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

Equilibrium of Solid α-Silver–Zinc Alloys with Zinc Vapor[1]

BY GEORGE SCATCHARD AND ROY A. WESTLUND, JR.

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The vapor pressure of zinc from solid silver–zinc alloys has been measured by the absorption of the resonance line at 3076 Å. from pressures of about 1 mm. nearly to the melting point and through the range of α-alloys, 0 to 30% zinc. The vapor pressures are expressed analytically. The activity coefficient of zinc passes through a minimum and does not vary greatly with composition over this range. The corresponding partial entropy is surprisingly large and appears to persist in the liquid alloys.

The method used by Herbenar, Siebert and Duffendack[2] to measure the vapor pressures of zinc in copper–zinc alloys is particularly adapted to the study of solid alloys because the amount of volatile metal removed is extremely small. We have copied it closely to study the vapor pressures of zinc in silver–zinc alloys. The method is to compare the absorption of the 3035.81 Å. (6^3S_1–4^3P_1) and 3075.88 Å. (4^3P_1–4^1S_0) lines from the zinc spark by the vapor in equilibrium with the alloy. These lines have approximately equal intensities. The first arises from transitions between highly excited states and is therefore not absorbed appreciably by zinc vapor at the temperatures of our measurements. The second is a resonance line, and is absorbed by zinc vapor.

Absorption Cell.—The absorption cell, illustrated in Fig. 1, was made of fused quartz by the Nieder Fused Quartz Company of Wellesley, Massachusetts. The absorption part is made of two concentric cylinders, each with a plane-parallel, optically flat window at one end. The outer diameter of the inner cylinder is 18 mm. and the inner diameter of the outer cylinder is 20 mm. Three small silica rods, equally spaced around the circumference at this end keep the two windows parallel and 10 mm. apart, and keep the tubes concentric. The opposite ends are sealed together and have two smaller tubes leading to supporting legs. One leg is a tube of about 10 mm. internal diameter, parallel to the cylinders. It contains the solid alloy. The other leg is merely a continuation of the 3-mm. connecting tube which can easily be bent to locate the center of windows at the light beam and which makes a convenient place to break the vacuum. The changes from the cell of Herbenar, Siebert and Duffendack[2] are the increase of light path from 1 mm. to 10 mm. and the replacement of two equal legs by one much larger and one much smaller leg. The internal volume is about 32 ml. of which about 4 ml. is occupied by 40 g. of alloy. The maximum pressure is limited by the melting points to about 10 mm., so the maximum zinc content of the vapor phase is 2–3 $\times 10^{-14}$ g. The minimum zinc in the solid phase was 2 g.

Observation Furnace.—It is essential that the furnace maintain a temperature which is uniform throughout the cell and constant for long periods of time, and it is important that the change from one temperature to another be reasonably rapid.

The core of the furnace is an Alundum tube of three-inch inside diameter 18.5″ long, grooved spirally with a 0.25″ pitch on the outer side. In this groove is wound No. 20 chromel A resistance wire covered with Alundum cement. The center 12″ of the core is surrounded by a 6″ diameter steel tube filled with Sil-O-Cel insulation. This core fits in a stainless steel shell 18″ long, 12″ high and 12″ deep, which is cut horizontally at the middle and hinged at the back. The shell is lined with Babcock and Wilcox K-30 firebrick which fits rather closely at the ends but leaves an air gap $^1/_4$″ thick around the iron cylinder.

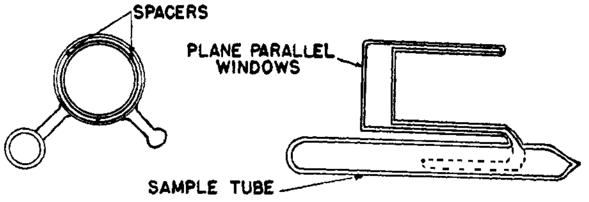

Fig. 1.—Absorption cell.

Within the core, centered longitudinally is a 12″ tube of $^1/_{16}$″ nickel, with an outside diameter of 2$^7/_8$″. Each end is closed by a pair of removable radiation shields of $^1/_{12}$″ nickel spaced two inches apart, with a 1″ hole for the passage of light and a smaller hole below it for the insertion of thermocouples. The purpose of the nickel lining is to give an even temperature distribution.

