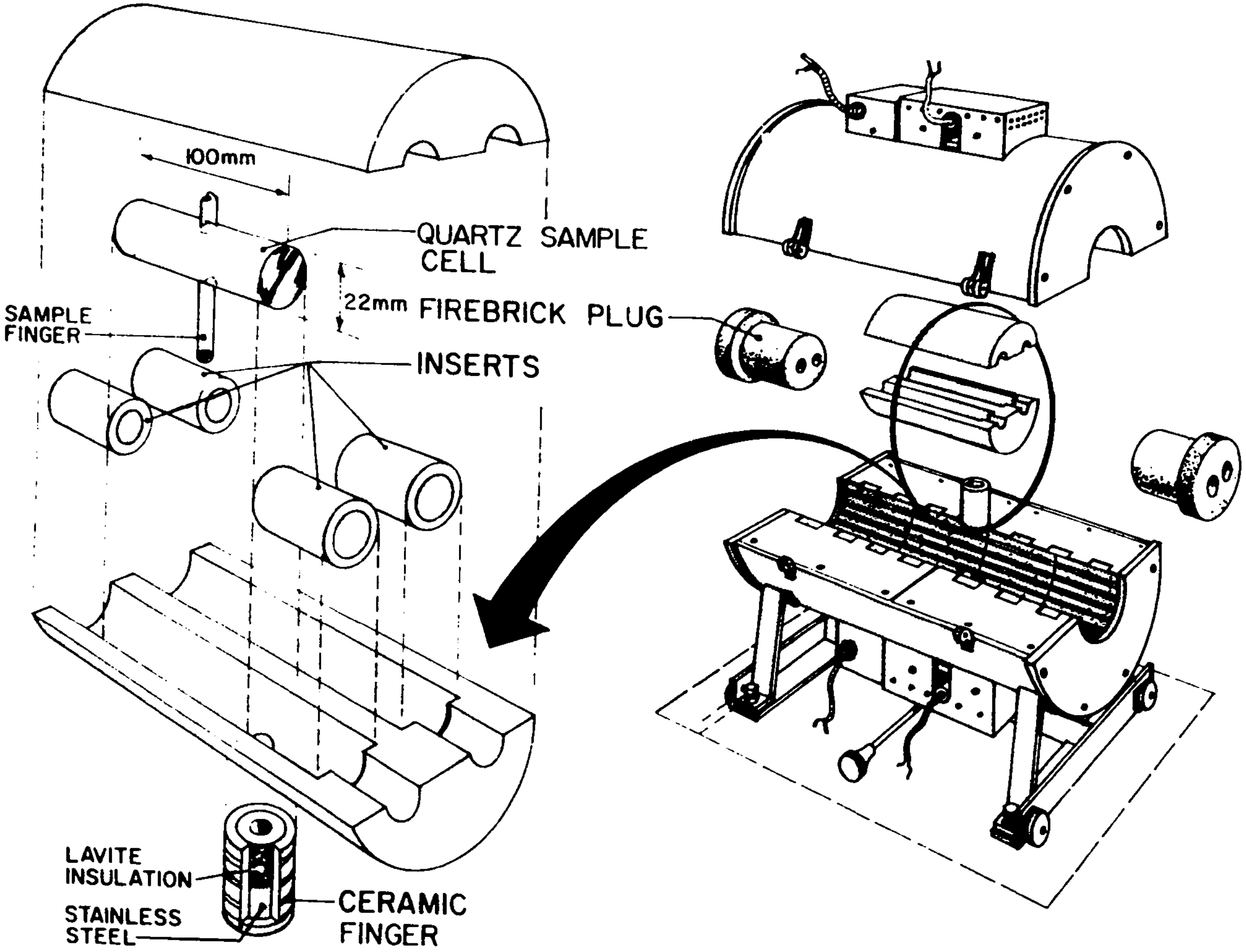

Fig. 4. Furnace assembly, block, and sample cell

cell, i.e. on the "bottom".

Furnace Assembly

The furnace was a 16 inch, hinged, tubular, muffle furnace (Heavy Duty, model M3016) mounted on four feet. These same feet were used to mount the furnace on a mobile platform fashioned from one inch angle iron and resembling a wide "H" when viewed from the top. Four ball bearing wheels were mounted to the "legs" of the platform and a simple rod was screwed into the cross bar to provide control of the movement. The inclination and height of the furnace were moderately adjustable by means of inserts placed between the feet of the furnace and the platform.

Heater Sections

The heater sections were constructed for the purpose of maintaining the sample within one degree of any temperature between 25 and 800° while insuring against any condensation outside of the finger of the absorption cell. The central component of the sections was the muffle furnace. This furnace normally consists of four 4 inch, semicylindrical, heating element sections wired in series, top and bottom. To accommodate the particular demands of this investigation, the sections were purchased unwired and unassembled so that the furnace could be modified as follows (see also Fig. 4).

Four of the sections were individually wired and the wiring sealed with the high temperature, insulating cement, Sauereisen No. 7. These sections were then installed in the ends of the top and bottom of the furnace with the top and bottom sections respectively wired in series. The coupled sections were then joined in parallel to meet the manufacturer's specifications for operation at 110 volts. (This collection is hereafter termed the "end" heaters.) Two of the remaining sections were wired together to form an eight inch section and installed so as to fill the middle of the top section of the furnace. The remaining two sections were also wired together, after a hole, 1 1/2 inches in diameter, had been cut where the sections join, the center of this hole being offset 5/8 inch from the center of this semicylinder to permit a fit over the auxiliary heater for the finger of the sample cell. The hole was cut with a high speed carborundum saw and the wiring facilitated by appropriate "chiseling" with a Burgess Vibra-graver. This modified section was installed in the middle of the bottom of the furnace after a cylindrical hole (one inch deep, 1 3/8 inch diameter) had been carved in the furnace insulation under the hole in the heating section. The middle heating sections were then connected in series, forming a system (termed the center heater) which met the specifications for operation at 220 volts. It should be noted that experience indicates that each section should be "Sauereisened" individually; six sections were burned out before the practice of collective cementing was eliminated. Apparently the spaces left are necessary to prevent localized over-heating. The electrical leads of all sections were threaded through the furnace insulation, passed through the steel furnace shell in alumina thermocouple shields, and attached to the power lines via bolts mounted on Transite boards at the top and bottom of the furnace.

A small auxiliary heater was constructed to provide temperature control for the sample finger of the actual sample cell. This "finger" heater was built from a two inch length of 1 1/4 inch diameter alumina furnace tubing which was wound with some six feet of 26 gauge Chromel-A wire. The heater was equipped with a 1/4 inch thick fire brick bottom, then cemented with Sauereisen and attached to the power lines as described above. A five millimeter hole was drilled 1/2 inch from the bottom of the finger heater and a corresponding hole made in the insulation and shell of the muffle furnace to accommodate a measuring thermocouple and its quartz shield.

When in operation the "three" heaters were each individually controlled; the middle and finger heaters by Brown proportioning controllers, the end heater by a Celectray off-on controller. The variation in the critical finger temperature was observed to be less than 0.5° over a half hour period.

Steel Blocks

Within the center heater a stainless steel block was positioned to provide a large heat capacity and a well-aligned holder for the absorption cells. This block is eight inches long and three inches in diameter to neatly fit the interior of the center heater. The block was fashioned in halves (see Fig. 4) for easy accessibility and introduction of the cells. Two holes (22.5 mm in diameter) seven inches deep were drilled into the block to accommodate cells. These holes were centered 5/8 inch from the axis of the block and both bisect the split between the halves. The remainder of the light path was formed by drilling 14 mm holes the rest of the way through the block. Pairs of cylindrical stainless steel inserts (also with 14 mm holes) were slipped into the end of the larger hole to provide exact accommodation for cells, 50, 100, or 150 mm in length. The end result was much as if two "rolling pins" had been hollowed out of the steel block.

