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# Polarographic Studies of Metal Complexes. I. The Copper(II) Tartrates

BY LOUIS MEITES

The first study of the polarographic behavior of copper(II) in a tartrate supporting electrolyte was made by Suchy,[1] who found a single wave, with a half-wave potential of −0.14 v. *vs.* the saturated calomel electrode, in a 10% (0.35 *M*) potassium sodium tartrate solution of unstated *p*H. Kolthoff and Lingane[2] found, in 0.5 *M* tartrate, $E_{1/2} = -0.10$ v., again at an unspecified *p*H value, and stated that the wave height corresponded to reduction to the metal. More recently, Lingane[3] has shown that the polarographic behavior of the system is significantly dependent on the *p*H: in particular, he found that the half-wave potential is displaced to very negative potentials in strongly alkaline solutions containing gelatin, in agreement with the earlier observation of Kolthoff and Lingane.[2]

Inasmuch as some preliminary experiments with alkaline tartrate solutions were in sharp disagreement with previous data, it was deemed desirable to make a complete study of the effects of *p*H and tartrate concentration on the system.

## Experimental

The polarographic apparatus used was that described by Meites and Meites.[4] All measurements were made at 25.00 ± 0.02° in a water thermostat. The cell is a modification of the H-cell described by Lingane and Laitinen.[5] The solution compartment of this cell has a capacity of about 450 ml.; it is fitted with a no. 14 rubber stopper, through which are inserted the dropping electrode, a tube for leading oxygen-free hydrogen over the solution, the tips of two calibrated 10-ml. microburets, and the glass and calomel electrodes of a Beckman Model G *p*H meter. A known volume of air-free acid or base is added to the solution, which is then stirred briefly by a stream of gas, the *p*H is measured, and the polarogram is recorded; or, alternatively, one of the microburets may be filled with a standard solution of the metal ion and the diffusion current constant[6] measured by the technique previously described.[7-9] The entire time consumed is very little more than that required by the polarographic measurements themselves.

The Beckman *p*H meter used was set to read 3.57 in a saturated potassium hydrogen tartrate solution at 25°.[10] All *p*H values above 10 were measured with a Type E glass electrode, using as standard a potassium borate-boric acid buffer whose *p*H had been checked against the National Technical Laboratories buffer of *p*H 10.00. Suitable corrections for the alkali errors of the glass electrode have been made: they were minimized by the use of potassium hydroxide instead of sodium hydroxide.

Oxygen was removed from the tank hydrogen used by a vanadous sulfate wash train.[11]

## Results and Discussion

Typical polarograms of copper(II) in potassium sodium tartrate solutions at varying *p*H values in the absence of gelatin are shown in Figs. 1, 2 and 3. In solutions containing the hydrogen tartrate ion at concentrations considerably greater than that of the copper(II), only a single wave is found. It is characterized by a very sharp maximum whose relative height decreases with increasing *p*H, but the plateau finally attained is very well defined. Lingane's data[3] indicate that the maximum in this wave is suppressed by as little as 0.005% gelatin.

The half-wave potential of this wave is only slightly affected by changes in *p*H: in 0.1 *M* tartrate $E_{1/2}$ is −0.003 v. at *p*H 1.70 and −0.084 v. at *p*H 5.73 (all potential measurements are referred to the saturated calomel electrode), and they are

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(1) K. Suchy, *Coll. Czechoslov. Chem. Commun.*, **3**, 354 (1931).

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 280.

(3) J. J. Lingane, THIS JOURNAL, **65**, 866 (1943).

(4) L. Meites and T. Meites, to be submitted.

(5) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 504 (1939).

(6) J. J. Lingane, *ibid.*, **15**, 583 (1943).

(7) J. J. Lingane and L. Meites, *ibid.*, **19**, 159 (1947).

(8) L. Meites, Ph.D. Thesis, Harvard University, 1947.

(9) L. Meites, *Anal. Chem.*, **20**, 895 (1948).

(10) J. J. Lingane, *Ind. Eng. Chem.*, *Anal. Ed.*, **19**, 810 (1947).

(11) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

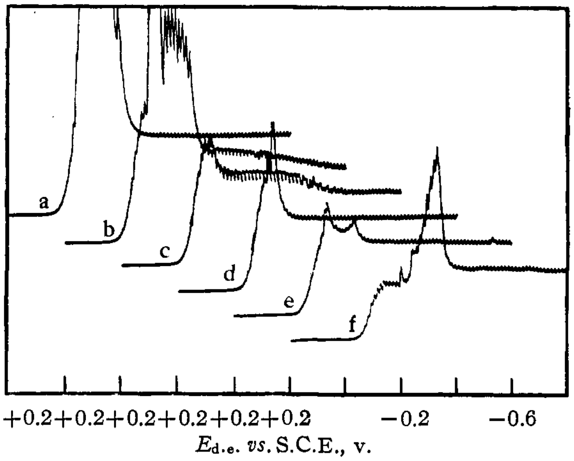

Fig. 1.—Polarograms of 3.23 millimolar copper (II) in 0.5 *M* potassium sodium tartrate at *p*H (a) 1.74, (b) 2.70, (c) 3.71, (d) 4.80, (e) 5.62, and (f) 6.27.