At each end of the core is a 6″ Alundum tube of 2$^3/_4$″ diameter, grooved and wound like the central core. The Alundum is thick enough to give a snug fit within the core. One inch from each end of each tube is an alumina disc shaped like the nickel radiation shields and held in place by an Alundum cement. These heaters compensate for heat losses at the ends of the core. They also permit maintaining the windows at a higher temperature than the rest of the cell during cooling. These end heaters are adjusted manually.

The main heater on the central core is regulated by a Tag Celectray throttling controller indicating pyrometer made by the C. J. Tagliabue Company of Brooklyn, N. Y. This controller gives an on-off heating cycle with a period of 12 seconds, and a ratio of time on to off varying with the difference in temperature from the selected temperature. The heating, which may be either 115 or 230 v., is adjusted so that the ratio of time on to time off is near unity, which gives the most accurate temperature control. The controller is governed by a Chromel–Alumel thermocouple in the cell chamber, similar to those used for temperature measurement. Therefore the short period fluctuations are less than can be measured. At 600–800° the temperature remains constant to 1° for many hours, and to better than 0.5° for short periods.

The temperature is measured by three Chromel–Alumel thermocouples with a common cold junction in an ice-water bath and the hot junctions in the cell chamber, one at the center and one about 2″ inside the inner radiation shield at each end. The potential of each couple may be measured separately, or the difference between any two may be measured. The potentials are measured with a Leeds and Northrup Type K-2 potentiometer and No. 2430 galvanometer, and Eppley Standard cell. The precision is one microvolt, or one-fortieth of a degree centigrade. The couples were calibrated against a platinum–platinum–10% rhodium couple which had been standardized by the National Bureau of Standards.

Optical Measurements.—The light source is a spark between two zinc electrodes, each 3″ long and $^3/_{16}$″ in diameter, spaced $^1/_8$″ apart. The electrodes, which were reported to be 99.99% zinc, were supplied by the Herrick Company, East Boston, Mass. The sparking potential comes from a 10,000 v. transformer on a 110-v. 60-cycle line, on which no other equipment is operated. A condenser across the electrodes increases the intensity, and an inductance with 4 taps reduces the number of "air lines" and also permits some variation of the relative intensities of the 3076 and 3035 Å. lines. The tap is chosen which makes this ratio nearest

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[1] Adapted from the Ph.D. Thesis of Roy A. Westlund, Jr., M.I.T., 1953. The spectroscopic work was carried out in the Spectroscopy Laboratory at M.I.T. This work received financial support from the Atomic Energy Commission, Contract No. AT-30-GEN-1002.

[2] A. Herbenar, C. A. Siebert and O. S. Duffendack, *J. Metals*, **188** 323 (1950).

unity. Freshly polished electrodes are used for each exposure. The exposure begins 15 seconds after the spark is started and usually lasts 3 seconds. For the calibration of the plates, however, 120 second exposures are used.

The light from the spark passes first through the absorption cell, then through a plano-convex quartz condensing lens with a diameter of one inch and focal length of 9.842 inches and through an exposure timer to the spectrograph. The exposure timer is a simple chopping disk mounted on the optical bench near the spectrograph with both vertical and horizontal adjustments so that the edges of the sector are parallel to those of the spectrograph slit. A Telechron clock motor drives the disk at one rotation per minute. The size of the aperture is adjustable to give exposures of 1, 3, 5, 7, 10, 15 or 20 seconds.

The spectrograph is a Hilger E-498 medium quartz spectrograph. It has a single prism, adjustable lenses, and a plate holder with templates to bend the photographic plates to the proper curvature.

The photographic plates were standard 10″ by 4″ Spectrum Analysis No. 2 plates of the Eastman Kodak Company. They were developed by a carefully standardized procedure. The percentage transmission of each line compared to the clear plate was measured in a JA-200 microphotometer of the Jarrell–Ash Company of Boston.

