produced by water.[14] Comparing the bands of the anhydrous nickel(II) acetylacetonate with the hydrated ion, one observes that the effective ligand field splittings are approximately equal.

Ni(AA)_2 (cm.$^{-1}$)[6]	$\text{Ni(AA)}_2\cdot 2\text{H}_2\text{O}$ in CH_3OH (cm.$^{-1}$)[6]	$\text{Ni(H}_2\text{O)}_6^{++}$ (cm.$^{-1}$)[15]
8,810	9,217	8,500
12,900	(13,423)	13,500
15,280	15,873	15,400

The decrease in the apparent ligand field strength of the acetylacetonate anion relative to water in the Ni(II) complex presumably can be described in part as due to the specific configuration of the anhydrous nickel(II) acetylacetonate. In the trimer, the Ni–Ni distance is ~2.8 Å.,[16] implying metal–metal interaction. Since the t_{2g} orbitals of the nickel atoms give maximum density between the ligand atoms, the presence of filled t_{2g} orbitals from the adjacent nickel atom or atoms in the octahedral faces should lead to decreased stability of the t_{2g} orbitals and increased stability of e_g orbitals. Consequently the ligand field splitting produced by the acetylacetonate in the trimer would be smaller than expected in the absence of nickel–nickel interactions. The approximately equal splittings observed in the trimeric acetylacetonate and the aqueous Ni(II) complex qualitatively coincide with a weakened acetylacetonate field. Nickel–nickel interaction is removed in forming the $\text{Ni(AA)}_2\cdot 2\text{H}_2\text{O}$. Thus one expects a slightly larger ligand field splitting in this molecule compared with the aqueous Ni(II) species. The observed spectrum[6] of $\text{Ni(AA)}_2\cdot 2\text{H}_2\text{O}$ does not contradict this conclusion. The spectral shifts are too small to conclusively show the above reasoning to be valid, however. Furthermore the effect of distortion from an octahedral configuration should be considered when quantitatively comparing the spectra of the acetylacetonates with the aqueous Ni(II) species.

Acknowledgments.—Gratitude is expressed to Professors W. B. Schaap and R. E. Connick for their helpful discussion of this work and to Professor F. Albert Cotton for his stimulating thoughts leading to other communications on this subject.

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[14] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 311 (1956), indicate that both the acetylacetonate anion and water produce stronger fields than the oxalate anion but weaker fields than ammonia. R. H. Holm (Ph.D. Thesis, M.I.T., 1959) has compared spectral data for M(OX)_3, $\text{M(H}_2\text{O)}_6$ and M(AA)_3 complexes of V(III), Cr(III), Mn(III), Fe(III), Co(III) and Rh(III). It appears that the fields in $\text{M(H}_2\text{O)}_6$ are ~5% greater than those in M(OX)_3 and ~5% less than in M(AA)_3, but there are complications in some of these spectra which raise some doubt about the validity of these crude generalizations.

[15] A. D. Liehr and C. J. Ballhausen, *Ann. phys.*, **6**, 134 (1959).

[16] G. J. Bullen, *Nature*, **177**, 537 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.]

The Equilibrium of α-Silver–Zinc–Cadmium Alloys with Zinc and Cadmium Vapors[1]

BY GEORGE SCATCHARD AND TUNG-PO LIN

RECEIVED MAY 13, 1961

An improved hollow cathode discharge tube has been developed which gives simultaneously the spectra of zinc and cadmium intense enough to be measured with a photomultiplier tube and galvanometer without further amplification, even after the light beam is halved by splitting mirrors and monochromated in a spectrograph. The vapor pressures of both zinc and cadmium in four ternary α-silver–zinc–cadmium alloys have been determined at several temperatures by means of the absorption of their resonance lines. The results are combined with earlier ones for the binary α-silver–zinc and α-silver–cadmium alloys to determine the thermodynamic properties of the ternary alloys.

The method of determining vapor pressures by the measurement of the absorption of the resonance line is particularly adapted to the study of mixed vapors because it determines directly the concentration of each component. The method of Scatchard and Boyd[2] of measuring the absorption photoelectrically has been applied to the vapor pressures of both zinc and cadmium from four ternary α-silver–zinc–cadmium alloys and the results have been combined with those of Scatchard and Westlund[3] for α-silver–zinc and those of Scatchard and Boyd for α-silver–cadmium[2] binary alloys to obtain analytic expressions for the thermodynamic properties of the ternary alloys.

A marked improvement in the hollow cathode discharge tube has permitted several developments which have increased the precision of the measurements.

Light Source.—It was important to have a single light source for both cadmium and zinc to avoid realigning the apparatus after each measurement. Hollow cathode lamps with the two metals electroplated successively were unsatisfactory because they became unsteady and flickering after a short time. The fact that they required at least seven days baking to give a satisfactory small degassing rate indicated that the difficulty was due to contamination from the plating solutions. We made a satisfactory source by reducing the impurities to a very low level. It was essentially the same as the one previously used,[2] but several changes were made.

The first change was to replace the Pyrex window with a quartz window and a graded quartz–Pyrex

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[1] Taken from the Ph.D. Thesis of Tung-Po Lin, M.I.T., 1958; Frank M. Shu Scientific Fellow during 1955–1957. The spectroscopic work was carried out in the Spectroscopy Laboratory of M.I.T. This work received financial support from the United States Atomic Energy Commission.