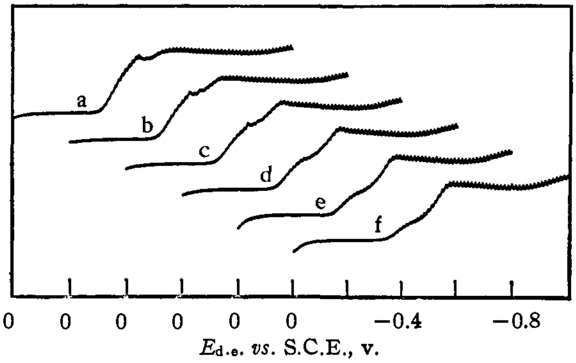

Fig. 2.—Polarograms of 3.23 millimolar copper (II) in 1.0 *M* potassium sodium tartrate at *p*H (a) 7.02, (b) 7.24, (c) 7.47, (d) 7.69, (e) 7.93, and (f) 8.12.

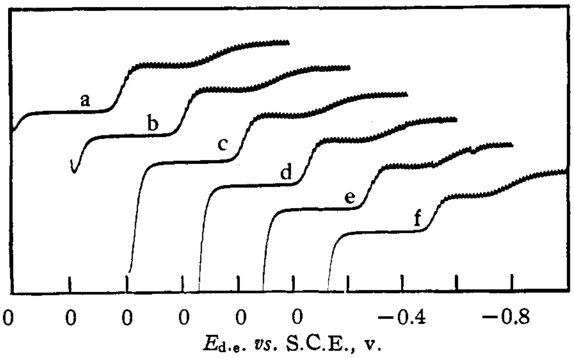

Fig. 3.—Polarograms of 3.23 millimolar copper (II) in 1.0 *M* potassium sodium tartrate at *p*H (a) 11.78, (b) 12.07, (c) 12.38, (d) 12.72, (e) 13.12, and (f) 13.50.

almost exactly the same in 0.5 or 1.0 *M* tartrate. This is in accordance with the fact that, in this *p*H range, the composition of the solution is determined, not by the total amount of tartrate present in the cell, but by the solubilities of sodium and potassium hydrogen tartrates. The presence of the maximum makes it impossible to attach any thermodynamic significance to the measured half-wave potentials.

As the *p*H is increased above about 6, the former single wave splits quite sharply into two waves. The first of these is fairly well defined, but the second has a maximum, sharper in 0.1 and 0.5 *M* tartrate than in 1 *M* tartrate (*cf.* curve *f*, Fig. 1, and Fig. 2), which again is suppressed by increasing *p*H. Concurrently, the height of the first wave is decreased, while that of the second increases. The sum of these two waves, at *p*H values near the bottom of this range, is about 10% smaller than the total wave height in more acid solutions where only one wave appears. The variation with *p*H of the relative heights of these waves in 0.5 *M* tartrate is shown in Fig. 4.

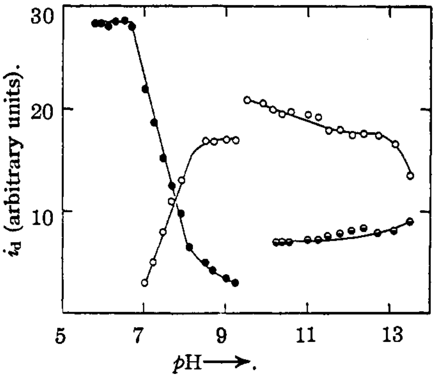

Fig. 4.—Effects of *p*H on the diffusion currents of the copper (II) waves in 1.0 *M* potassium sodium tartrate. Solid circles represent the first wave, open circles the second, and half-solid circles the third.

From Figs. 4, 5 and 6, which show the effect of *p*H on the half-wave potential of copper in tartrate solutions of various concentrations, the first indication of the appearance of two waves is found at *p*H 5.5 in 0.1 *M* tartrate, *p*H 6.3 in 0.5 *M* tartrate, and *p*H 6.7 in 1.0 *M* tartrate. The concentration of copper in all of these solutions was 3.23 millimolar, and from this datum and the values of $K_1$ and $K_2$ for tartaric acid given by Jones and Soper,[12] one calculates that the concentration of free hydrogen tartrate ion becomes equal to four times the copper concentration at *p*H 5.7 in 0.1 *M* total tartrate, at *p*H 6.4 in 0.5 *M* tartrate, and at *p*H 6.7 in 1.0 *M* tartrate. This appears to constitute conclusive proof that the complex formed in these acidic solutions has the formula $\mathrm{Cu(H\ Tart)_4^{-}}$, a deduction further supported by the results of an amperometric titration shown in Fig. 7.