Perpendicular to the light path and four inches from the ends of the block a single 10 mm hole was bored through the lower half of the block from the center of the sample cell area. This hole accommodates the finger of the sample cell. Small holes (5/8 inch deep) were likewise drilled from both cell areas into the upper half of the block to accommodate the seal-off stubs. A thermocouple groove (5 mm wide) was milled adjacent to the sample cell and paralleling its length to permit determination of the temperature variations along the length of the cell. A similar groove was milled down the center of the top of the upper block half for insertion of the controller thermocouple for the center heater. When in operation the block was found to be particularly susceptible to corrosion on the faces of the split. Subsequently a 3 mil sheet of platinum (two inches by six inches) was placed across the split to prevent possible heat losses through that avenue.

A small, cylindrical stainless steel block (29/32 inch in diameter, one inch high) was also fashioned. This block was placed in the bottom of the finger heater to provide additional heat capacity for the condensed sample. A hole, 10 mm in diameter, 3/4 inch deep, was drilled lengthwise into the center of the block to accept the finger. A hole (5 mm in diameter) was drilled perpendicular to the axis of the block to intercept the finger hole at its bottom. This hole provides access for the controlling thermocouple of the finger heater. (The same thermocouple is used to measure the sample temperature by inserting a Rubicon potentiometer across the thermocouple between the sample and the controller.) The remaining space in the finger heater was filled with a cylindrical, fired Lavite insulator (3/4 inch long, 29/32 inch in diameter with a 10 mm hole drilled lengthwise through its center). The purpose of the insulator is to separate the finger from the influence of the center heater as much as possible (since the finger must be kept cooler than the gas phase to prevent condensation outside the finger).

Insulator Blocks

Fire brick blocks (4 1/2 inches long) were hand carved to snuggly fit within the end heaters of the furnace assembly. These blocks were carved in two pieces and both drilled with light path holes, 5/8 inch in diameter. The outer section of each set of blocks was carved so as to leave a rim (four inches in diameter, 1/2 inch thick) on the outside of the furnace when the blocks were in position. The block to be inserted nearest the light source was also appropriately provided with holes for the lateral thermocouples which extend into the grooves in the steel block. A groove (three inches long) was also constructed in the bottom of this block so that a controlling thermocouple could be placed adjacent to the end heater. The insulator blocks helped to provide a buffer zone that could be heated sufficiently to maintain the absorption cell windows at the same temperature as the rest of the cell body.

EXPERIMENTAL PROCEDURE

Sample Preparation

Before each run the absorption cells were carefully cleaned, washed in dilute nitric acid, rinsed, first with deionized water and finally with doubly-distilled water. The cells were then sealed to the necessary auxiliary apparatus and connected to the vacuum line (by way of a trap cooled with liquid nitrogen) for evacuation. The liquid nitrogen trap was placed between the cell and the vacuum line at all times after one metal sample "collected" a 2% mercury impurity from the manometer while on the line overnight. The empty reference cells were heated to 500° under dynamic vacuum (ca. 10^{-7} Torr) to aid degassing and after an hour at this temperature were sealed off from the line for use.

Each sample cell required a somewhat different method of loading depending upon the particular sample to be studied. For the condensed phase cadmium runs the metal was distilled twice at 415° in an attached, segmented, Vycor tube, the second time directly into the cell. The cell was then sealed off and the metal "chased" into the finger with a hand torch. All measurements of $CdCl_2$ and $Cd\text{-}CdCl_2$ were made in cells that had been chlorinated at 500° in the manner described under Materials. Following the chlorination of the cells the samples were sublimed in a segmented Vycor tube at 525°, the second time into the cell. (In the case of the dichloride the sample and cell were chlorinated before sublimation to minimize the production of free metal during the sublimation.) These cells were then sealed off from the line and the samples sublimed into the fingers with the aid of several tubular furnaces.

The cells for the all-gas phase measurements were degassed and then taken to the dry box where the weighed samples were loaded directly. After being loaded the cells were again evacuated and then sealed off for use. It should be noted that the cells used for the cadmium metal samples were not chlorinated. Preliminary runs demonstrated that either chlorination or rinsing with hydrochloric acid tended to introduce monochloride peaks in the metal spectra.

Optical Alignment and Reference Selection

Prior to any quantitative measurements, the apparatus was completely focused, aligned, and calibrated. During the preliminary work it was noted that satisfactory alignment and focusing could only be achieved after "warping" the sample compartment base to counter the distortion introduced in welding the cooling coils to the base. The compartment was "warped" by inserting thin spacers under one of its legs until the source could be properly focused according to the recommended procedure. The sample and reference were then aligned by a trial and error scheme of inserting thin spacers between the "feet" of the furnace and its carriage until both light paths indicated 100% transmission. The wave length calibration of the assembly was checked and found to be satisfactory using the Beckman 2260 mercury source according to the Company's instructions.

Following the condensed phase measurements a check of the sample and reference cells revealed that the cells were no longer matched. Apparently over the period of several runs the cell windows were slightly, but significantly, attacked. (It was earlier noted that $CdCl_2$, in particular, will severely attack quartz in the presence of a slight amount of moisture; 50 hours at 700° is sufficient to effectively frost a cell.) The loss of the matched cell and the difficulty encountered in positioning the firebrick blocks before each run prompted a decision to discard the use of a reference cell and all subsequent measurements were made using the empty reference hole as "reference".

Measurements

Spectral measurements of the gas phase above condensed cadmium, cadmium chloride, and a saturated solution of cadmium in the dichloride were taken between 2000 and 5000 Å. Similar measurements were also taken of the all-gas systems of cadmium metal, and mixtures of cadmium and cadmium(II) chloride. These measurements and those on empty cells were in each case made from room temperature through 750°. The choice of the particular spectral region investigated was made after preliminary studies with a tungsten source disclosed no interesting detail from 5000 to 20,000 Å. Higher temperatures were not investigated since above 800° the absorptions of the samples in a 100 mm cell were too large to be measured with any appreciable degree of accuracy.

During the runs the end heaters of the furnace were maintained 50° hotter than the center section in order to keep the cell windows at the same temperature as the rest of the cell. During the condensed phase measurements the finger was kept 15° cooler than the cylindrical portion of the cell. In this manner the finger temperature determined the vapor pressure of the sample and provided an area outside the light path for condensation.

Transmission measurements were made only after allowing the cell and sample to equilibrate for 45 minutes at each new temperature. It was noted during the initial survey runs that equilibrium conditions were actually attained in 10 to 12 minutes. Temperature measurements were made with the finger thermocouple immediately preceding and following each series of spectral measurements at a given temperature. Measurements during each run were taken both with increasing and decreasing temperature with reproducible results. During the cooling periods particular care was taken to see that the finger remained cooler than the rest of the cell. The actual transmission measurements were taken by balancing the reference signal on the reference cell or hole at a selected wavelength, then determining the relative per cent transmission of the sample cell and contents. This procedure was repeated for each wavelength at which measurements were taken. The wavelength was approached from the violet for every measurement to minimize errors due to "backlash" by the wavelength selector. A Corex filter (Beckman No. 2311) was employed as recommended between 3200 and 4000 Å to eliminate scattered light. The slit widths during the series of measurements dropped quickly from 1.4 mm at 2000 Å to 0.15 mm at 2288 Å and then gradually to 0.04 mm at 4000 Å after which it rose slightly due to the continued use of the hydrogen source in this region.

RESULTS

Excluding preliminary work some 10,000 individual transmission measurements were made during the course of this study. The sheer mass of this data prevents its reproduction in total in this thesis. Each piece of data was recorded as a per cent transmission (compared to a known reference) at a measured thermocouple EMF. To obtain the actual sample absorption and temperature it was necessary to correct and convert each measurement individually.

Data Correction

Thermocouple corrections were made directly from the calibration equation:

$$\Delta T_{corr.} = -3.83 \times 10^{-4}\ T_{meas.}\ (^{\circ}K) - 0.197,$$

after converting the thermocouple EMF to °K. The transmission corrections were more difficult. It was previously mentioned that the all-gas phase measurements were made without the use of an actual reference cell after it was noted that the sample and reference cells were no longer matched. A careful examination of the two cells subsequently revealed the sample cell transmitted only slightly less light than it did originally while the reference cell was substantially less transparent. This unexpected change was apparently due to exterior attack by a small piece of the Sauereisen which had become trapped between the cell window and the block. As a result suspicion was cast on the reliability of the runs made using this cell as the reference. Further studies indicated that the transmission of this reference cell, although poor, did not change appreciably over the normal period of a run, 50 to 100 hours. It was also noted that the transmission of an empty cell changed less than 5% from room temperature to 800° with 95% of that change occurring above 400°. After consideration of these factors the following correction scheme was adopted for the transmission values.