[2] G. Scatchard and R. H. Boyd, *J. Am. Chem. Soc.*, **78**, 3889 (1956).

[3] G. Scatchard and R. A. Westlund, Jr., *ibid.*, **75**, 4189 (1953).

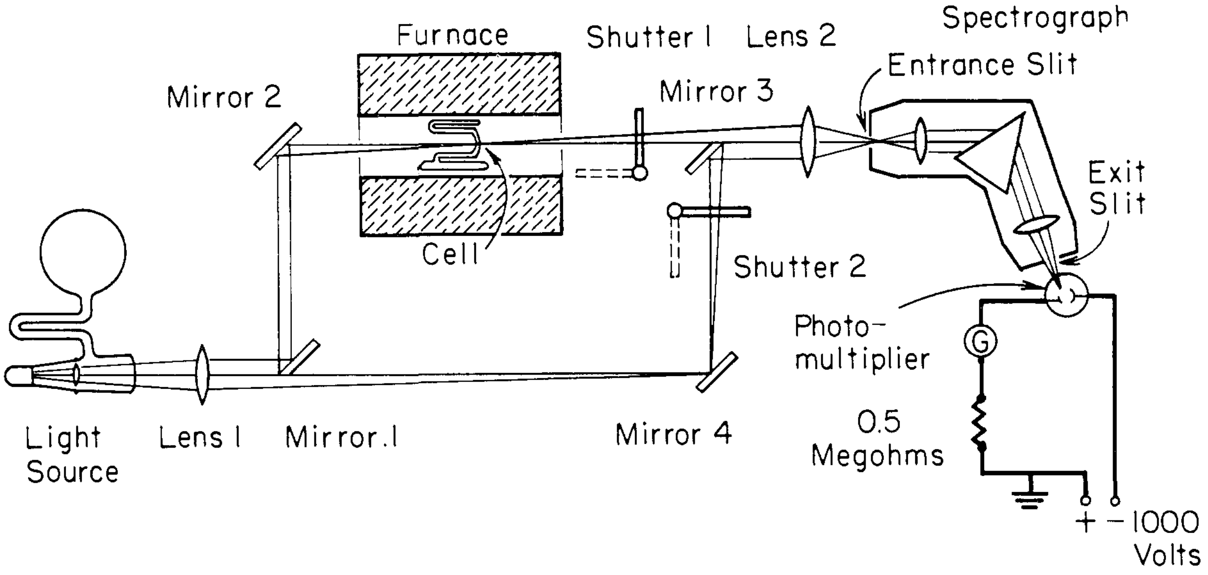

Fig. 1.— Optical system.

seal to permit transmission of the zinc line and more complete transmission of the cadmium line.

The second change was to replace the aluminum anode by a tungsten ring which was much less oxidizable in the fabrication of the tube and could be cleaned if necessary by electrolysis in 20% potassium hydroxide with 10 volts alternating current after the tube was assembled.

The third change was to attach to the tube a two-liter bulb to give a large reservoir of argon.

The fourth and most important change was to coat the cathode with the metals by melting them in the arc instead of by electroplating. After the tube was assembled, the kovar cup for the cathode was cleaned successively with 6 *N* HCl, water, 12 *N* HCl, water, 9 *N* HNO_3, water, 6 *N* HCl, water, pure acetone. The tube was dried in a stream of nitrogen and then in an oven at 120° Pure zinc and pure cadmium chips were dropped into the cup, and the tube was attached to the vacuum line with the cup at the bottom and the window at the top. The tube was evacuated to 10^{-5} mm., then about 10 mm. of pure argon was admitted and the tube was evacuated again to 10^{-5} mm. A cylindrical electrical oven was slipped over the tube, an insulating cap was placed around the bottom and the tube was baked at 150° for at least 4 hr. Near the end of the baking period the flask was flamed for at least ten minutes. The insulating cap was removed and the furnace raised slightly, and the tube was heated for twenty minutes more to drive any metal from the window and upper part of the tube back to the cup. About 7 mm. of pure argon was admitted, about 250 volts d.c. was applied across the electrodes and the discharge was started with a Tesla coil. A current of about 20 mamp. was maintained for several hours without cooling water around the kovar cathode. The heat melted the metal chips and molten alloy formed a film on the cathode walls. The discharge was stopped after the chips were almost completely melted, and the tube was again evacuated to 10^{-5} mm. About 4 mm. of pure hydrogen gas was admitted and the discharge was maintained for about an hour without cooling the cathode. The tube again was evacuated to 10^{-5} mm. Then cooling water was circulated around the cathode, 2–3 mm. of argon were admitted and the discharge started with about 30 volts d.c. The voltage and the argon pressure were adjusted until both zinc and cadmium spectra were clearly visible through a hand spectroscope. An argon pressure of 2.5 mm. and a current of 40 mamp. were usually satisfactory. After a discharge of at least 4 hr. the tube was sealed off from the vacuum line.

A tube thus prepared gives strong resonance lines of both zinc (3076 Å.) and cadmium (3261 Å.). The two lines are of about equal intensity so the vapor pressures of both metals from the ternary alloy can be measured without interruption and realignment of the optical system. The intensities are great enough so that it is possible to use fixed splitting mirrors instead of rotating ones and also to measure the output of the photomultiplier tube with a sensitive galvanometer without amplification. The intensities are sufficiently free from flicker and fluctuations so that they may be measured directly without a reference beam.