The second of these two waves increases in height at the expense of the first as the concentration of the hydrogen tartrate ion decreases with increasing *p*H until only a single wave is observed. Over a *p*H range whose lower limit is the first appearance of a double wave and whose upper limit is the point at which the wave begins a grad-

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[12] I. Jones and F. G. Soper, *J. Chem. Soc.*, **136**, 1836 (1934).

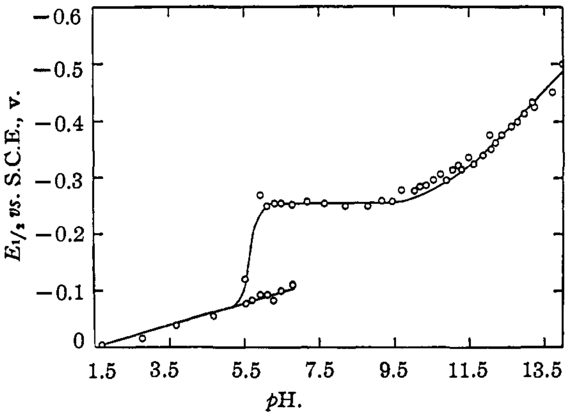

Fig. 5.—Effects of *p*H on the half-wave potentials of the copper (II) waves in 0.10 *M* potassium sodium tartrate.

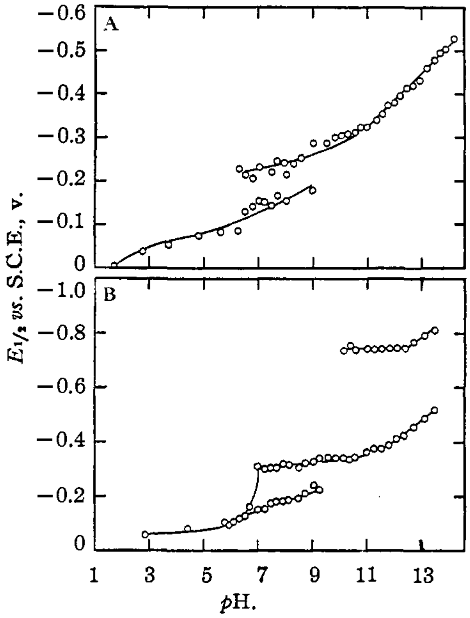

Fig. 6.—Effects of *p*H on the half-wave potentials of the copper(II) waves in (A) 0.50 *M* and (B) 1.0 *M* potassium sodium tartrate.

ual continuous shift to more negative values, the half-wave potential of this wave is fairly constant.

From measurements of the relative heights of the two waves in a similar critical region, Lingane[13] was able to establish the formula of the ferric hydrogen tartrate complex in solution as Fe(H Tart)$_3$, and theoretically it should also be possible, if the tartrate and hydrogen tartrate complexes were sufficiently slowly interconvertible, to calculate the ratio of their dissociation constants from such diffusion current measurements. In the present case, however, the ratio secured exhibits a consistent trend with *p*H: this is the behavior which would be expected if the two species were in moderately rapid equilibrium at the surface of the drop.

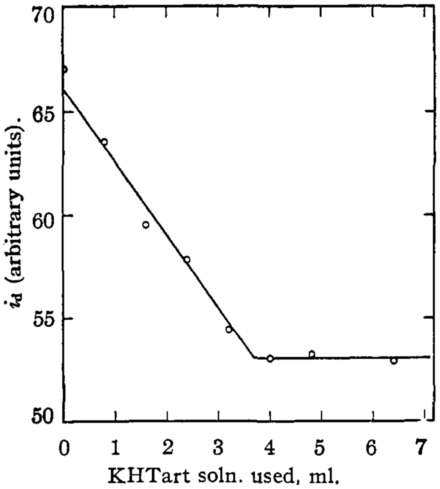

Fig. 7.—Amperometric titration of 250 ml. of 0.400 millimolar copper (II) in an 0.5 *M* acetate buffer of *p*H 3.59 with 20 millimolar potassium hydrogen tartrate, at $E_{\mathrm{d.e.}} = -0.50$ v.

As the *p*H is further increased so that the concentration of hydroxyl ion becomes significant in comparison with the copper concentration, the wave begins the slow shift to more negative potentials described above. This shift is first observed at *p*H 9.0 in 0.1 *M* tartrate, at *p*H 9.5 in 0.5 *M* tartrate, and at *p*H 10.5 in 1.0 *M* tartrate. It is surprising that the hydroxyl ion concentration in every case is much too small to correspond to conversion of an appreciable fraction of the copper into a hydroxytartrate complex. Nevertheless, the waves observed in this region are very well defined and show, on mathematical analysis, none of the phenomena frequently observed[9,14] in systems where other evidence points to the co-existence of two ionic species in moderately slow equilibrium.