To calibrate the photographic plates the lens was removed and the exposure timer was replaced by a step sector mounted on the optical bench very close to the spectrograph, with horizontal and vertical adjustments so that the sector edges may be placed parallel to the spectrograph slit, and the light may be passed through any one of eight steps each three millimeters high. The steps are adjusted so that each permits half as much light to pass as the preceding one. The disk is $^1/_{16}$″ sheet aluminum with 8″ diameter. It is rotated by a $^1/_{50}$th horsepower motor at 6000 r.p.m. Usually four steps are sufficient to calibrate a plate.

The absorption cell was calibrated by measuring the vapor pressure of liquid zinc in the range 0.2 to 12 mm. Fifteen minutes was more than sufficient to reach equilibrium after the temperature was changed. It was assumed that the vapor is so nearly a perfect gas at these pressures that the concentration is equal to p/RT. The equation for the vapor pressure calculated from free energies determined by Overstreet,[3] as published by Kelley,[4] is

$$\log P_{\text{mm}} = 12.760 - \frac{6749}{T} - 1.316 \log T - 0.060 \times 10^{-3}\, T \qquad (1)$$

Combination of Beers law for the 3076 line with constant k and cell length l, and for the 3035 line with constant zero, gives, with numerical values for p in mm. in the 10-mm. cell

$$\log \frac{I_{3035}}{I_{3076}} = \log \frac{I^0_{3035}}{I^0_{3076}} + \frac{klp}{T} = 0.179 + 36.9\, p/\text{T} \qquad (2)$$

Two points would have been sufficient to determine this equation. The good agreement over the whole range confirms the method and also the equation for the relative vapor pressure of zinc in this region. In cooling after a run with liquid zinc the temperature was held for a long time at 430° and the end heater furtherest from the cell windows was turned off. This caused the zinc to solidify in that end of the sample tube. Since the tube always cracked where liquid zinc solidified, it was important that condensation should not occur on the windows or the upper part of the cell.

The vapor pressures of the solid alloys were obtained in the same way as the calibration curve except that after each temperature change, three hours was allowed for reaching equilibrium since preliminary experiments showed that two hours were sometimes necessary. The pressure was always so low relative to that of liquid zinc at the same temperature that there was no difficulty with liquid zinc condensing on the walls.

Jacket Furnace.—The preparation of the alloys requires a jacket furnace which can be slid around a tube on the vacuum line. The core of this furnace is a horizontal cylindrical magnesia crucible 9″ long, $^1/_4$″ thick and with an outside diameter of 4″. It is spirally wound on the outside with No. 22 Chromel resistance wire with a $^1/_4$″ pitch, insulated and supported by Alundum Cement. This core is surrounded by Babcock and Wilcox K-30 firebrick in a shell of $^1/_{12}$″ stainless steel 12″ × 9″ × 9″. Two pieces of angle iron welded on the bottom of the shell parallel to the core serve as mounts for four wheels, which run on tracks on a wooden board which rests on a wooden platform through three leveling screws. This permits adjustments of about two inches. The mouth of the furnace is closed with a plug of glass wool. Power is provided through a Variac V-5 condenser on the 110-volt line. It gives a maximum temperature of 550°. The temperature can be held constant within a few degrees for many hours. The temperature is measured by a Chromel–Alumel thermocouple, a Leeds and Northrup Type K-1 potentiometer and No. 2420B galvanometer, which is sensitive to 40 microvolts, or 1°.

Preparation of Alloys.—The zinc used in the calibration and in the preparation of the alloys was obtained from the Research Laboratories of the American Smelting and Refining Company, Barber, N. J., and reported by them to be 99.998% zinc. The silver was obtained from the Handy and Harman Company, New York, and was reported by them to be 99.95% silver.

Andrews, Davies, Hume-Rothery and Oswin[5] determined the first triple point of the silver–zinc system as 32.5% zinc in α, 37% zinc in β and 38% zinc in the liquid at 710°. The solidus curve is only slightly concave upward to the melting point of silver at 960°. Seven alloys were prepared covering the range of α-alloys. One hundred fifty grams of silver was used for the alloy least concentrated in zinc, 100 g. for each of the others. The silver was placed in a clean unused graphite crucible and covered with a powdered graphite cover. The crucible was placed in the core of an Ajax water-cooled induction furnace in the Department of Metallurgy, M.I.T., and heated until the silver melted. Heating was stopped and sufficient zinc was added to give the desired concentration with a slight excess to allow for evaporation. The liquid mixture was then stirred several times with a pure graphite rod. Finally the furnace was restarted and allowed to run for some time. After cooling, the alloy was removed from the crucible and surface cleaned.