Optical System.—The optical system consisted of two quartz lenses, four first-surface mirrors, two rotary shutters and a Hilger Medium Quartz Spectrograph (Fig. 1). Mirrors 1 and 3 stood half way in the optical path so that one half the beam was reflected by mirrors 1 and 2 through the cell and the other half was reflected by mirrors 4 and 3 around it. Both shutters stood ordinarily in the optical paths so that no light would go through lens 2. The mirrors were first-surface-aluminized mirrors purchased from the Edmund Scientific Corporation of Barrington, New Jersey. They were firmly fastened with beeswax to brass stands which were clamped to the optical bench by contour clamps. Their positions and orientations were adjusted so that the two light paths were parallel and of the same length. Lens 1 was adjusted so that the image of the source was focused on the windows of the absorption cell in the furnace, and lens 2 was adjusted to focus the image on the entrance slit of the spectrograph.

The use of beam-splitting mirrors and shutters rather than rotating mirrors reduces the experimental error greatly by eliminating all moving parts in the optical system.

The exit slit assembly was the same as that used by Boyd[2] except that a set of gears was attached to maneuver the micrometer and a new scale was made for the micrometer reading. Its smallest division represents 12.70 microns and is readable to 0.5 division. The entrance and exit slit openings were 25 and 50 microns, respectively.

The photomultiplier was a 1 P 28 (R.C.A.) tube sensitive in the ultraviolet. It was powered by the 1000 volts regulated d.c. supply described by Boyd.[2] It was connected through a 0.5 megohm resistance to a Leeds and Northrup Type E self-contained galvanometer No. 2430d. The sensitivity is 0.0005 microampere per division, and it can be read to 0.2 division.

The photocurrent produced was of the order of 0.02 microampere. The dark current, almost entirely from leakage through the base of the photomultiplier, was about 0.004 microampere and stayed fairly constant. It was subtracted from the current reading during an intensity measurement.

The absorption cell was the quartz vessel used by Boyd which differs from that used and described by Westlund[3] only by having the vapor space between the windows 1 mm. instead of 10 mm. The furnace and controller were the same as those used by Westlund and Boyd, but the power supply for the heaters was changed from d.c. to a.c. and the currents were regulated by Variacs. Preliminary experiments determined the appropriate settings for the Variacs and the difference between the heating currents during the on and off parts of the controller cycle.

Materials.—The hydrogen was supplied by the Air Reduction Company in high pressure tanks. It contained less than 0.5% impurities.

Highest grade argon was supplied by the Air Reduction Company in one-liter flasks with drop-break seals. It was guaranteed to contain less than 0.01% impurities.

Silver pellets, guaranteed to contain less than 0.05% total impurities, were obtained from Handy and Harman Company, New York, New York.

Cadmium bars, guaranteed to contain less than 0.02% total impurities, and zinc bars, guaranteed to contain less than 0.002% total impurities, were obtained from the American Smelting and Refining Company. Granular Zinc, 30 mesh, containing less than 0.02% total impurities, was obtained from the Mallinckrodt Chemical Company. The granular zinc was used to calibrate the absorption cell, zinc from the bars was used for the light source and for the alloys.

The alloys were prepared by melting the silver in an induction furnace, stirring in small pieces of zinc and cadmium and continuing to heat the resultant alloy for a few minutes to permit homogenization. To avoid undesirable chemical reactions, graphite crucibles and rods were used and the surface of the molten metal was covered with graphite powder. After cooling the alloy was placed in a Pyrex tube, evacuated to 10^{-5} mm. and sealed under vacuum. It was then annealed at 500° for 5 days and cooled gradually to room temperature. The surface of the alloy was machined off and the inner part was milled into fine chips.

Since from 7 to 30% of the added zinc or cadmium was lost during the preparation of an alloy, each one was analyzed for each of the components.

The silver was determined gravimetrically as silver chloride as described by Kolthoff and Sandell.[4] In the three more concentrated alloys the cadmium was determined gravimetrically as sulfide after several reprecipitations to remove the zinc from the precipitate.[5] The combined filtrates were concentrated and the zinc precipitated with sodium anthranilate. For some unknown reason we could not use this method for zinc and cadmium in the most dilute alloy, so they were determined by plating the metals successively on a platinum cathode upon which a thin film of copper previously had been plated. The apparatus was essentially the same as that of Hammond[6] and the method that of Lingane.[7]

The compositions of the alloys are given in Table I.

TABLE I

COMPOSITIONS OF ALLOYS IN ATOM PER CENT.

Alloy	Silver (1)	Zinc (2)	Cadmium (3)
1	70.83	21.63	7.54
2	73.54	13.91	12.55
3	71.48	6.66	21.86
4	85.46	7.42	7.12

Measurements of Absorption.—The absorption cell was calibrated by measuring the absorption of saturated vapors of zinc and of cadmium as functions of the temperature. Before use with each pure metal or alloy, the absorption cell was cleaned for several hours with hot nitric acid, then with water and finally with acetone. It was dried in a current of pure nitrogen gas and then in an oven at 110°. The metal was placed in the sample leg and the cell sealed to the vacuum system. If the sample was an alloy, as much as possible was used and the sample leg was cooled in liquid nitrogen during the sealing. The cell was evacuated to 10^{-5} mm., filled with pure argon and evacuated again to 10^{-5} mm. The cell was heated to 150° for several hours. The oven was removed and the cell sealed off *in vacuo*.