A comparison of the half-wave potentials of this wave at a constant hydroxyl ion activity gives results typified by those at *p*H 12, which are −0.346 v. in 0.1 *M* tartrate, −0.378 v. in 0.5 *M* tartrate, and −0.409 v. in 1.0 *M* tartrate. Applying to these data the theoretical equation for the reduction of metal complexes derived by Lingane,[15,16] one calculates that, in the generalized equation for the reduction

$$[\mathrm{Cu(OH)}_p(\mathrm{Tart})_q]^{2-(p+2q)} + ne \longrightarrow \mathrm{Cu}^{(2-n)}\,(\mathrm{OH})_r(\mathrm{Tart})_s^{2-(n+r+2s)} + (q-s)\,\mathrm{Tart}^{=} + (p-r)\mathrm{OH}^- \quad (1)$$

$(q - s)$ is equal to $n$. Lingane[3] and Kolthoff and Lingane[17] are agreed that the reduction of copper from these solutions proceeds all the way to the metal. In confirmation of this, the slopes of plots of $-E_{\mathrm{d.e.}}$ against $\log [i/(i_d - i)]$ for the waves given by these solutions are uniformly 36 ± 2 mv., cor-

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[13] J. J. Lingane, This Journal, **68**, 2448 (1946).

[14] J. J. Lingane and L. Meites, *ibid.*, in press.

[15] J. J. Lingane, *Chem. Rev.*, **29**, 1 (1941).

[16] Ref. 2, pp. 161–165.

[17] Ref. 2, p. 280.

responding approximately to the expected value for a thermodynamically reversible two-electron reduction.[16] Therefore equation (1) becomes

$$[Cu(OH)_p(Tart)_2]^{-(2+p)} + 2e \longrightarrow Cu(Hg) + 2\ Tart^= + p\ OH^- \quad (2)$$

Now the rate of change of the half-wave potential with $pH$ in this region is shown by Figs. 5 and 6 to be nearly linear, and from them the average values of $\Delta E_{1/2}/\Delta(pH)$ are estimated to be −50 mv. in 0.1 *M* tartrate, −60 mv. in 0.5 *M* tartrate, and −63 mv. in 1.0 *M* tartrate. The differences in these values may well be due to the effects of the changing ionic strength on the activity coefficients of the various species involved in the equilibrium. However, they are all in satisfactory agreement for the predicted effect of $pH$ on the half-wave potential for $p = 2$ in equation (2), so that, finally

$$Cu(OH)_2(Tart)_2^{-4} + 2e \longrightarrow Cu(Hg) + 2\ Tart^= + 2OH^- \quad (3)$$

At $pH$ 14.0, and at a total tartrate concentration of 1.0 *M*, the half-wave potential is −0.563 v. Then, neglecting, perforce, activity effects, we write, using the value for $E_{1/2}$ of the aquo-cupric ion given by Kolthoff and Lingane[18]

$$K = \frac{[Cu^{++}][OH^-]^2[Tart^=]^2}{[Cu(OH)_2(Tart)_2^{-4}]} = 1.4 \times 10^{-10}$$

and, for the standard potential of the reduction corresponding to equation (3), by combining this value for $K$ with the $E_0$ for the copper–cupric ion couple given by Lewis and Randall,[19] we secure

$$Cu + 2OH^- + 2\ Tart^= \longrightarrow Cu(OH)_2(Tart)_2^{-4} + 2e;\ E^0 = +0.24\ v.$$

corresponding to a standard free energy change of 13.4 kcal.

Jellinek and Gordon[20] report, from potentiometric measurements, that $K = [Cu^{++}]^2[OH^-]^4\cdot[Tart^=]^2/[Complex]$ and state that $[Cu^{++}] = 10^{-15}$ *M* when $[OH^-] = 1$ *M* and the concentration of the complex is $10^{-3}$ *M*. Latimer[21] has called attention to the uncertainty regarding the formula of the complex ion.

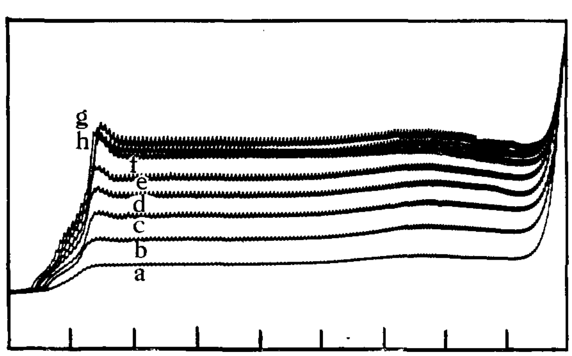

Fig. 8.—Polarograms of (a) 0.385, (b) 0.741, (c) 1.071, (d) 1.380, (e) 1.667, (f) 2.064 (g) 2.424, and (h) 2.86 millimolar copper (II) in 1.00 *M* potassium hydroxide.