Under the assumption that the low temperature measurements (approximately 100°) of a run represent the relative transmission of an empty cell very closely (a good assumption since at this temperature the sample absorption is undetectable), these values were adopted as an internal corrected reference. This procedure has the advantage of implicitly correcting for any mismatching of the absorption cells in cases where a reference cell was employed and providing a "matched reference" for the other runs while correcting for any errors that may have been introduced through faulty positioning of the firebrick blocks or, indeed, the steel block itself. The actual corrections were obtained by drawing a calibration curve of %T (transmission) vs. wavelength for the low temperature values of each run and interpolating the correction values from this graph. The slight change in cell transmission exhibited at higher temperatures was accommodated by shifting the transmission values of the correction curve so that transmissions in the empty 4000 to 5000 Å region of both the correction and the sample curves were identical.

The corrected values of %T should by definition equal the quantity of light transmitted by the sample and cell divided by the quantity of light transmitted by the cell times 100,

$$\%T_{\text{corrected}} = I_{\text{sample + cell}} \times 100 / I_{\text{cell}}.$$

With

$$\%T_{\text{measured}} = I_{\text{sample + cell}} \times 100 / I_{\text{reference}}$$

and the above assumption that

$$\%T_{100^\circ} = I_{\text{cell}} \times 100 / I_{\text{reference}},$$

the corrected values of %T were calculated for each run by evaluating $\%T_{\text{measured}} / \%T_{100^\circ}$. Plots of these corrected transmissions vs. wavelength were used for all quantitative calculations and discussions herein.

Spectra

The spectra of cadmium vapor was measured over the condensed metal from room temperature through 750° and as an all gas system from 700 to 780°. The system is described in Table 1 and is illustrated in Fig. 5a. The spectra of

Table 1. Spectral systems of gaseous cadmium metal

Transition	Appearance[a]	Description
2288 Å	4.5×10^{-4} Torr 475°K	The major resonance peak broadens slowly and symmetrically at the base (100%T) from 0.5 Torr. By 10 Torr the peak begins to broaden asymmetrically to the red and by 135 Torr it has formed a sharp edge at 2200 Å and a wing extends to 3000 Å in the red.
3261 Å	0.08 Torr 585°K	The secondary resonance line, broadens symmetrically from the base at 85 Torr and asymmetrically to the red above 500 Torr.
2123 Å	2.5 Torr 700°K	A sharp peak which broadens very slowly and symmetrically from its first appearance.
2214 Å	2.5 Torr 700°K	A sharp peak which is absorbed into the 2288 Å band at 135 Torr.
3178 Å	50 Torr 840°K	A sharp band which tends to be absorbed by the 3261 Å line at pressures above 1 atm.

[a] Pressures and temperatures for the minimum detection of the vapor spectrum through a 100 mm path length.

gaseous $CdCl_2$ was only measured above the condensed phase from room temperature through 750° and is in itself rather uninteresting. The spectra is described in Table 2 and a typical absorption curve may be seen in Fig. 5b. The vapor phase spectra of the Cd-$CdCl_2$ mixture were measured over the two phase saturated solution and for a series of gaseous