The 3076 Å. line of zinc and the 3261 Å. line of cadmium are separated by about 11 mm. on the focal plane of the spectrograph, and there are no other strong lines in this region. After their approximate positions were determined from a photograph of the spectrum, there was no difficulty in identifying each line with the galvanometer, although the exact positions varied somewhat with the setting of the absorption cell, and the positions of the maxima for the two paths might differ as much as 0.06 mm. So the position of the maximum, a_i, was determined for each measurement of current J_i.

The light source was operated only during a set of measurements, which usually occupied about

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(4) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1938, p. 286.

(5) "Scott's Standard Methods of Chemical Analysis," Vol. I, D. Van Nostrand Co., New York, N. Y., 1939, p. 200.

(6) W. H. Hammond, *Trans. Electrochem. Soc.*, **88**, 393 (1945).

(7) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953, p. 310.

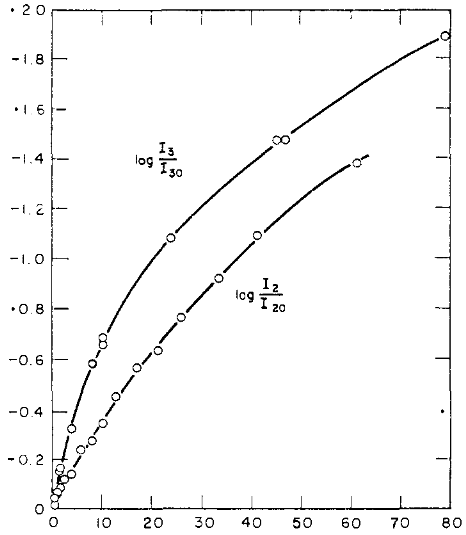
fifteen minutes and a preliminary warming up period of at least three minutes.

In each series shutter 1 was opened and J_2 and a_2 were determined for the zinc line by moving the exit slit slowly and always in the same direction. The shutter was closed and the corresponding dark current D_2 was measured. Then shutter 2 was opened and J_2^R, a_2^R were determined in the same way from the reference beam. This alternation was repeated for three measurements of J_2 and two of J_2^R, and the corresponding intensities ratio was determined from the averages as $I_2/I_2^R = (J_2 - D_2)_{av}/(J_2^R - D_2^R)_{av}$. The same procedure was then followed to determine I_3/I_3^R for the cadmium line. Due to the intermittent operation of the light source, the absolute intensities of the lines in the source fluctuated slightly, but the ratio of the intensity of each line before entering the absorption cell, I_i^0, to that of the corresponding line in the reference beam was assumed to be constant and therefore equal to $(I_i/I_i^R)_0$, the ratio when the absorption cell was at room temperature. Then $I_i/I_i^0 = (I_i/I_i^R)/(I_i/I_i^R)_0$. The validity of this assumption was checked for the calibration measurements by the constancy of I_i/I_i^R for the metal not present in the absorption cell. For the measurements with alloys the temperature ranges of which were higher, there were two complications because the laboratory temperature controlling system did not maintain the temperature of the small room constant at 18° when the furnace was heated to above 500°.

The first effect was that the exit slit positions for both lines shifted to longer wave lengths as the room temperature increased. The magnitude of the shift was the same for each of the four maxima a_2, a_2^R, a_3 and a_3^R and was nearly proportional to the increase in the reading of a thermometer placed near the prism of the spectrograph, with $\Delta a/(t - 18) = 0.012$ mm./°C. This relation held for each of the four runs on the alloys and for a fifth run under approximately the same conditions except that the absorption cell was not in the furnace. This effect caused a minor inconvenience and helped remedy the more serious second effect.

The absorption measurements were made at room temperature and then about every twenty degrees through the range of measurements ascending and then descending and again at room temperature. The furnace was held at each temperature for 2 to 3 hr. The value of $(I_i/I_i^R)_0$ after the high temperature runs was not the same as before, but $(I_2/I_2^R)_0/(I_3/I_3^R)_0$ remained the same. At the lower temperatures for the measurements with cadmium, the absorption of zinc was negligible, so $(I_2/I_2^R) = (I_2^0/I_2^R)$ was observable for some time. It was found to be a function of the displacement of the slit position at maximum intensity but with a lag of 4 hr., such that $\log (I_2^0/I_2^R)$ was not constant but was equal to $\log (I_2/I_2^R)_0 + k\Delta_a'$, where Δ_a' is the shift in the slit position four hours earlier, and k is about 0.0040 absorption unit per micron. The measurements at room temperature and in the blank run without absorption cell show that the same constants should apply to $\log (I_3^0/I_3^R)$. We have therefore corrected each value of $\log (I_i/I_i^0)$ by adding $k\Delta_a'$. The maximum value of the correction is 0.17, while the maximum absolute value of $\log (I_i/I_i^0)$ is more than 2.0.