The second wave visible on the curves of Fig. 4 appears only at $pH$ values above about 10. Since its height, although to some extent a function of the tartrate concentration, is never quite equal to that of the first wave, and in 1 *M* tartrate is only about one-third of the height of the first wave, it cannot indicate stepwise reduction of the copper, but must be due to the presence of a second complex in very slow equilibrium with the first. Its height is quite insensitive to gross changes in $pH$, and its half-wave potential is similarly independent of $pH(E_{1/2} = -0.744 \pm 0.004$ v. *vs.* the S.C.E. in 1.0 *M* tartrate) up to $pH$ 12.5. Because it was thought that this wave might be due to the reduction of a cuprate ion, the polarograms shown in Fig. 8 were recorded. At low concentrations (0.4 millimolar) only a single wave, with a half-wave potential of −0.410 v., is observed. The value of $E_{3/4} - E_{1/4}$ for this wave is −42 mv., showing that the two-electron reduction to the metal proceeds somewhat irreversibly from these solutions. As the total copper concentration is increased, the wave appears to divide into two poorly separated waves nearly equal in height, of which the second is much more nearly reversible than the first, and at the same time a small maximum develops. These facts strongly indicate that the cuprate species which predominates in these solutions is reduced to the metal *via* an intermediate cuprite ion. At copper concentrations above 2.5 millimolar, a dark brown solid phase, presumably cupric oxide, separates, and further additions of copper then have little effect on the diffusion current observed. The complexity of the wave form does not appear to affect the constancy of $i_d/C$, as shown in Fig. 9, which shows a sharply defined limiting concentration of dissolved +2 copper of $2.18 \times 10^{-3}$ *M*. This is considered more reliable than the solubility computed by Latimer.[22]

$$Cu(OH)_2 + 2OH^- \longrightarrow CuO_2^= + 2H_2O;\ K = 1.2 \times 10^{-3}$$

For the moment, we can at least conclude that the wave at −0.744 v. is not due to the reduction of a cuprate ion, but no better explanation has as yet suggested itself.

Lingane,[3] working with solutions containing 0.01% gelatin, found that the copper wave in 0.5 *M* tartrate containing 0.1 *M* sodium hydroxide was shifted to a very negative potential ($E_{1/2}$ = *ca.* − 1.6 v.), while a small "pre-wave" was observed starting at about −0.4 v. He considered the "pre-wave" to be produced by the same species present in the neutral and slightly acid solutions, which, on the basis of the present discussion, is plainly impossible. The appearance of the main

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[18] Ref. 2, p. 279.

[19] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Publishing Co., New York, N. Y., 1923, p. 433.

[20] K. Jellinek and H. Gordon, *Z. physik. Chem.*, **112**, 207 (1924).

[21] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 175.

[22] Ref. 21, p. 174.

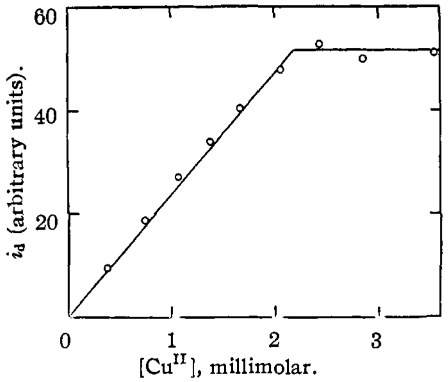

Fig. 9.—The diffusion current of copper (II) in 1.00 *M* potassium hydroxide. $E_{d.e.} = -0.80$ v.

wave at −1.6 v. is also in contradiction of the present data. The apparent controversy is resolved by Fig. 10, which shows the effect of adding 0.010% gelatin to a solution of +2 copper in 0.5 *M* tartrate containing 1 *M* potassium hydroxide. Similar effects are caused by the addition of gelatin to every other system discussed in this paper: a discussion of these effects is now in preparation. Once again it must be stressed that the indiscriminate addition of gelatin to a solution except for the specific purpose of suppressing a maximum, and then only in an amount barely sufficient to accomplish this purpose, is to be looked upon with the gravest suspicion.

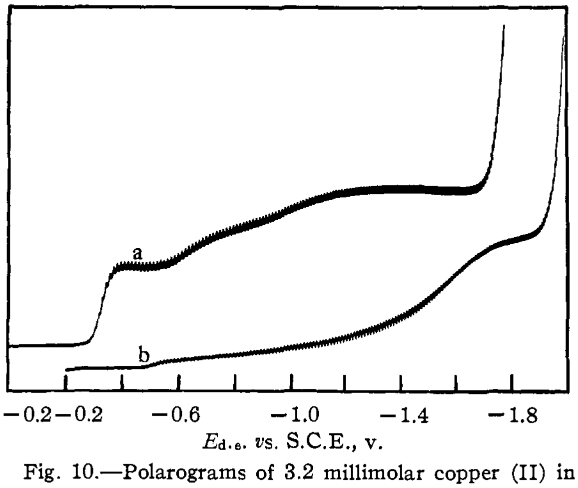

Fig. 10.—Polarograms of 3.2 millimolar copper (II) in 0.50 *M* potassium sodium tartrate and 1.0 *M* potassium hydroxide, (a) without gelatin, (b) with 0.010 % gelatin.