Each alloy was sealed in a Pyrex tube, evacuated to 1×10^{-5} mm. and then heated to 550° for five days. It was then removed from the tube, the surface was machined off, and the rest was milled into fine chips. These chips were cleaned successively with dilute sodium hydroxide, ethanol and ethyl ether and dried in a stream of pure dry nitrogen. At this point, a portion was reserved for analysis. The sample tube of the absorption cell was filled with 35 to 40 g. of these chips, the cell was sealed onto the vacuum line through a graded quartz–Vycor–Pyrex seal, evacuated to 1×10^{-5} mm., heated to 350° for several hours under constant pumping. It was then sealed from the vacuum line, tested with a spark tester immediately and again after standing overnight. The absorption was then measured over a series of temperatures. After the run the alloy was analyzed for silver gravimetrically as silver chloride. The two least concentrated solutions were also analyzed for zinc gravimetrically as zinc anthranilate. The analysis for the two components checked within 0.1%. The samples after heating contained less zinc than those before heating by 0.02–0.10 (average 0.05) %. This is about the precision of analysis but, since a slight loss of zinc during the evacuation is to be expected, the values after heating were selected.

For the calibration of the absorption cell, fine chips of zinc were treated just as the chips of the alloys. Since the vapor pressures were measured above the melting point of zinc, the precautions discussed above were taken on cooling to avoid cracking the cell at an important point.

Results.—Since $RT \ln p_2$ is the difference in the molar chemical potential (partial molar free energy) of zinc in the alloy and in the vapor at 1 mm. pressure, p is the activity of zinc in the alloy with zinc vapor at the same temperature and 1 mm. pressure as the standard state. It is therefore convenient to work with the activity coefficient p_2/x_2. At each composition our measurements are fitted by the linear relations

$$\log p_2/x_2 = B - A/T \qquad (3)$$

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(3) R. Overstreet, Master's Thesis, University of California, 1930.

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

(5) K. W. Andrews, H. E. Davies, W. Hume-Rothery and C. R. Oswin, *Proc. Roy. Soc.* (*London*), **177A**, 149 (1941).

or

$$(T/T_0) \log p_2/x_2 = (B - A/T_0) + B(T/T_0 - 1) \quad (4)$$

in which x_2 is the mole fraction of zinc in the alloy, T_0 is an arbitrary temperature, and A and B are functions of the composition. Since 1000°K. is a round temperature near the middle of the range, we smooth for temperature with equation 4 and $T_0 = 1000$. The composition smoothing is complicated by the facts that the temperature range varies with the composition, and that the composition range is rather large to treat satisfactorily by the methods of dilute solutions but not large enough to give good indications of the form of the variations. The potentials should correspond to the equation for the excess free energy per mole

$$G^E_x = x_1x_2[G^0_{12} + G'_{12}(x_2 - x_1) + G''_{12}(x_2 - x_1)^2 + \ldots] \quad (5)$$

in which G^0_{12}, G'_{12}, etc., are functions of the temperature (and pressure). The corresponding equation for excess potential of component 2 is

$$\bar{G}^E_2 = x_1^2[G^0_{12} + G'_{12}(3 - 4x_1) + G''_{12}(1 - 2x_1)(5 - 6x_1) + \ldots] \quad (6)$$

The parameter B is linear in x_1^2 but the slope is surprisingly large for an excess entropy

$$B = 10.692 - 3.300x_1^2 \quad (7)$$

The enthalpy contribution, A, needs an additional term, but the range is not large enough to decide between A'_{12} and A''_{12}. The fit is about the same for the equations

$$A = 6865 + [837 + 1744(3 - 4x_1)]x_1^2 \quad (8)$$

and

$$A = 8045 - [1441 + 704(1 - 2x_1)(5 - 6x_1)]x_1^2 \quad (9)$$

and would be as good for many combinations of the two. Table I lists the values of $(B - 0.001A)$ and of B. Those in the second and fifth columns headed Eq. 4 are determined from the measurements on a single solution with no composition smoothing. The sixth column gives the values of B from equation 7. The third and fourth headed Eq. 8 and Eq. 9, give the values of A calculated from equations 4, 7 and 8 or 9. In the further discussion we have used equation 8, since it gives simpler results in other forms of expansion.