The agreement between the effect for the two metals and the agreement between the four runs indicates that this effect is due to some change in the geometry of the optical system which responds slowly to changes in temperature. It seems probable that this change is in one or both of the supports for the beam splitting mirrors.



$(P_2/T) \times 10^4$ or $(5P_3/T) \times 10^4$.

Fig. 2.—Calibration curves.

Calibration.—The absorption by zinc or cadmium vapors does not follow Beer's law strictly, but we have made the reasonable assumption that in the range of absolute temperature from 450 to 1100°K. the absorption is a function only of $p_i/T = Rc_i$.[8] We have calculated p_i/T from the free energy equations of Kelley[9] which yield (with all p's in mm.)

$$\log p_2/T = 9.692 - 6860/T - 1.140 \log T - 0.295 \times 10^{-3}\, T \text{ for solid zinc } (T < 693\text{°K.}) \quad (1)$$

$$\log p_2/T = 12.721 - 6753/T - 2.318 \log T - 0.060 \times 10^{-3}\, T \text{ for liquid zinc } (693 < T < 1180\text{°K.}) \quad (2)$$

$$\log p_3/T = 9.819 - 5902/T - 1.247 \log T - 0.269 \times 10^{-3}\, T \text{ for solid cadmium } (T < 594\text{°K.}) \quad (3)$$

$$\log p_3/T = 11.655 - 5706/T - 2.086 \log T \text{ for liquid cadmium } (594 < T < 1038\text{°K.} \quad (4)$$

The values of $\log I_2/I_2^0$ and of $\log I_3/I_3^0$ are exhibited in Fig. 2.

Measurements with Alloys.—Our measurements with ternary alloys, like those with the binary alloys,[2,3] may be represented by equations of the

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(8) It has been suggested that pressure broadening of the zinc lines by cadmium might affect our results. Since the pressure is an exponential function of the temperature, the effect should be a sharp hook in the curves of Fig. 3 at the highest temperatures. The highest cadmium pressure is 30 mm. at 1000°K. for alloy 3. No effect is apparent. See also discussion in Ref 2.

(9) K. K. Kelley, Bureau of Mines Bulletin, 383 (1935).

type

$$T \log p_i = B_iT - A_i + T \log x_i \qquad (5)$$

They are displayed in Fig. 3 as

$$Y = T \log p_2 - 7(T - 820) + T \log x_2 \qquad (6)$$

$$Z = T \log p_3 - 7(T - 820) + T \log x_3 + 1000 \qquad (7)$$

The second terms on the right hand side of these equations serve to reduce the slopes nearly to zero since each B_i is approximately 7. The terms (T log x_2) and (T log x_3 + 1000) serve merely to separate the points of the different runs so that they may all be exhibited in a single diagram.

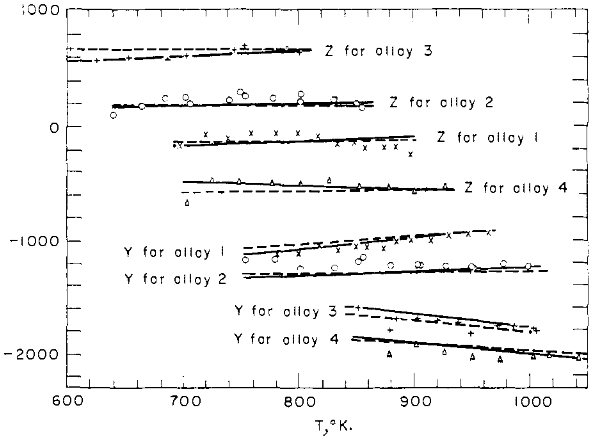

Fig. 3.—$Y = T \log p_2 - 7(T - 820) + T \log x_2$; $Z = T \log p_3 - 7(T - 820) + T \log x_3 + 1000$.

The excess free energy per mole of alloy, G^E/N $(=G/N - \Sigma_i x_i\ [G_i^0 + RT \ln x_i])$ may be represented by the equation

$$G^E/N = \sum_{j > 1} x_ix_j \sum_{t \geqslant 0} G_{ij}^{(t)}(x_i - x_j)^t + \sum_{k > j > i} x_ix_jx_k\, G_{ijk}^{(1)} + \cdots \qquad (8)$$

in which G is the free energy of the system, N is the total number of moles, x_i the mole fraction of component i, etc. and the G_i^0's, $G_{ij}^{(t)}$'s and $G_{ijk}^{(1)}$, etc. are functions of the temperature (and pressure) independent of the composition. Since $G = H - TS$, the excess enthalpy per mole $H^E/N(=H/N - \Sigma_i x_i H_i^0)$ and the excess entropy per mole S^E/N $(=S/N - \Sigma_i x_i[S_i^0 - R \ln x_i])$ must be represented by analogous expressions, and each $G_{ij}^{(t)} = H_{ij}^{(t)} - TS_{ij}^{(t)}$. The parameters H_i^0, S_i^0 and $G_i^0 = H_i^0 - TS_i^0$ are the enthalpy, entropy and free energy per mole of the pure components at the same temperature and in the same state of aggregation. For the α-alloys, this state of aggregation is the face-centered cubic form which is metastable for both pure zinc and pure cadmium. We have found that the terms of fourth and higher orders in mole fractions may be ignored. Then for the ternary systems

$$G^E/N = x_1x_2[G_{12}^{(0)} + G_{12}^{(1)}\ (x_1 - x_2)] + x_1x_3[G_{13}^{(0)} + G_{13}^{(1)}(x_1 - x_3)] + x_2x_3[G_{23}^{(0)} + G_{23}^{(1)}(x_2 - x_3)] + x_1x_2x_3\ G_{123}^{(1)} \qquad (9)$$