Figures 11, 12 and 13 show the effect of *p*H on the reduction of +2 copper from ammoniacal ammonium tartrate solutions: the values of $E_{1/2}$ are plotted in Fig. 14 as functions of the *p*H. Below *p*H 5.6 there appears to be no difference between the waves in these solutions and those in solutions containing only alkali metal ions, except that the maximum seems to be somewhat accentuated. The appearance of a double wave at *p*H 7.9 in 0.1 *M* ammonium tartrate, and at *p*H 8.2 in 0.25 *M* ammonium tartrate, is accompanied by the development of a very peculiar hump in the

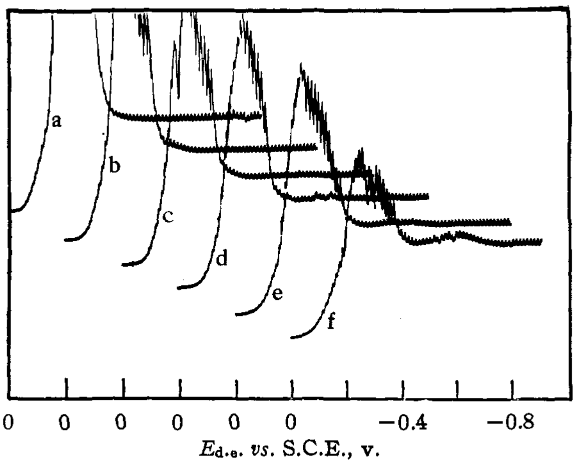

Fig. 11.—Polarograms of 3.23 millimolar copper (II) in 0.100 *M* ammonium tartrate at *p*H (a) 6.07, (b) 6.49, (c) 6.89, (d) 7.21, (e) 7.60, and (f) 7.95.

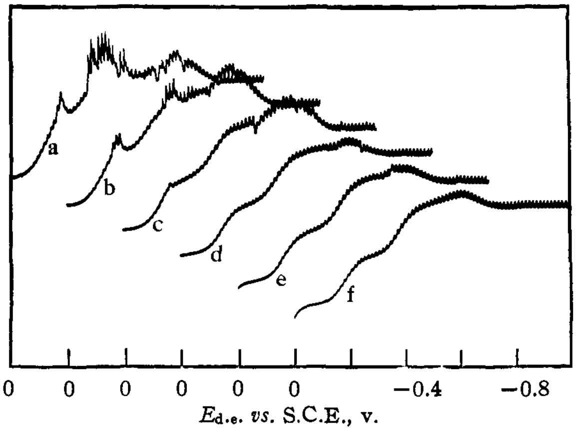

Fig. 12.—Polarograms of 3.23 millimolar copper (II) in 0.100 *M* ammonium tartrate at *p*H (a) 8.25, (b) 8.58, (c) 8.82, (d) 9.11, (e) 9.41, and (f) 9.72.

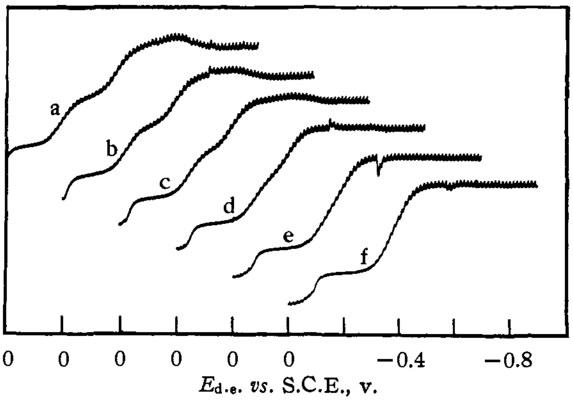

Fig. 13.—Polarograms of 3.23 millimolar copper (II) in 0.100 *M* ammonium tartrate at *p*H (a) 10.03, (b) 10.50, (c) 10.90, (d) 11.38, (e) 11.90, and (f) 12.22.

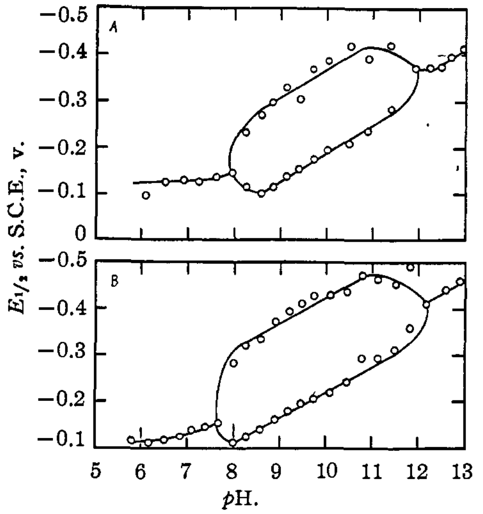

Fig. 14.—Effects of *p*H on the half-wave potentials of the copper (II) waves in (A) 0.10 *M* and (B) 0.25 *M* ammonium tartrate.

plateau of the second wave about 0.2 v. after this plateau is reached. This hump is observed at all *p*H values at which a double wave is found. These two waves are, within the limits of accuracy of the measurements, equal in height throughout this *p*H range, which indicates that reduction to the metal proceeds through the +1 state. For each of the waves $E_{3/4} - E_{1/4}$ is found to be −66 ± 4 mv., in approximate agreement with the expected value for a reversible one-electron reduction.