TABLE I

PARAMETERS FOR VAPOR PRESSURE EQUATIONS

Atomic % Zn,	$(B - 0.001A)$ Eq. 4	Eq. 8	Eq. 9	B Eq. 4	Eq. 7
(3.98	1.434	1.365	1.388	7.721	7.649)
8.01	1.311	1.329	1.334	7.821	7.900
13.08	1.341	1.330	1.327	8.244	8.199
16.43	1.347	1.356	1.354	8.396	8.387
19.65	1.401	1.397	1.397	8.565	8.563
26.63	1.535	1.539	1.540	8.889	8.916
30.10	1.643	1.632	1.629	9.098	9.080

Figure 2 shows the quantity $Y = 0.001\ T \log p_2 - (0.001T - 1)(8 + \log x_2) = (B - 0.001A) + (B - 8)(0.001T - 1) + \log x_2$ plotted against T for each of the seven alloys. At 1000°K. this is $\log p_2$, chosen rather than $\log p_2/x_2$ because it gives a reasonable spread to the measurements. The term $\log x_2$ is proportional to the ideal entropy and 8 is equal to B for an alloy of about 10% zinc.

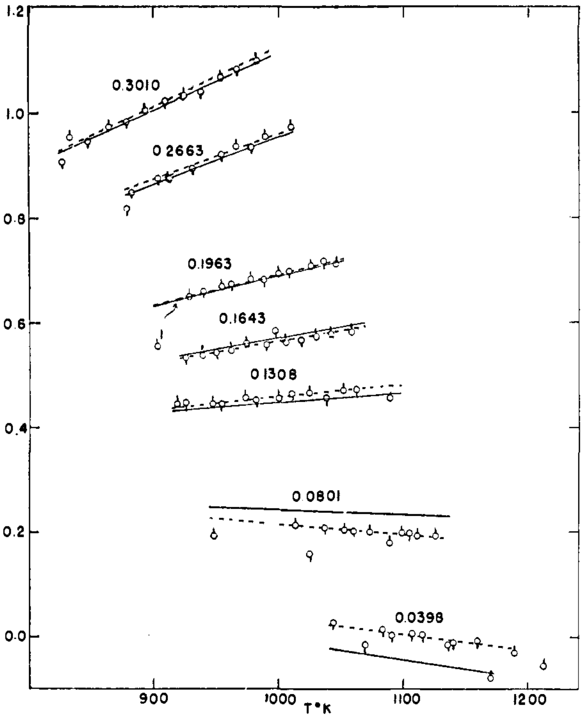

Fig. 2.—Experimental measurements of α-silver (1)–zinc (2) alloys: $Y = 0.001T \log p_2 - (0.001T - 1)(8 + \log x_2) = (B - 0.001A) + (B - 8)(0.001T - 1) + \log x_2$.

It is introduced to make the slopes nearly zero so that the differences in slope are readily visible. The circles are our individual measurements. Those with tails on top were made with increasing temperature, those with tails on the bottom were made with decreasing temperature. The broken

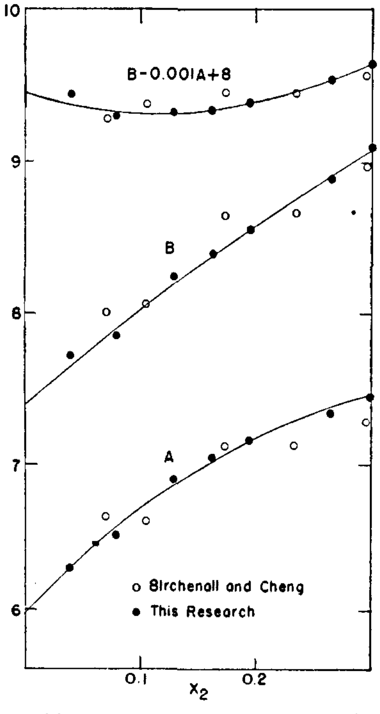

Fig. 3.—Smoothing parameters of α-silver (1)–zinc (2) alloys: $\log p_2/x_2 = B - A/T$.