The corresponding equations for the vapor pressures of components 2 and 3, are

$$RT \ln p_2 = RT \ln p_2^0 + RT \ln x_2 + G_{12}^{(0)}x_1(1 - x_2) + G_{12}^{(1)}x_1(x_1 - 2x_2 - 2x_1x_2 + 2x_2^2) - G_{13}^{(0)}x_1x_3 - 2G_{13}^{(1)}x_1x_3(x_1 - x_3) + G_{23}^{(0)}x_3(1 - x_2) - G_{23}^{(1)}\ x_3(x_3 - 2x_2 - 2x_2x_3 + 2x_2^2) + G_{123}^{(1)}\ x_1x_3(1 - 2x_2) \qquad (10)$$

$$RT \ln p_3 = RT \ln p_3^0 + RT \ln x_3 + G_{13}^{(0)}x_1\ (1 - x_3) + G_{13}^{(1)}x_1(x_1 - 2x_3 - 2x_1x_3 + 2x_3^2) - G_{12}^{(0)}x_1x_2 - 2G_{12}^{(1)}\ x_1x_2\ (x_1 - x_2 + G_{23}^{(0)}\ x_2(1 - x_3) + G_{23}^{(1)}\ x_2(x_2 - 2x_3 - 2x_2x_3 + 2x_3^2) + G_{123}^{(1)}\ x_1x_2\ (1 - 2x_3) \qquad (11)$$

in which p_2^0 and p_3^0 are the vapor pressures of the pure components at the same temperature and state of aggregation.

The fact that the T log p_i is a linear function of T shows that the enthalpy and entropy of evaporation of the pure substances, each $H_{ij}^{(t)}$ and each $S_{ij}^{(r)}$ may be considered to be independent of the temperature. $RT \ln p_2^0$, $RT \ln p_3^0$, and the parameters with subscripts $_{12}$ and $_{13}$ were determined in previous studies from this Laboratory.[2,3,10] Those with subscripts $_{23}$ are determined by least squares from the vapor pressures of ternary mixtures.

$$RT \ln p_2^0 = 48.93T - 31.42 \times 10^3 \qquad (12)$$

$$RT \ln p_3^0 = 33.35T - 18.21 \times 10^3 \qquad (13)$$

with RT in cal. mole^{-1} and p's in mm.

$H_{12}^{(0)} = -3.83$ $\quad S_{12}^{(0)} = +15.10$
$H_{13}^{(0)} = -22.39$ $\quad S_{13}^{(0)} = -14.07$
$H_{23}^{(0)} = -8.44$ $\quad S_{23}^{(0)} = -6.73$
$H_{12}^{(1)} = +7.98$ $\quad S_{12}^{(1)} = 0.00$
$H_{13}^{(1)} = +9.11$ $\quad S_{13}^{(1)} = +8.62$
$H_{23}^{(1)} = -75.89$ $\quad S_{23}^{(1)} = -82.48$

$H_{23}^{(0)*} = +122.6$ $\quad S_{23}^{(0)*} = +140.5$
$H_{23}^{(1)*} = -91.5$ $\quad S_{23}^{(1)*} = -106.2$
$H_{123}^{(1)*} = -200.9$ $\quad S_{123}^{(1)*} = -225.0$

with H's in kcal. mole^{-1} and S's in cal. mole^{-1} °K.$^{-1}$. The unstarred $H_{23}^{(0)}$, etc. were determined with the assumption that $H_{123}^{(1)}$ and $S_{123}^{(1)}$ are zero. They correspond to the full lines in Fig. 3. We much prefer them to $H_{23}^{(0)}$*, etc., which are represented by the broken lines, because they reproduce the measurements with four adjustable parameters almost as well as the others do with six and because the values of $H_{23}^{(0)}$ correspond more closely to those for the binary alloys.

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(10) There are numerical errors in equations 1, 10, 14, 15, 16 and 17 in ref. 3, which we will designate as W-1, etc. The correct (W·1) is given in (2) of this paper. The others are (with all p's in atmospheres):

$$\log p_2/x_2 = (5.60 - 7720/T) + (0.78 + 53/T)x_1^2 + (1105/T)(3 - 4x_1)x_1^2 \qquad (\text{W}\cdot 10)$$

$$0.001\ T \log P_{21} = -0.944 + 5.194\ (0.001T - 1) \qquad (\text{W-}14)$$

$$0.001\ T \log p_{2h} = -0.778 + 5.740\ (0.001T - 1) \qquad (\text{W}\cdot 15)$$

$$0.001\ T \log p_{20} = -0.234 + 7.811\ (0.001T - 1) \qquad (\text{W}\cdot 16)$$

$$0.001\ T \log p_{20} = -2.12 + 5.60\ (0.001T - 1) \qquad (\text{W}\cdot 17)$$

Estimation of Errors.—The compositions of the alloys were determined to 0.1 weight per cent. The temperature of the furnace was measured reproducibly to 0.1° and the gradient through the furnace was always less than 0.5°. Any errors due to lack of proportionality of the current from the photomultiplier tube to the light intensity or to lack of linearity in the galvanometer reading should have been negligible. The photocurrents were reproducible to 0.0001 microampere, and at low vapor densities the photocurrents were of the order of 0.02 microampere. The error in I_i/I_i^R was therefore 0.01, so the calibration curve should be accurate to about 1%. The error in I_i/I_i^0 is larger for the measurements with alloys, however, because of the shift in I_i/I_i^R with room temperature. The total probable error of a single measurement is about 4%. The average deviation from the temperature smoothed value is 3%, and the average deviation from the temperature and composition smoothed value is 4%.