In 0.1 *M* ammonium tartrate, the half-wave potentials are given by the equations $E_{1/2}{}^1 = 0.458 - 0.065$ (*p*H) (±4 mv.) and $E_{1/2}{}^2 = 0.273 - 0.065$ (*p*H) (±14 mv.). The corresponding equations for 0.25 *M* ammonium tartrate solutions are $E_{1/2}{}^1 = 0.359 - 0.0583$ (*p*H) (±5 mv.) and $E_{1/2}{}^2 = 0.156 - 0.0583$ (*p*H) (±11 mv.). In each case the better agreement with the equation for the first wave is due to the considerably poorer definition of the second.

Now this effect of *p*H is exactly that to be expected if one molecule of ammonia is liberated in each one-electron reduction, so that the copper(II) complex must be formulated as $Cu(NH_3)_2(Tart)_x{}^{2-2x}$ and the copper(I) complex must be $Cu(NH_3)(Tart)_y{}^{1-2y}$. On making a correction of 0.40 *p*H unit to compensate for the different concentrations of ammonium ion, the half-wave potentials of the first waves (reduction to +1 copper) at the different concentrations of tartrate are found to be essentially equal (±10 mv.) at equal concentrations of ammonia. Therefore we must conclude that tartrate ions are not involved in the first step of the reduction, and, in equations 4 and 5

$$Cu(NH_3)_2(Tart)_x{}^{2-2x} + e \longrightarrow Cu(NH_3)(Tart)_y{}^{1-2y} + NH_3 + (x - y)Tart^= \quad (4)$$

$$Cu(NH_3)(Tart)_y{}^{1-y} + e \longrightarrow Cu(Hg) + NH_3 + yTart^= \quad (5)$$

$x = y$. The same correction to the data for the second waves reveals that, at a constant concentration of ammonia, a 2.5-fold increase in the tartrate concentration shifts the half-wave potential corresponding to equation (5) to a value more negative by about 30 mv. This corresponds to 75 mv. for a tenfold increase in tartrate concentrations, in approximate agreement with the theoretical effect if $y = 1$ in equation 5. Correcting the observed data to solutions containing *M* ammonia and tartrate, we then have

$$Cu(NH_3)(Tart)^- + NH_3 \longrightarrow Cu(NH_3)_2(Tart) + e;\ E^0 = -0.04 \text{ v.}$$

and

$$Cu(Hg) + NH_3 + Tart^= \longrightarrow Cu(NH_3)(Tart)^- + e;\ E^0 = +0.20 \text{ v.}$$

At *p*H values above about 11, when the concentration of hydroxyl ion becomes of the same order of magnitude as the concentration of copper, the two waves coalesce into one which, because of the equality of the $E_1/_2$ values, must be attributed to the reduction of the $Cu(OH)_2(Tart)_2{}^{-4}$ complex present in the ammonia-free tartrate solutions of the same pH..

Figure 15 illustrates the effect of gelatin on the waves in ammoniacal ammonium tartrate, and re-emphasizes the caution that must be observed in the use of gelatin.

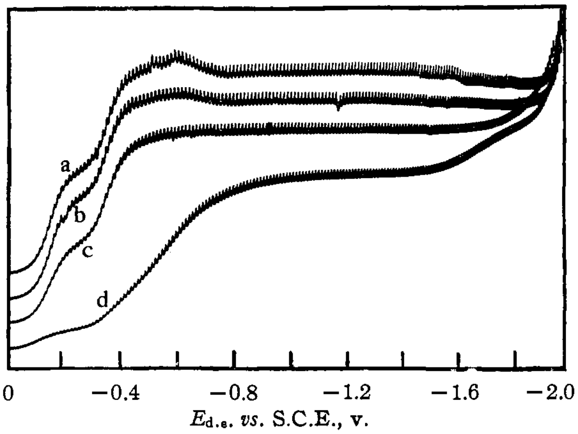

Fig. 15.—Polarograms of 3.2 millimolar copper (II) in 0.10 *M* ammonium tartrate, *p*H 9.55, with (a) 0, (b) 0.001, (c) 0.010, and (d) 0.050 % gelatin.