lines are determined from the second and fifth columns of Table I, with composition smoothing, and the full lines are determined by the values in the third and sixth columns. Each line stops at the solidus temperature determined by Andrews, Davies, Hume-Rothery and Oswin.[5] Figure 3 shows 0.001 A, B and $(B - 0.001A)$ as functions of the mole fraction x_2. The lines are calculated from equations 7 and 8, the filled circles represent our measurements, Eq. 4, unsmoothed for composition, and the open circles represent the measurements of Birchenall and Cheng[6] by the dew point method. The results with the 3.98% alloy were not used in determining the parameters because the second and third points were taken above the solidus temperature and the sample should have melted at least partially. There was no indication of this having occurred, however. Three samples taken after the run gave analyses which checked closely, and the deviations are about as much larger than for the other solutions as might be expected from the smaller concentration. The results on this particular alloy are presented without explanation for the sake of completeness.

The measurements of Birchenall and Cheng[6] are fitted by the curves determined from our measurements about as well as by any simple function. This agreement between two very different methods is most gratifying. We were surprised to confirm so closely the temperature variation from the dew point method.

Excess Entropy of Mixing.—The most remarkable result is the very large non-ideal entropy of mixing indicated by the large coefficient of $x^2{}_1$ in eq. 7, and by the large slope of B *vs.* x_2 in Fig. 3. Figure 2 is designed to show that this effect does not come from any of our smoothing but is shown by the measurements themselves. The variation in the slopes of the lines at different concentrations is the variation in B. It is obvious that the measurements demand such a variation, and that the variation of the points is expressed well by the variation in the curves used for smoothing.

If the excess entropy of mixing without change of volume is zero, there should be a term in the entropy of mixing at constant pressure which is approximately equal to the enthalpy of mixing multiplied by $\alpha/(1 + \alpha T)$ if α is the coefficient of thermal volume expansion,[7] but α is only about 6×10^{-5} for silver, so that can explain only a few per cent. of the entropy. Theories of order disorder[8] give terms in the entropy corresponding to G''_{12} in eq. 5 and to higher terms, but none corresponding to G^0_{12}.

It would be interesting to know whether this entropy depends upon the crystallinity. The measurements of the vapor pressure of liquid silver-zinc alloys are not very satisfactory and better results can probably be obtained by combining our equations with the solid–liquid equilibrium measurements of Andrews, Davies, Hume-Rothery and Oswin.[8] Table II shows the values of the solidus composition and equilibrium temperature corresponding to rounded values of the liquidus composition, minus the logarithm of the pressure–mole fraction ratio for the liquidus in column 3, and in column 4 the logarithm of the ratio of the vapor pressure of the solid of the same composition extrapolated to the liquidus temperature by equations 3, 7 and 8, p'_s, and the vapor pressure of the liquidus, p_l.

TABLE II

LIQUIDUS VAPOR PRESSURES

Atomic % Zinc,		Eq. temp.	−log $(p_2/x_2)_l$	log p_s'/p_l	−log $(p_l/x_2p_{l0}$
Liquidus	Solidus				
0	0	1233			
5	2.5	1197	2.103	0.291	1.437
10	5.5	1161	1.975	.276	1.328
15	9.5	1125	1.866	.250	1.186
20	14	1090	1.750	.245	1.042
25	19.5	1055	1.660	.223	0.854
30	24.5	1025	1.579	.231	.681
35	29.5	998	1.525	.244	.495
38	32.5	983	1.504	.252	.376

The change in ratio is within the error of determining the solidus composition. However, the results are fairly smooth and both the composition and temperature are changing, so the minimum may be real. The results do seem sufficiently accurate to show that the behavior of the liquid is not very different from that of the solid, and that there must also be a large excess entropy of mixing in the liquid. On the other hand, the measurements of Birchenall and Cheng[6] and those of Underwood and Averbach[9] on β-silver-zinc alloys in the range 43–54 atomic % zinc indicates normal entropies for those systems.