Any errors in the measurement of the parameters for the binary alloys or in extending their temperature range are, of course, carried over into our calculations of the parameters $G_{23}^{(0)}$, $G_{23}^{(1)}$ and $G_{123}^{(1)}$. The temperature range of the measurements of Scatchard and Westlund on α-silver–zinc alloys is 550–850° and that of Scatchard and Boyd on α-silver–cadmium alloys is 350–650°. In the ternary alloys we have measured the vapor pressure of zinc in the range 480–770° and that of cadmium in the range 350–650°.

The Binary α-Silver–Cadmium Alloys.—There have been five publications recently on this system. Two of them were published before the paper of Scatchard and Boyd[2] but did not come to our attention until afterward. Herasymenko[11] measured the vapor–solid equilibrium along a series of isobars. Kleppa[12] measured the integral heats of formation at 450° and Orr, Goldberg and Hultgren[13] measured them at room temperature. Anderson[14] calculated the integral heats from the partial heats of Herasymenko and of Scatchard and Boyd[2] and compared them with the two sets of direct measurements. The direct measurements agree within the scatter of either and indicate that the excess enthalpy and entropy are indeed independent of the temperature as we have assumed. They agree as closely with the results calculated from Scatchard and Boyd as they do with each other but differ widely from those of Herasymenko.

Although Herasymenko obtained smooth curves for each of his ten isobars and for the partial molal free energy of cadmium at 1000°K., he obtained very irregular values for the partial enthalpy which he calculated at each per cent. and therefore for the partial entropy. He found marked inflections at 4, 8.3, 25 and 33.3 atom % cadmium and attributed them to changes in the ordering of the alloys. He found maxima at 18 and 26% and minima at 24 and 32%. On the other hand, Scatchard and Boyd's equation yields a smooth curve with neither extremum nor inflection in the α range.

Entirely aside from the assumption of short range order which changes sharply at definite atomic ratios, Herasymenko's conclusions would be important, and very disturbing, if true, for they would prohibit the composition smoothing of the thermodynamic properties of solid alloys. None of the other measurements can be used to test these conclusions because they are made at too few concentrations. We have therefore made a careful study of some of Herasymenko's own measurements. His last two isobars, at 22.8 and 87 mm. are about 100° apart and may be compared from 23 to 35 atom %. We have calculated the partial enthalpy increase from liquid cadmium from these measurements alone at each per cent. increment in concentration. The second minimum is shifted from 32 to 29% and the second maximum from 26 to 25%. The first minimum apparently is shifted to a concentration below 23%. The difference between the minimum and the maximum enthalpy is reduced from 1000 cal. to 500 cal.

The samples were rings of coiled wire spaced about 5 mm apart. The temperature difference between adjacent wires was sometimes 12–14°. It seems improbable that the temperature of a sample in such a gradient can be correlated accurately with a thermocouple separated from it by two walls of quartz. Yet one degree error in the difference in temperature between two isobars makes an error of 250 cal. in the enthalpy.

From these three facts: (1) that Herasymenko's partial enthalpies differ by as much as 3000 cal. from those of Scatchard and Boyd, which agree with the calorimetric measurements of total enthalpy, (2) that a careful analysis of two of the more precise isobars halves the fluctuation in the more concentrated region and (3) that the apparatus appears ill designed for precision, we conclude that there is no reason to believe that the enthalpy of mixing of α-silver–cadmium alloys is not a smooth function of the composition.

Discussion

A graphical representation of either H^E/N or S^E/N would require three dimensions. We have chosen sections of these three dimensional figures at constant ratios y, defined by $y = x_2/(x_2 + x_3)$. Figures 4 and 5 exhibit these properties as functions of $x = (x_2 + x_3)$ for five values of y, 0.00, 0.25, 0.5, 0.75 and 1.00, with x varying from 0 to 0.4, which is a little beyond the stability range of the α alloys. The units are kcal. mole^{-1} for H and cal. mole^{-1} °K.$^{-1}$ for the entropy. The corresponding excess free energy at any temperature may be obtained by subtracting 10^{-3} T times the excess entropy from the excess enthalpy.