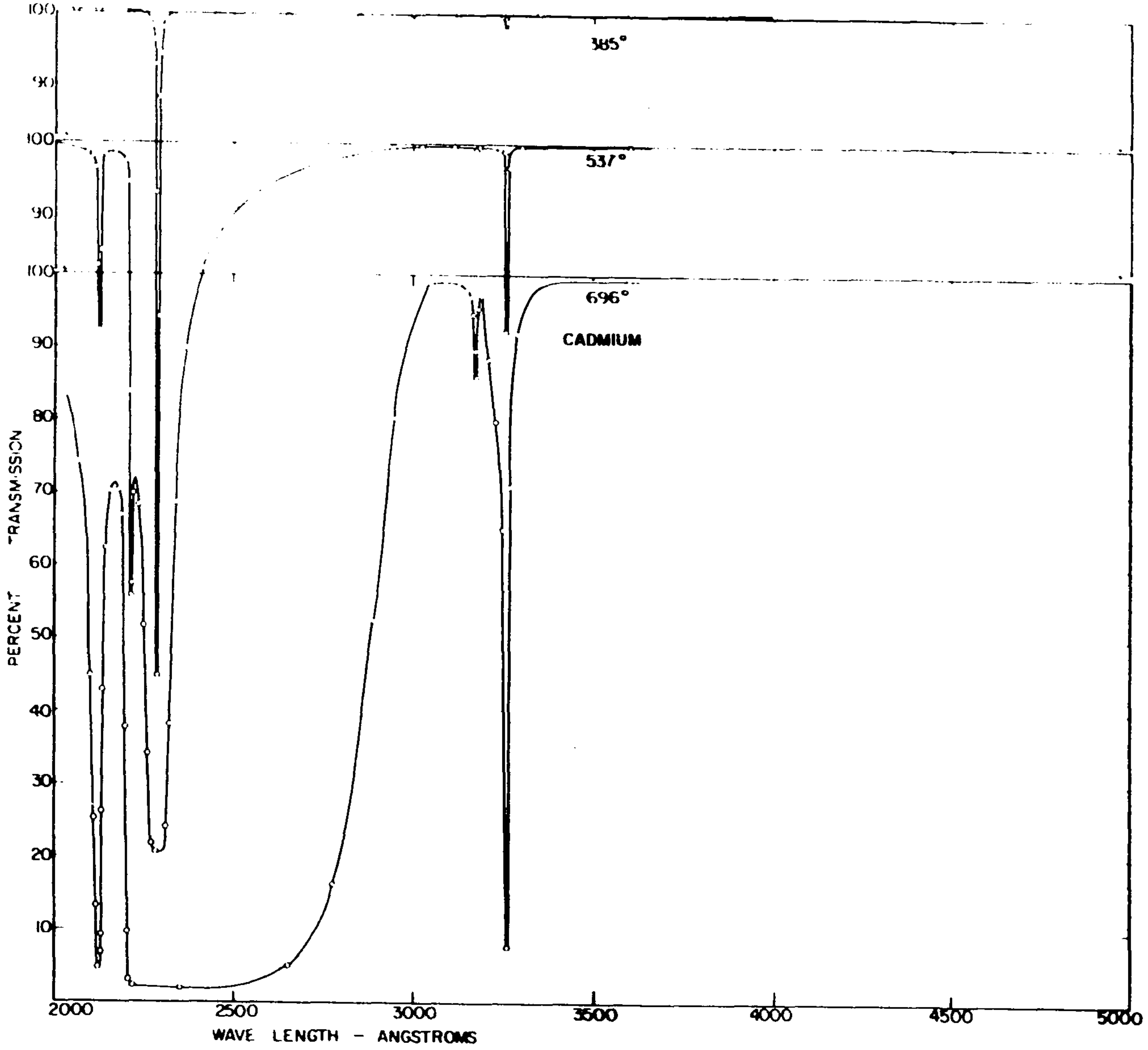

Fig. 5a. Typical Cd vapor phase spectra

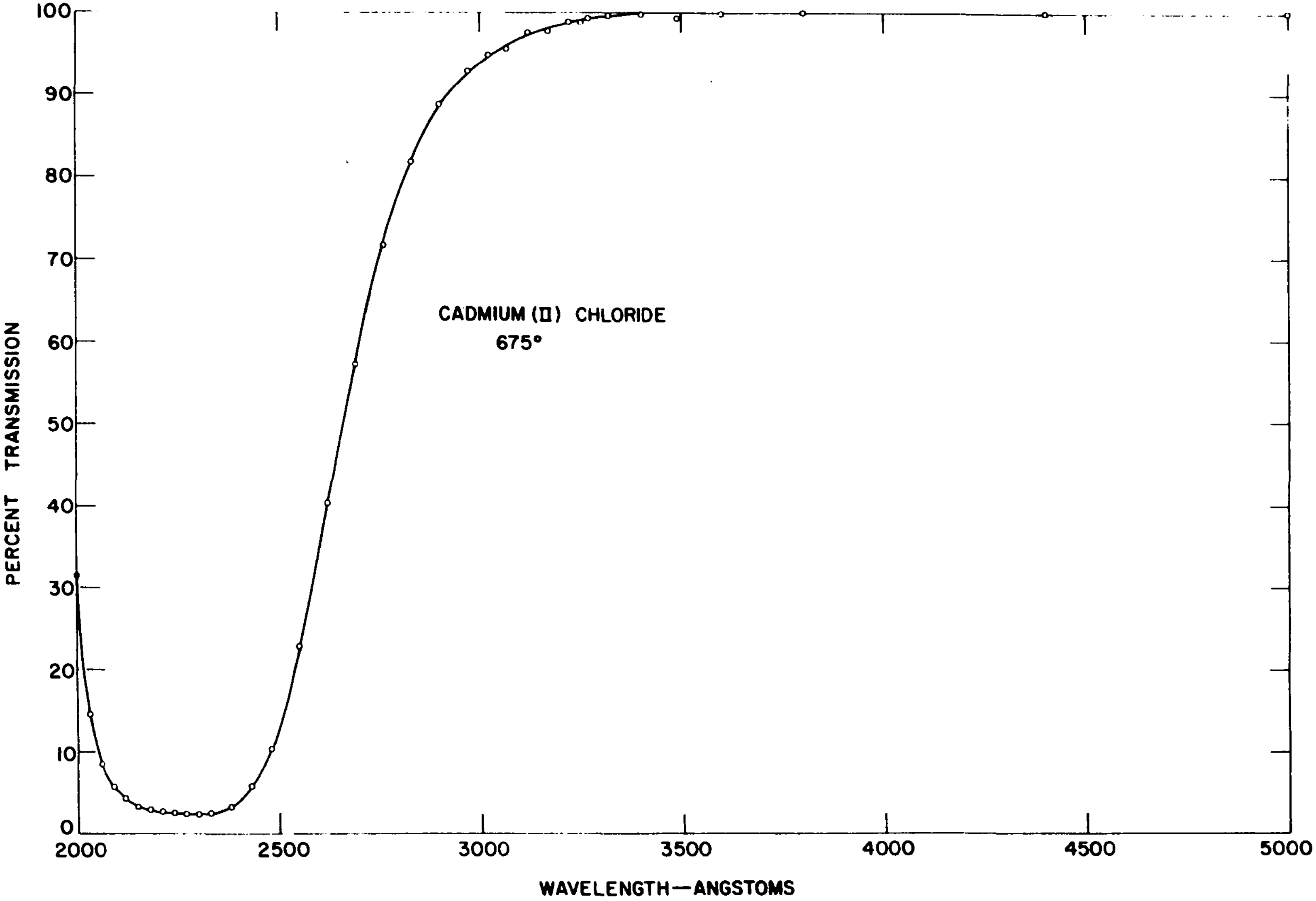

Fig. 5b. Typical $CdCl_2$ vapor phase spectra

Table 2. Spectral system of gaseous cadmium(II) chloride

Transition	Appearance[a]	Description
2000 Å	3×10^{-3} Torr 675°K	A broad, structureless band which is shaded to the red. With increasing pressure the band shifts to the red and is centered at 2400 Å and broadened to 3600 Å at 60 Torr (1025°K).

[a] Pressures and temperatures for the minimum detection of the vapor spectrum through a 100 mm path length.

mixtures of varying initial concentrations. The spectral components of these systems are summarized in Table 3 and a typical spectrum is presented in Fig. 6 with the Cd and $CdCl_2$ lines marked for reference. The most notable feature of the spectra of these mixtures was the observation of two series of lines extending toward the violet from strong transitions at 3070 and 3170 Å. These values correspond very well with the system of cadmium monochloride (CdCl) lines reported by Walters and Barratt (27). A thorough scanning of the entire spectral range of the instrument (2000 to 20,000 Å) failed to reveal any additional discrete lines or bands.

The spectrum of an empty absorption cell was quite uninteresting with one exception. It was found that the spectrum of an empty cell exhibited a sharp 2288 Å peak in

Table 3. Spectral systems of the gaseous cadmium-cadmium(II) chloride mixture

Transition	Assignment	Description
2050 Å	$CdCl_2$	Broad, structureless band shaded to the red at low concentration. Shifts to the red and is absorbed into a common continuum with Cd at high temperatures.
2123 Å	Cd	Small peak on the red edge of the 2050 Å. Absorbed into a common continuum at high temperature.
2214 Å	Cd	Small peak which is absorbed into the 2288 Å peak at higher temperatures.
2288 Å	Cd	Intense peak, broadened to the red and absorbed into a common continuum with $CdCl_2$ at higher temperatures.
3070 Å	CdCl[a]	Band head of a series of lines extending to the violet.
3170 Å	CdCl[a]	Band head of a series of lines extending to the violet.
3178 Å	Cd	Transition largely buried in the 3170 Å peak and detectable only at high concentrations.
3261 Å	Cd	Intense transition which broadens to the red at higher temperatures.

[a] See Appendix II for a compilation of the vibrational fine structure of the CdCl doublet.

every case after it had been used for a run with cadmium. This absorption corresponded to an apparent Cd pressure of 10^{-3} Torr and could not be removed by heating under vacuum or by washing with HNO_3 or aqua regia. The $CdCl_2$ runs also