Although the vapor pressure of zinc from an α-brass is less than that from an α-silver–zinc alloy of the same mole fraction of zinc, the non-ideal entropy of mixing is much smaller. The measurements of Herbenar, Seigel and Duffendack[2] may be represented by the equation

$$\log p_2/x_2 = 19.985 - 0.383\, x_1^2 - \{17{,}776 - [121 + 2545\,(3 - 4x_1)]x_1^2\}/T \quad (10)$$

Seigle, Cohen and Averbach[10] found an excess entropy of mixing for solid nickel-gold alloys about half as large as that we find for silver–zinc. The solid nickel–gold system, however, is very near the limit of partial miscibility, and the liquid system is very nearly ideal.

Standard States.—The equations we have used so far are equivalent to the choice of the gas at 1 mm. as the standard state of unit activity. The change of standard state to gas at one atmosphere involves only subtracting 2.881 from B to give

$$0.001T \log p_2/x_2 = 0.946 + 7.811(0.001T - 1) - [4.137 + 1.744(3 - 4x_1) + 3.300(0.001T - 1)]x^2{}_1 \quad (11)$$

The choice of the hypothetical face-centered cubic zinc as standard involves the dropping of the constant terms to give

$$0.001T \log p_2/x_2p_{2\text{o}} = - [4.137 + 1.744\,(3 - 4x_1) + 3.300(0.001T - 1)]x^2{}_1 \quad (12)$$

It follows that the vapor pressure in atmospheres

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(6) C. E. Birchenall and C. H. Cheng, *J. Metals*, **187**, 428 (1949).

(7) G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

(8) For example, J. G. Kirkwood, *J. Phys. Chem.*, **43**, 97 (1939).

(9) E. E. Underwood and B. L. Averbach, *J. Metals*, **3**, 1198 (1951).

(10) L. L. Seigle, M. Cohen and B. L. Averbach, *J. Metals*, **4**, 1320 (1952).

of this unstable zinc is given by the equation

$$0.001T \log p_{2o} = 0.946 + 7.811\,(0.001T - 1) \quad (13)$$

If liquid zinc be chosen as the standard state, the equation for its vapor pressure must be subtracted from equation 11. Over the range of our measurements the vapor pressure in atmospheres of liquid zinc may be expressed as

$$0.001T \log p_{2l} = -0.843 + 8.282\,(0.001T - 1) \quad (14)$$

If the unstable solid hexagonal zinc is chosen, its vapor pressure may be obtained by temperature extrapolation as

$$0.001T \log p_{2h} = -0.461 + 9.212\,(0.001T - 1) \quad (15)$$

It will be seen that the vapor pressure of hypothetical face-centered zinc is well above that of either the liquid or the unstable hexagonal zinc. Equation 9 gives

$$0.001T \log p_{2o} = -0.134 + 7.811\,(0.001T - 1) \quad (16)$$

which still indicates instability relative to liquid or to hexagonal zinc. Equation (10) for brass, however, gives

$$0.001T \log p_{2o} = -0.672 + 17.104\,(0.001T - 1) \quad (17)$$

If the extrapolation could be trusted, this would indicate that face-centered cubic zinc was the stable form.

The standard state of pure liquid zinc is particularly appropriate for the liquid alloys. The last column of Table II presents $-\log p_{2l}/x_2p_{2lo}$ which is equal to $-\log \gamma_2$ for this standard state.