A tangent to any of these curves intercepts the $x = 0$ axis at the partial excess enthalpy, $\bar{H}_1^E$, or entropy, $\bar{S}_1^E$ at the point of tangency, and intercepts the $x = 1$ axis at $[y\bar{H}_2^E + (1 - y)\bar{H}_3^E]$ or $[y\bar{S}_2^E + (1 - y)\bar{S}_3^E]$ also at the point of tangency. The determination of the individual partial molal properties for zinc or cadmium would require sections at constant ratios of the other two com-

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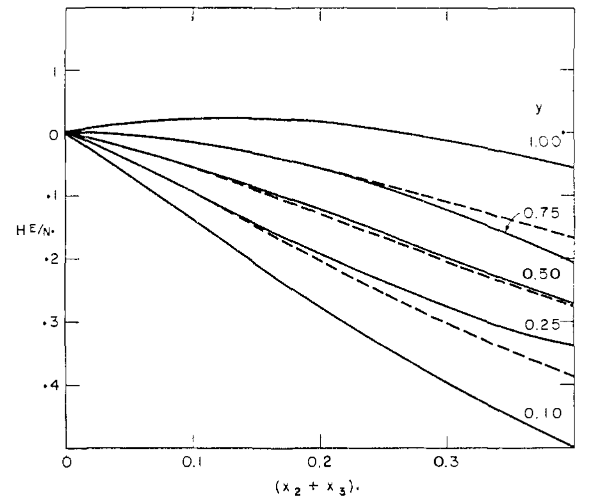

Fig. 4.—Excess enthalpy of α-silver–zinc–cadmium alloys.

ponents, at constant $(1 - y)x/(1 - x)$ or $yx/(1 - x)$.

The broken lines in Figs. 4 and 5 are y times the top curve plus $(1 - y)$ times the bottom one. The difference between any full curve and the corresponding broken one is the difference in excess enthalpy or entropy between one mole of the alloy and y moles of the silver–zinc alloy plus $(1 - y)$ moles of the silver–cadmium alloy, all with the same mole fraction of silver. In the dilute alloys these differences are extremely small. They are never large for $y = 0.5$. For $y = 0.25$ the differences in excess enthalpy and entropy are both positive, for $y = 0.75$ they are both negative.

$H_{23}^{(0)}$ is intermediate between $H_{12}^{(0)}$ and $H_{13}^{(0)}$, and $S_{23}^{(0)}$ is intermediate between $S_{12}^{(0)}$ and $S_{13}^{(0)}$, but we cannot take this relation too seriously. Assuming that $H_{123}^{(1)}$ was plus or minus 5% of the value which gives the best fit, instead of assuming that it is zero, would destroy this relation for one of the properties. Assuming plus 7% would change the sign of both $H_{23}^{(0)}$ and $S_{20}^{(0)}$. On the other hand $H_{23}^{(1)}$ and $S_{23}^{(1)}$ are an order of magnitude larger than the corresponding function for the binaries with silver. The two effects compensate in the excess free energy. The large values may arise from the fact that the parameters for silver–zinc were determined at higher temperatures and those for silver–cadmium at lower, or it may also be due to the difficulties of extrapolation. Although we have been successful in representing the thermodynamic properties of the α-alloys within their stability range, we have not obtained a unique function which warrants extrapolation.

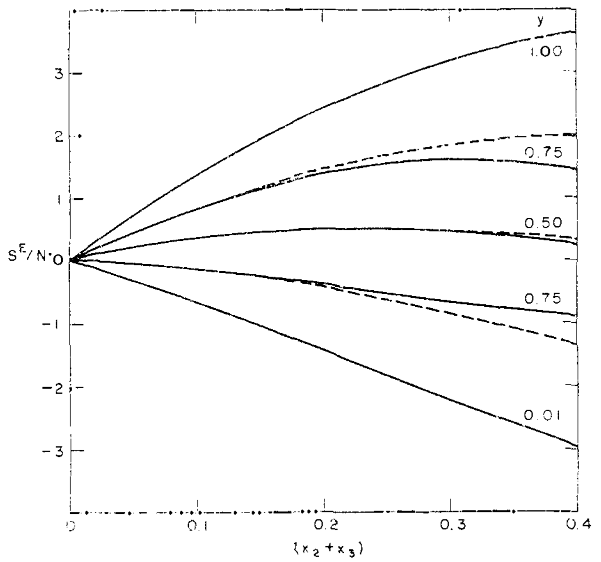

Fig. 5.—Excess entropy of α-silver–zinc–cadmium alloys.

[Contribution from the Chemistry Research Division, Armour Research Foundation of Illinois Institute of Technology, Technology Center, Chicago 16, Illinois]

Ammonium Ozonide

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The new compound, ammonium ozonide, has been prepared by the low temperature ozonization of ammonia. It has the characteristic five-peaked ozonide spectrum which shows a maximum in the vicinity of 450 mμ. The salt is thermally unstable and starts to decompose above −126°. Its decomposition products are ammonium nitrate, oxygen and water.

Introduction

The reaction of ozone with some of the alkali metal hydroxides to yield orange-red products has been known for some time.[1-5] Kazarnovskii, Nikolskii and Abletsova[6] identified the product of the potassium hydroxide reaction as potassium ozonide. Strecker and Thienemann[5] also observed that the reaction of dilute gaseous ozone with liquid ammonia at −78° created a transitory red color. Upon evaporation of the ammonia, a solid consisting of 98% ammonium nitrate was found. Since all of the known ozonides are red, it was believed that ammonium ozonide had been formed and had subsequently decomposed. Therefore, it was decided to undertake the preparation, isolation and identification of this red product.

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