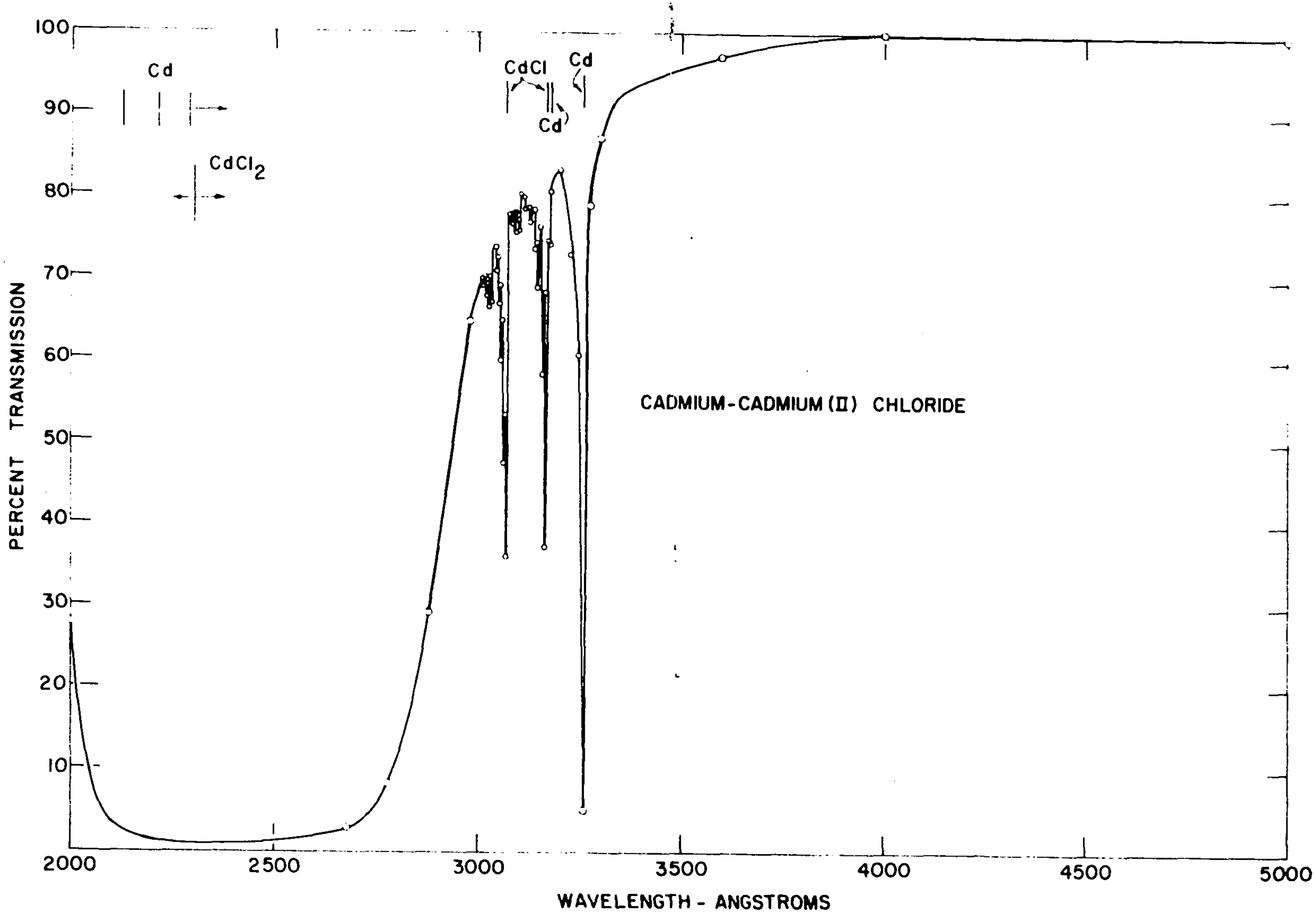

Fig. 6. Cd-CdCl$_2$ spectra with component bands indicated

exhibited a similar 2288 Å transition below 2 Torr which corresponded to a Cd pressure of 5×10^{-2} Torr or about 0.002% by weight of the $CdCl_2$, presumably due to a slight thermal decomposition. These observations are of no consequence in the quantitative studies that follow.

Numerical Data

The experimental data essential for the calculation of equilibrium species in the gas phase mixtures are tabulated in Appendix I. Appendix II contains the experimental values of interest for quantitative calculations of the condensed systems.

DISCUSSION

Identification of Species

A comparison of the transitions occurring in the spectra of the pure components with those present in the spectra of the Cd-$CdCl_2$ mixture clearly reveals the presence of the metal and the dichloride. The correspondence of the 3070 and 3170 Å transitions and their accompanying fine structure to the lines reported by Walters and Barrett (27) (see Appendix III) forms a positive identification for the presence of CdCl even though the wavelengths observed in this study are consistantly about 2 Å smaller. The inability to detect a transition at 3181 Å is most likely due to a faulty assignment on the part of the previous investigators. It seems quite likely that Walters and Barrett observed a transition due to the metal and erroneously assigned it to CdCl. Their failure to record the detection of the subsequently observed 3178 Å Cd line (31, 32) tends to support this contention.

It must be concluded from the absence of any further spectral systems that any additional species are absent or present in undetectable amounts unless masked by the broad Cd-$CdCl_2$ continuum, since it is unlikely that they would fail to exhibit some transition in the normal ultraviolet-visible region. If masked, evidence for the necessarily polymeric species could only be obtained by other means such as high temperature mass or far infrared spectra. There is, however, no evidence to suggest that such a species was present in significant concentration.

Vibrational Bands of CdCl

With the primary exception of the aforementioned 3181 Å transition and 2 Å wavelength displacement, the observations of the CdCl lines correspond very well with the reported literature values. However, while these discrepancies did not obviate the identification of the monochloride species they did indicate a need to re-examine the vibrational analysis Howell has presented (33) on the basis of Walter and Barratt's data. To this end Deslandres tables were prepared using the observed wavelengths and relative intensities. Assuming that the CdCl systems observed were due to a $^2\Pi - ^2\Sigma$ system and that only the Q heads were likely to be resolved, the intense 3070 and 3170 Å bands were assigned to the 0-0 transitions for the two expected systems and the other bands exhibiting relative intensities greater than one were assigned in decreasing order of intensity to the 1-1, 2-2, and 3-3 transitions (which have the greatest transition probability). It was then possible to assign all of the other bands in a very consistent manner, using Cornell's (34) value of 330.5 cm^{-1} for ω_e'' as a guide. The resulting table differs from Howell's in many assignments and is reproduced in Appendix III. Analysis of the first system, which is more complete, yields an average value of 328.24 cm^{-1}

for $\Delta G''$ or 334.5 and 1.25 cm^{-1} for ω_e'' and $\omega_e''x_e''$, respectively. ($\Delta G(\nu+1/2) = \omega_e - 2\omega_e x_e - 2\omega_e x_e \nu$ and $\omega_o = \omega_e x_e$.) These values and the values of 397.1 cm^{-1} and 0.92 cm^{-1} for ω_e' and $x_e'\omega_e'$ of the $^2\Pi_{1/2}$ state should be much more reliable than the data from Howell's assignments, being much more consistent and not including the 3181 Å band. A value of 419 cm^{-1} for ω_e' of the $^2\Pi_{3/2}$ state is less reliable, but in all cases the ground state values are in good agreement with Cornell's values.

Calculation of Equilibrium Species

Initially it was planned to individually measure the absorption of Cd and $CdCl_2$ vapors in equilibrium with their pure condensed phases over a range of temperatures and to calibrate these absorptions as a measure of the concentration with the aid of the known vapor pressures of the pure substances (see Appendix IV). To this end the transmission values for Cd and $CdCl_2$ at 3261 Å and 2900 Å, respectively, were plotted as log %T vs. P/T (which is proportional to concentration). The 2900 Å value for $CdCl_2$ was chosen as it offers the least interference with other transitions observed in the spectra of the mixtures. The plot of the Cd data can be very well described by a straight line between 10 and 100%T which indicates that the extinction coefficient (2.14×10^4 cm^2/mole) is independent of temperature over this range. The $CdCl_2$ plot deviated slightly from Beer's Law, displaying a slight curvature.

Using these calibration curves, the metal concentrations of the mixed gas phase runs were calculated and found to be in good agreement with those calculated from the amount of metal added initially. However, the calculated concentrations of $CdCl_2$ exceeded the initial concentrations even after correction for the background absorption of Cd at 2900 Å. This failure was apparently due to line broadening induced by the high concentration of metal vapor. The net effect was to obviate this avenue of concentration evaluation.

The second approach attempted was to use the apparent difference between the observed concentrations and that calculated from the weight added to evaluate the equilibrium concentrations of both $CdCl_2$ and CdCl using the stoichiometry, $CdCl_2(g) + Cd(g) = 2CdCl(g)$. In this manner a series of apparent equilibrium constants were evaluated over a range of temperatures and plotted as log K vs. 1/T ($\log K = -\Delta H°/2.3RT + \Delta S°/2.3R$). These values yielded a linear plot at low temperatures (700°), but the data rose almost exponentially at higher temperatures.

A second series of pseudo equilibrium constants were calculated from the relation,

$$K_a = (A_{CdCl})^2 / (C_{Cd}) (C_{CdCl_2}),$$

using the absorbance of CdCl at 3070 Å and deduced values for

Cd and $CdCl_2$ on the assumption that the observed absorbance values for the individual measurements would be a better measure of the relative concentration of CdCl after correction for the background absorbance of Cd and $CdCl_2$ (since the deduced values had been obtained as small differences between two sets of large numbers). In principle these values should produce a plot with the same slope as the first case, and an intercept which is offset by 2 log (ab) since the absorbance of a substance equals its extinction coefficient times the product of the sample path length and concentration. In practice the two plots were not quite parallel. Upon experimentation it was noted that very slight changes in the postulated CdCl concentrations, and consequently a small change in the concentrations of Cd and $CdCl_2$, resulted in significant improvements in the curves. A series of successive approximations produced two parallel, straight lines without changing the deduced concentration of the monochloride more than 8%.

Using the linear plot of log K_c vs. 1/T, a heat and an entropy for the reaction of the gaseous mixture were calculated. The heat of 39.5 kcal/mole seemed reasonable, but the entropy was an alarmingly large 31.8 eu (a ΔS of 10 being expected). Although it may be noted in Appendix I that the per cent transmission of cadmium in the mixture increases and thus the absorbance decreases with increasing temperature, the above results indicate that these values probably should not be taken literally as indicating a corresponding decrease in the metal concentration even though the absorbance of the CdCl species is simultaneously increasing. The most plausible reason for the apparent decrease in metal concentration is that there is a small decrease in the absorbance accompanying temperature dependent line broadening of the metal resonance line at constant concentration.