Probably the most useful reference state for solid alloys is that of unit activity coefficient in an infinitely dilute solution of zinc in silver. By subtracting the value at $x_1 = 1$ from eq. 11 we obtain for $\gamma_2 = a_2/x_2$

$$0.001T \log \gamma_2 = [4.137 + 3.300(0.001T - 1)](1 - x_1^2) + 1.744[1 - x_1^2(3 - 4x_1)] \quad (18)$$

The corresponding equation for the activity coefficient of silver $\gamma_1 = a_1/x_1$

$$0.001T \log \gamma_1 = -[4.137 - 1.744(3 - 4x_2) + 3.300(0.001T - 1)]x_2^2 \quad (19)$$

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

The Chemistry of Niobium and Tantalum. I. Reduction in Solution[1]

BY R. E. ELSON[2]

RECEIVED MARCH 24, 1953

Polarographic and spectrophotometric evidence is presented for the existence of the +3 and +4 oxidation states of niobium and tantalum in solution. Irreversible, one electron reductions are observed at potentials ranging from −1.05 to −1.95 v. *vs.* S.C.E. for niobium and −1.16 to −1.58 for tantalum. Spectral changes in the visible and ultraviolet produced by reduction, are attributed to the (IV) and (III) states.

Wohler, Osborne and others[3] have shown that niobium(V) in sulfuric or hydrochloric acid can be reduced electrolytically or by zinc to a brown or blue solution. The color has been shown to be a function of acid concentration. Titration of this solution has established it to be Nb(III), and potential measurements by Grube and Grube[4] have given values of 0.344 v. for the Nb(III)–Nb(V) couple in 2–6 *N* hydrochloric and 0.342 v. in 3–6 *N* sulfuric.

Zeltzer[5] reported niobium to be polarographically reduced to the III state at −0.8 v. *vs.* S.C.E. in 1 *M* HNO_3 but was unsuccessful in obtaining reduction in other media. Several workers have reported the possible existence of Nb(IV). Ott[6] reduced sodium niobate electrolytically in hydrochloric acid and obtained a green color which he attributed to Nb(IV). He also reduced niobium pentachloride in concentrated sulfuric acid and obtained a blue solution from which a compound was isolated which he postulated to be the mixed oxide $Nb_2O_5{\cdot}NbO_2$. No direct evidence of the oxidation state in solution was presented and it is probable that he was working with the (III) state.

There are no data available on the direct reduction of tantalum in solution but lower valence chlorides have been prepared in the dry state by reduction of tantalum pentachloride with aluminum. Ruff and Thomas[7] report that tantalum trichloride dissolves in water to give an intensely green colored aqueous solution which is fairly stable. Tantalum dichloride is also reported by these workers to dissolve with the evolution of hydrogen and the production of the green Ta(III) solution. Zeltzer[5] could not obtain any reduction wave for tantalum in hydrochloric or strong alkali solutions by polarographic techniques.

In this work, evidence was obtained for the existence of the (IV) and (III) states of niobium and tantalum by means of polarographic and spectrophotometric techniques. Most of the reductions were carried out in oxalate and tartrate solutions. It has been found that niobium and tantalum are difficultly soluble in most acids and tend to hydrolyze in these except at high acid concentrations. It was therefore felt advisable to work with strong complexing solutions such as oxalate and tartrate. Some additional polarograms

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[1] Presented in part before the XIIth International Congress of Pure and Applied Chemistry, New York, New York, Sept., 1951.

[2] California Research and Development Co., P. O. Box 751, Livermore, Calif.

[3] (a) F. Wohler, *Pogg. Ann.*, **48**, 93 (1839); (b) W. J. Osborne, *Am. J. Sci.*, [3] **30**, 331 (1885); (c) F. J. Metzger and C. E. Taylor, *J. Soc. Chem. Ind.*, **28**, 818 (1909); (d) S. J. Kiehl and A. Hart, THIS JOURNAL, **50**, 2337 (1928); (e) W. D. Treadwell and R. Nieriker, *Helv. Chim. Acta*, **25**, 474 (1942).

[4] G. Grube and H. L. Grube, *Z. Electrochem.*, **44**, 771 (1938).

[5] S. Zeltzer, *Collection Czechoslov. Chem. Communs.*, **4**, 319 (1932).

[6] F. Ott, *Z. Elektrochem.*, **18**, 349 (1912).

[7] (a) O. Ruff and F. Thomas, *Ber.*, **55B**, 1466 (1922); (b) O. Ruff and F. Thomas, *Z. anorg. Chem.*, **148**, 1 (1925).