## Summary

Acidic tartrate solutions of +2 copper contain the $Cu(H\ Tart)_4{}^=$ ion which is reduced directly to the metal at about −0.1 v. (*vs.* S.C.E.). At *p*H values between about 7 and 11, the copper is present mainly as a tartrate complex whose formula cannot be determined from polarographic measurements, and in still more alkaline solutions the $Cu(OH)_2(Tart)_2{}^{-4}$ ion is formed. The dissociation constant of this ion is $1.4 \times 10^{-10}$.

The same phenomena are found in ammonium tartrate solutions of *p*H below 7 or above 12, but in the intermediate range an amminocupric tartrate ion is formed. This is reduced to the metal *via* the +1 state, the reactions being

$$Cu(NH_3)(Tart)^- + NH_3 \longrightarrow Cu(NH_3)_2(Tart) + e;\ E^0 = -0.04 \text{ v.}$$

and

$$Cu(Hg) = NH_3 + Tart^= \longrightarrow Cu(NH_3)(Tart)^- + e;\ E^0 = +0.20 \text{ v.}$$

The solubility of +2 copper in $M$ hydroxide is $2.18 \times 10^{-3}$ $M$.

Gelatin severely distorts the waves of all these species, especially at concentrations above 0.001%. Great stress is laid on the caution that should be observed in its use if polarographic data are to be considered to represent the true electrochemical behavior of substances in solution.

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# A Thermodynamic Study of Liquid Metallic Solutions. I. The System Lead–Gold

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## Introduction

In a detailed experimental study of the thermodynamic properties of binary liquid alloy systems, there are two general ways of approach. One method is to evaluate the activity of a volatile component (Hg, Zn, Cd, Mg) from vapor pressure measurements. The other method depends on measuring the electromotive force in reversible galvanic cells of the type

$$A(l)/A^{n+}/(A + B)(l)$$

where A denotes the baser (more electropositive) metal, B the other metal.

If carried out over a sufficiently large composition and temperature range, both methods will give us, in principle, all the data required for a complete evaluation of the thermodynamic properties (*i. e.*, free energy, entropy and heat of mixing) for the mixture, using the pure components as reference states. Both methods have also found extensive application at moderately high temperatures during the past twenty to twenty-five years.[1]

It has not, however, so far been possible to tie the results of these researches in with any existing theory of solutions.[2] This paper is the first report on a series of investigations started in order, if possible, to arrive at a clearer understanding of the factors governing the properties of such liquid metallic solutions.

**Experimental Method.**—The system lead–gold is well suited for application of the electromotive force method.

Measurements of the electromotive force, $E$, of various liquid alloy compositions *versus* pure liquid lead immediately give us the relative chemical potential $\mu_{Pb}$ in the mixture through the relationship $\mu_{Pb} - \mu_{Pb}^0 = -2FyE$ where $Fy$ is the faraday constant. The superscript$^0$ in this paper refers to the pure component.

The temperature gradient of the electromotive force, $dE/dT$, will give the relative partial molar entropy $\Delta\bar{S}$ in the mixture in a similar way, through the relationship

$$\Delta\bar{S} = \bar{S} - S^0 = 2Fy(dE/dT)$$

These quantities are thus directly available from measurements. Through the equation

$$\mu - \mu^0 = \bar{L} - T\Delta\bar{S}$$

we can also immediately calculate the relative partial molar heat content, $\bar{L}_{Pb}$, for lead in the mixture.

A knowledge of the partial molar properties for one of the components over the whole concentration range makes possible a calculation of the same properties for the other component by (graphical) integration of the Gibbs–Duhem–Margules equation

$$x_1 d\bar{Y}_1 + x_2 d\bar{Y}_2 = 0$$

where $\bar{Y}_1$ is any partial molar quantity for component 1, $x_1$ is the corresponding mole fraction (or here atomic fraction).

It should, however, be noted that in the case of lead–gold, where it was not possible to extend the measurements into the gold-rich region beyond an atomic fraction of gold of 0.79, the calculation of the partial molar properties for gold in the mixtures is associated with some uncertainty. This uncertainty is carried through in any calculation of the integral thermodynamic properties $Y$ through the equation

$$Y = x_1\bar{Y}_1 + x_2\bar{Y}_2$$

## Experimental Procedure

The type of cell used in this investigation was similar to the H-shaped cell extensively applied by H. Seltz and co-workers.[3] However, as the study of the lead–gold system required measurements up to 800–850°, temperatures at which Pyrex will no longer stand up, the cells were made from fused silica. Although extended heating at the highest temperatures caused some devitrification of the cell walls, it was found that these silica cells in general stood up quite well to the attack of the electrolyte used. This consisted of a eutectic mixture (m. p. 360°) of lithium

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[1] A fairly complete bibliography is recently given by John Chipman, *Discussions Faraday Soc.*, **4**, 23 (1948).

[2] J. H. Hildebrand, "Solubility," Reinhold Publishing Corp., New York, N. Y., 1936.

[3] H. Seltz, *Trans. Electrochem. Soc.*, **77**, 233 (1940).