For the third approximation it was assumed that the concentration of the CdCl produced was too small to decrease the initial concentrations of the reactants significantly. Acting on this assumption a corresponding plot of log K_a vs. 1/T was constructed and found to yield a straight line without correction (see Fig. 7). This line has a slope yielding an apparent heat of 34.15 kcal/mole at 1000°K for three different experiments. It should also be noted that a high concentration run which could not be fit to the line in the first two treatments now yields a line parallel to the line of this calculation, differing therefore only by an additive constant which could be due to temperature dependent line broadening or a weighing error.

The reliability of this estimation of the heat can be established in two ways, by its internal variation or self consistency and by the agreement between the original assumptions and the equilibrium concentrations calculated

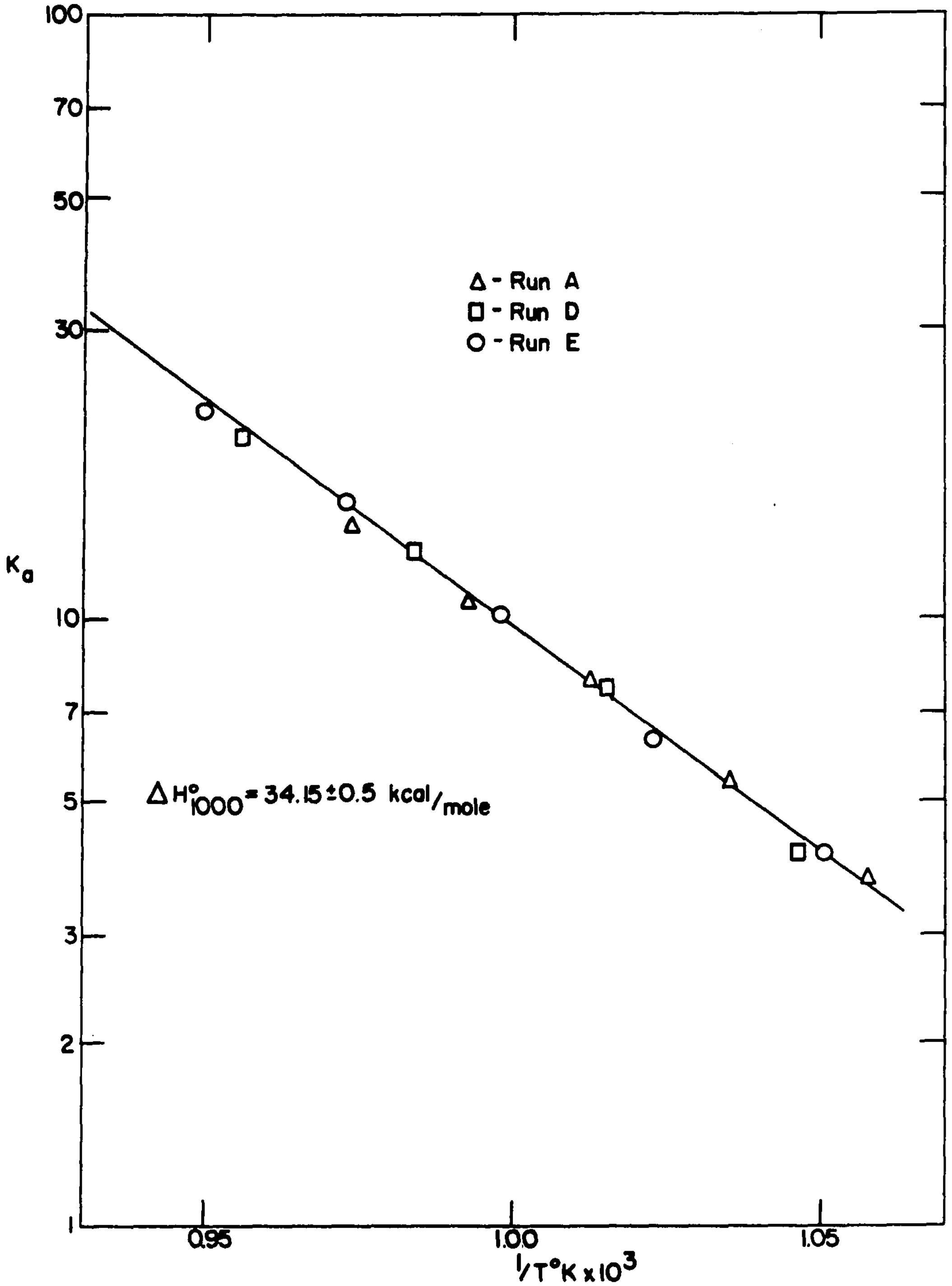

Fig. 7. Temperature variation of pseudo equilibrium constant, K_a

with the use of this heat and a third law entropy for the reaction. First, a least squares analysis of the data indicated a 95% confidence value of ± 0.5 kcal/mole for the heat and a 99.5% confidence level of ± 0.75 kcal/mole. Second, utilizing the thermodynamic values summarized in Appendix IV, one obtains 23.58 kcal/mole for ΔF°_{1000} of the reaction, $CdCl_2(g) + Cd(g) = 2CdCl(g)$, and hence an equilibrium constant of 7.03×10^{-6}. This value corresponds to a change of less than 1% in the reactants of the three runs and thus is consistent with the assumption that relatively little CdCl was produced. It would in principle be possible to accommodate these small concentration changes and slightly modify the resulting ΔH, but such a correction (0.2 kcal/mole) is probably not too meaningful considering the magnitude of the overall experimental error.

Thermodynamic Calculations

Having experimentally determined ΔH°_{1000} for the gaseous Cd-$CdCl_2$ reaction, it is interesting to consider some of the reactions for which thermodynamic values may now be derived or improved using this heat. Using the solubility data of Topol and Landis (3), it is possible to estimate a heat of reaction of 5.67 kcal/mole at 1000°K for cadmium metal dissolving in cadmium(II) chloride to form Cd_2Cl_2. This value combined with the heats of vaporization of Cd and $CdCl_2$ at 1000° and the heat of the gas phase reaction above yields a value of 84.45

kcal/mole for the heat of the reaction Cd_2Cl_2 (dissolved in $CdCl_2$) = $2CdCl(g)$.

One may also indirectly obtain a measure of the dissociation energy of CdCl, a quantity which is variously listed as being between 2.2 and 2.8 e.v. (35), by evaluating the relationship, $\Delta F^\circ/T = \Delta(F_T^\circ - H_{298}^\circ/T) + \Delta H_{298}^\circ/T$, for the reaction, $CdCl_2(g) + Cd(g) = 2CdCl(g)$. ΔF_{1000}° was previously found to be 23.58 kcal/mole and the data in Appendix IV give a value of -11.76 cal/mole-deg for $\Delta(F_T^\circ - H_{298}^\circ/T)$ at 1000°K thus requiring that $\Delta H_{298}^\circ = 35.34$ kcal/mole. Using the following heats:

$$\begin{array}{ll}
CdCl_2(g) = Cd(s) + Cl_2(g) & \Delta H_{298}^\circ = 50.40 \text{ kcal/mole} \\
Cd(s) = Cd(g) & \Delta H_{298}^\circ = 26.78 \text{ kcal/mole} \\
2Cd(g) + 2Cl(g) = 2CdCl(g) & \Delta H_{298}^\circ \quad -2D_o^\circ \text{ kcal/mole} \\
Cl_2(g) = 2Cl(g) & \Delta H_{298}^\circ = 57.88 \text{ kcal/mole} \\
\hline
CdCl_2(g) + Cd(g) = 2CdCl(g) & \Delta H_{298}^\circ = 135.06 - 2D_o^\circ
\end{array}$$

one may arrive at a value of 49.86 kcal/mole (2.17 e.v.) for the dissociation energy of the monochloride using no thermodynamic value more uncertain than 0.5 kcal. This corresponds well with Gaydon's estimate of 2.0 ± 0.5 e.v. (35) and indicates that the value obtained by a linear Birge-Sponer extrapolation and cited by Herzberg (26) is too large.

It is also possible to estimate a heat for the dissociation of the Cd_2 molecule from the spectra of the Cd vapor.

Using the values in Appendix I for the 3178 Å transition of Cd_2 and proceeding in a manner analogous to that described for the Cd-$CdCl_2$ reaction one obtains a value of 1.67 ± 0.2 kcal/mole in good agreement with the 2.0 ± 0.5 kcal/mole quantity reported by Kuhn and Arrhenius (36).

Predictions and Correlations

Collected in Table 4 is a compilation of the dissociation energies of the gaseous zinc, mercury, and cadmium monohalides and the heats of reaction of group IIb metal-metal halide mixtures. Where possible experimental or calculated data are provided; the remaining values are estimates or interpolations by the author. $\Delta S°$ for the reactions tabulated is generally of the order of 11 e.u. so that equilibrium concentrations can be readily calculated.

Future Work

Even a short perusal of Table 4 serves to indicate the lack of accurate thermal data in this area of high temperature chemistry. While in a sense it would be desirable to extend this study and systematically determine the properties of the other halides of this group, there remains the fact that this study has really served to definitively establish the existence of group IIb subhalides in the gas phase under equilibrium conditions. (All other experimental values listed in Table 4 were derived from studies of the dissociation of

Table 4. Group IIb monohalides: D_o for MX(g) and ΔH° for $MX_2(g) + M(g) = 2MX(g)$

Monohalide	D_o (source)[a]	ΔH° (source)[a, b]
ZnF	75 (est.)	34 (est.)
ZnCl	59 (35)	49 (est.)
ZnBr	50 (est.)	32 (est.)
ZnI	41 (35)	18.5 (est.)
CdF	65 (est.)	23.3 (est.)
CdCl	49.85 (this study)	35.48 (this study)
CdBr	37 (35)	43 (est.)
CdI	32 (35)	21.5 (37) - 0°K
HgF	32 (35)	60.5 (est.)
HgCl	23 (26)	53 (38) - 0°K
HgBr	16 (26)	57 (est.)
HgI	8.3 (39)	51.95 (39) - 0°K

[a] Given in kcal/mole.

[b] T°K = 298.15°K unless otherwise specified.

the dihalides - in no case was the monohalide concentration directly measured.) Likewise the thermodynamic values obtained for this system are sufficiently accurate to serve as a guide for predictions and estimations for the other members of the group IIb family, although additional experimental data are always desirable.

There remains the promise of the spectroscopic method as a neat and readily adaptable tool for making high temperature identifications and quantitative analyses. The method is particularly well suited for the study of equilibriums because of its ability to simultaneously measure values for a number of components, any one or all of which may be present in significant quantities.

A few specific problems have arisen or have been suggested during the course of this work and should be mentioned here. The observation that cadmium can act as a mercury "getter" at room temperature prompts one to feel that a study of the Cd-Hg gas phase system might yield an interesting equilibrium and an original determination of the molecular constants of the hypothetical CdHg molecule. The experimental conditions for this study would be well within the reach of most modified spectrophotometers.

The repeated observation of the Cd 2288 Å line in "empty" cells also indicates an area needing investigation. The significant question is whether this line is due to cadmium atoms trapped or bound to the cell walls. The extremely small amounts of metal involved make this a most difficult problem for conventional methods of surface chemistry and might present an excellent opportunity to expand the application of high temperature infrared spectroscopy.

Another problem which involves many aspects of surface chemistry, as well, is the corrosion of the quartz cell by $CdCl_2$ containing small traces of moisture. The spectroscopic techniques described herein should suffice to at least identify the species involved and probably would permit a determination of the equilibrium thermodynamics and the kinetics as well.

Lastly, two problems typical of those suggested by the early literature consulted during the course of this work should be mentioned. Twenty years ago, Howell (33) noted that the reported spectra of ZnBr could not be analyzed in a manner consistent with the other group IIb monohalides. He stressed the need for a re-examination of this system - to date no further work has been performed. Nearly forty years ago, Gucker and Munch (17) studied the sublimation of "calomel", noting that above 250° it quantitatively disproportionated. They also observed, however, that below 200° it was possible to sublime the salt without decomposition while $HgCl_2$ and Hg under the same conditions did not combine to form Hg_2Cl_2. The nature of the vapor phase species in this system certainly should be investigated. Initially, a survey of the visible and ultraviolet region would probably be most interesting provided that the length absorption cell required at this low temperature could be accommodated. If, indeed, there is a dimeric species present the infrared spectra should also be studied.

Almost every family in the periodic table has been investigated spectroscopically, but the large majority of these investigations were also made in the late 1920's and early 1930's. Not only have there been many technical advances since then, but upon consideration there appears in many cases to be considerable doubt about the assignments and even the actual species being observed (most often due to the lack of really pure materials). In addition few of these studies have pertained to equilibrium systems, but rather most have been attempts to detect new spectroscopic entities (often in arcs, flames, or discharge tubes). A large percentage of the thermal data presently available for high temperature reactions rests only on statistical calculations based on these early measurements. There very obviously exists a need to selectively provide corroborating experimental evidence.

Among the systems which might well be advantageously studied spectroscopically are the metal-metal halide systems of Ba, Sn, Sb, Ga, Te, Pb, and Be. In each case the metals have significant vapor pressures at rather low temperatures making ordinary static pressure measurements impossible and transpiration studies difficult. Even more significant, each metal has at least one moderately strong absorption transition which could be used to monitor its concentration. Although such metals as Cr and Mn are not low melting, nor are their salts, they too exhibit strong absorption transitions and thereby, in principle, could be studied in a gas phase reaction by spectral means.

Experimentally, the problem of high temperature absorption spectroscopy rests not so much with attaining the temperature or containing the sample as with retaining the accuracy and precision of measurement under the influence of furnace radiation above 500°. There is now little question, that reversed optics are essential. The second problem is that of source intensity. Gas phase absorption measurements require a long absorption cell and consequently conventional sources are often unable to provide sufficient intensity with the slit widths needed for good resolution. Recently, however, high pressure xenon lamps, 100 times more intense than an H_2 lamp, have become available and should alleviate this problem.

A number of small problems have occurred in the course of this study and should be considered when modifying or purchasing a spectrophotometer. In view of the labor required to carefully scan the optical range of the modern manual instruments, it is almost essential that one utilize a recording instrument. A large part of the optical problem periodically experienced in this study was attributable to the fact that the sample cell of this instrument assembly was continually moved back and forth and thereby lacked a stable and secure positioning. It is strongly recommended that a double-beam instrument be employed whether or not actually using matched cells for quantitative runs. Lastly, it is exceedingly important to very thoroughly insulate the sample cell. At 1000°K even hair lines become heat leaks. It is particularly essential to protect the cell windows and to this end it is recommended that extra quartz plates be inserted at the ends of the furnace assembly to aid in maintaining the cell windows at the same temperature as the cell body. This study has also led the author to believe that it would be extremely advantageous and perhaps even necessary to have an instrument capable of operating with sample temperatures up to 1500°C.

For the present, this study should also provide encouragement for those researchers with a limited budget and an excess of spare time. For certainly very stimulating and significant research can be accomplished with a modest expenditure utilizing a spectroscopic system like that described herein.

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APPENDIX I

Table 5. Cadmium metal all-gas phase data

Temp. °K	%T (3261 Å)	%T (3178 Å)	P/T (Cd)[a]	Absorbance (Cd_2)
989.2	8.7	83.8	0.3167	0.077
1008.0	8.8	84.1	0.3133	0.0775
1048.5	9.2	84.3	0.3080	0.074

[a] Based on the 3261 Å transmission.

Table 6. Cadmium-cadmium(II) chloride

Temp. °K	%T (3261 Å)	%T (3070 Å)	%T (3170 Å)	Absorbance (CdCl)[a]
951.9	26.2	75.8	76.0	0.102[b]
977.7	26.4	71.4	71.2	0.128[b]
1001.9	26.7	66.1	65.9	0.162[b]
1027.7	26.7	60.3	59.8	0.201[b]
1052.4	27.3	55.0	53.8	0.241[b]

[a] Corrected for Cd and $CdCl_2$ background.

[b] Run E: P/T(Cd) = 0.1841; P/T($CdCl_2$) = 0.0140.
All P/T values are in Torr/°K.

Table 6. (Continued)

Temp. °K	%T (3261 Å)	%T (3070 Å)	%T (3170 Å)	Absorbance (CdCl)[a]
945.6	26.2	81.0	82.0	0.078[c]
965.6	26.5	78.1	77.6	0.094[c]
987.4	26.8	74.7	74.6	0.014[c]
1006.4	26.8	71.6	70.5	0.133[c]
1026.4	27.5	68.2	70.2	0.153[c]
955.6	28.2	74.7	75.4	0.107[d]
985.4	28.4	68.3	69.9	0.146[d]
1016.1	28.5	62.4	61.9	0.189[d]
1045.6	28.7	55.5	58.2	0.236[d]

[c] Run A: P/T(Cd) = 0.1884; P/T($CdCl_2$) = 0.0090.

[d] Run D: P/T(Cd) = 0.1623; P/T($CdCl_2$) = 0.0171.

APPENDIX II

Table 7. Cadmium metal

Temp. °K	%T (3261 Å)	%T (3178 Å)	%T (3072 Å)	P/T[a]	Absorbance (Cd_2)
928.4	19.2	94.2	99.2	0.2052	0.0155
968.0	7.6	85.8	98.9	0.3412	0.066
987.8	4.8	80.5	98.7	0.4242	0.084
1003.5	3.8	72.1	98.6	0.5062	0.142
1018.34	3.0	64.1	98.5	0.6037	0.194

[a] Calculated from the known vapor pressure - Appendix IV.

Table 8. Cadmium(II) chloride

Temp. °K	%T (3070 Å)	%T (3170 Å)	P/T[a]
899.3	99.2	99.6	0.00712
923.4	97.5	98.5	0.0112
947.6	96.1	98.1	0.0172
972.0	94.6	97.4	0.0259
997.9	89.8	94.6	0.0388
1022.1	84.1	91.3	0.0555

[a] Calculated from the known vapor pressure - Appendix IV.

Table 9. Cadmium-cadmium(II) chloride

Temp. °K	%T (3261 Å)	%T (3070 Å)	%T (3170 Å)	P/T (Cd)[a]
817.6	74.7	98.0	98.1	0.039
869.1	52.5	94.3	94.6	0.089
902.3	34.3	86.2	85.0	0.144
936.3	18.6	69.1	68.0	0.227
968.7	6.1	43.9	43.8	0.340
993.2	3.3	25.0	25.0	0.451
1018.0	1.8	11.0	12.4	0.592

[a] Calculated from the known vapor pressure - Appendix IV.

APPENDIX III

Table 10. Vibrational bands of the CdCl spectrum

Wavelength[a] (Å)	Wavelength[b] (Å)	Wavenumber (cm^{-1})
3181 (5)[c]		
3174 (2)	-[d]	
3172 (5)	3170 (10)[c]	31545
3163 (3)	3161 (4)	31635
3152 (1)	3150 (1)	31746
3145 (0)	3141 (0)	31816
3134 (0)	3128^{+}(00)	31964
3127 (0)		
3120 (00)		
3115 (00)		
3104 (0)	3102^{+}(1)	32242
3100 (0)		
3097 (0)	3095 (1)	32310
3090 (0)	3089 (0)	32372
3083 (0)	3082^{+}(00)	32440
3077 (0)		
3074 (2)	-[d]	
3072 (5)	3070 (10)	32573
3066 (4)	3064 (7)	32637
3060 (3)	3058 (3)	32701
3054 (2)	3052 (2)	32765
3047 (1)	3046 (0)	32830
3042 (1)		
3036 (0)	3033 (1)	32970
3030 (0)	3027^{+}(1)	33030
3023 (0)	3022 (00)	33091
3018 (0)	3016 (00)	33156

[a] Walters and Barratt (27).

[b] This study.

[c] Relative intensities in parentheses.

[d] P bands which would have been masked by the intense Q center.

Table 11. Deslandres table of the CdCl bands with vertical and horizontal differences

v' \ v"	0		1		2		3		4
0	32573(10)	331	32242(1)						
	397		395						
1	32970(1)	333	32637(7)	327	32310(1)				
			393		391				
2			33030(1)	329	32701(3)	329	32372(1)		
					390		393		
3					33091(00)	326	32765(2)	325	32440(0)
							391		390
4							33156(00)	326	32830(0)
0	31545(10)		–[a]						
	419								
1	31964(00)	329	31635(4)		–[a]				
2					31746(1)				
3							31816(0)		

[a] The slight bulge observed near 3200 Å in the violet wing of the 3261 Å Cd line may indicate the presence of these bands.

APPENDIX IV

Table 12. Collected thermodynamic properties - cadmium

Property	Value	Source
$\Delta H^\circ_{sub.}(0^\circ K)$	26.78 kcal/mole	(40)
$\Delta H^\circ_{vap.}(1038^\circ K)$	23.86 kcal/mole	(41)
Cp(g)	4.97 cal/mole	(42)
Cp(l)	7.10 cal/mole	(42)
Cp(s)	$5.31 + 2.94 \times 10^{-3}$ T cal/mole	(42)
S°_{298}	40.07 e.u.	(43)
S°_{1000}	46.08 e.u.	(43)
$H^\circ_T - H^\circ_o(298.15^\circ K)$	1481.36 cal/mole	calculated statistically
$H^\circ_T - H^\circ_o(1000^\circ K)$	4968.5 cal/mole	calculated statistically
$(F^\circ_T - H^\circ_{298}/T)_{(1000^\circ K)}$	-42.60 cal/mole deg.	(43)

Table 13. Collected thermodynamic properties - cadmium (II) chloride

Property	Value	Source
$\Delta H^{\circ}_{sub.}(0°K)$	42.03 kcal/mole	(44)
$\Delta Cp(s-g)$	$-2.23 -1.452 \times 10^{-2}$ T cal/mole	estimated from data in (45)
$\Delta Cp(l-g)$	-10 cal/mole	(45)
$\Delta H^{\circ}_{f}(gas)(298.15°K)$	-50.4 kcal/mole	(46)[a]
S°_{298}	68.03 e.u.	(46)
S°_{1000}	85.55 e.u.	calculated statistically using molecular constants from (46)
$H^{\circ}_{T} - H^{\circ}_{0}(298.15°K)$	3432.25 cal/mole	calculated statistically using molecular constants from (46)
$H^{\circ}_{T} - H^{\circ}_{0}(1000°K)$	13665.56 cal/mole	calculated statistically using molecular constants from (46)
$(F^{\circ}_{T} - H^{\circ}_{298}/T)$ (1000°K)	-75.35 cal/mole deg.	(46)

[a] This reference includes data on all of the group IIb halides.

Table 14. Collected thermodynamic properties - cadmium monochloride

Property	Value	Source
S°_{298}	60.4 e.u.	(42)
$S^\circ_T - S^\circ_{298}$(1000°K)	10.65 e.u.	(47)
$H^\circ_T - H^\circ_0$(298.15°K)	2316.31 cal/mole	calculated using molecular constants from (47)
$H^\circ_T - H^\circ_0$(1000°K)	8511.04 cal/mole	(47)

Table 15. Vapor pressure equations[a]

	Equation
Cd(liq.):	$\log P_{Torr} = -5697.5/T - 1.07 \log T + 11.5584 + 3.65 \times 10^{-5} T$
Cd(sol.):	$\log P_{Torr} = -5903.2/T - 0.171 \log T - 0.321 \times 10^{-3} T + 9.6234$
$CdCl_2$(liq.):	$\log P_{Torr} = -9183/T - 5.03 \log T + 25.876$
$CdCl_2$(sol.):	$\log P_{Torr} = -10{,}462/T - 1.59 \times 10^{-3}T - 1.13 \log T + 17.3248$

[a] Adjusted to be consistent at the melting point and calculated from the thermodynamic properties listed in this appendix with the exception of $CdCl_2$(l) for which the equation was taken from reference (44).