are not susceptible to chemical or thermodynamic interpretation in the absence of confirmatory information secured from other sources.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Polarographic Studies of Metal Complexes. III. The Copper(II) Oxalates and Carbonates

BY LOUIS MEITES*

The present paper is a continuation of a series whose earlier members have been devoted to the tartrate[1] and citrate[2] complexes of +2 copper.

Experimental

The experimental apparatus and techniques were essentially identical with those used previously.[1,2]

Data and Discussion

Polarography of Cu(II) in Oxalate Media.—Figure 1 shows the relationship between the half-wave potential of copper(II) in 0.09 *F* potassium oxalate and the *p*H of the solution between 0.8 and 11. The waves are well defined at all *p*H values, but in solutions more acidic than *p*H 2 a maximum develops whose height is greatly increased by decreasing oxalate concentration.

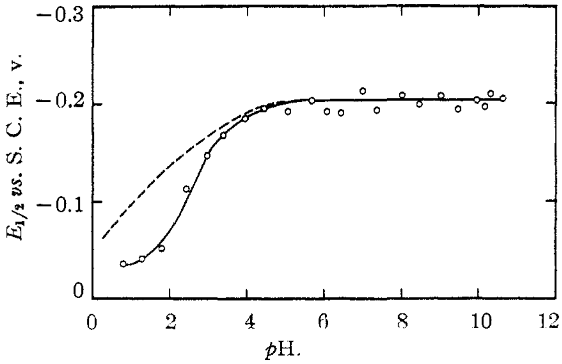

Fig. 1.—Half-wave potentials of 3.2 millimolar copper(II) in 0.09 *F* potassium oxalate: the dashed line represents the theoretical values if no hydrogen oxalate complex is formed.

Above *p*H 5.7, where substantially all of the oxalate has been converted into the C_2O ion, no change in half-wave potential is observed. As in this *p*H range, the concentrations of all other anions in the solution are small compared to the copper concentration (usually 3m*M*), the greenish-blue complex must be of the type $Cu(C_2O_4)_x^{2-2x}$. For the reversible $(\Delta(-E_{d.e.})/\Delta \log (i/(i_d - i)$ = 28–31 mv.[3]) reduction of this complex to the metal, the half-wave potential is −0.204 ± 0.006 v. (*vs.* S.C.E.) in 0.090 *F* oxalate and −0.271 ± 0.006 v. in 0.95 *F* oxalate. Then, from the general equation[8] for the half-wave potential of a reversible *n*-electron reduction, we have

$$\frac{\Delta E_{1/2}}{\Delta \log [C_2O_4^=]} = \frac{-0.067}{1.024} = -\frac{0.0591}{n}x \qquad (1)$$

whence, since $n = 2$, $x = 2.2$. Therefore the complex must be $Cu(C_2O_4)_2^=$.

From equation (1) and the measured half-wave potentials in 0.95 *F* oxalate, the half-wave potential for the reduction of the $Cu(C_2O_4)_2^=$ ion from 1.00 *F* oxalate should be −0.272 v. For the reduction of the aquo-copper(II) ion at the dropping electrode, Kolthoff and Lingane[4] give $E^0 = +0.033$ v. The difference between this and the above figure is related to the dissociation constant of the complex by the expression[3]

$$-0.272 - 0.033 = (0.0591/n) \log K \qquad (2)$$

whence

$$K = [Cu^{++}][C_2O_4^=]^2/[Cu(C_2O_4)_2^=] = 4.8 \times 10^{-11} \qquad (3)$$

and, using the standard free energies of the cupric and oxalate ions computed by Latimer,[5] $F°$-$Cu(C_2O_4)_2^=$ = −315.5 kcal.

For the reaction Cu → $Cu^{++} + 2e$, Lewis and Randall[6] give E^0 = −0.3448 v. (*vs.* N.H.E.). Then from equation (3) we deduce

$$Cu + 2\,C_2O_4^= \longrightarrow Cu(C_2O_4)_2^= + 2e; \qquad E^0 = -0.04\ v.\ (N.\ H.\ E.) \qquad (4)$$

The dashed line in Fig. 1 corresponds to the half-wave potentials in 0.094 *F* oxalate calculated from equation (1) on the assumption that no hydrogen oxalate complex is formed. The line is coincident with the experimental points down to a *p*H of about 3, but in more acidic solutions the deviation is appreciable. This *p*H corresponds quite closely to that at which, from the values of K_1 and K_2 for oxalic acid quoted by

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* Harvard University Ph.D., 1947.

(1) L. Meites, THIS JOURNAL, **71**, 3269 (1949).

(2) L. Meites, *ibid.*, **72**, 180 (1950).

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 161-164.

(4) Ref. 3, p. 176.

(5) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, N. Y., 1938.

(6) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

Gane and Ingold,[7] the concentration of oxalate ion becomes equal to twice that of the copper(II) present. Even though aquo- or binoxalatocopper ions must therefore be formed in the body of the solution below this *p*H, one would expect that they would react in the diffusion layer with the oxalate ions liberated at the electrode surface, and, hence, that the predicted potential relationships would be at least approximately fulfilled. That they are not indicates that the rate of combination of the ions to form the oxalate complex must be fairly slow. A similar behavior is also found with the tartrate[1] and citrate[2] complexes.

Although the measured half-wave potentials in acid media are about 70 mv. more negative than that[8] found for the reduction of the aquocopper(II) ion, the data afford no substantial evidence for the existence of a hydrogen oxalate complex.

At *p*H values above about 10 in 0.1 *F* oxalate, or 11.4 in 1 *F* oxalate, addition of more potassium hydroxide causes the single $Cu(C_2O_4)_2^=$ wave to break up into a doublet wave (curve *g*, Fig. 2). As the first wave is always considerably greater in height than the second, this cannot represent stepwise reduction *via* the +1 state, but must indicate the formation of a second ionic species, probably of the type $Cu(OH)_x^{2-x}$. Simultaneously a light greenish-blue semi-gelatinous precipitate forms and the wave height decreases as precipitation continues on further addition of hydroxide. Taking the over-all wave height to be accurately proportional to the concentration of dissolved copper(II) (*i. e.*, assuming that the two species have equal diffusion coefficients, which seems to be justified by the fact that, at equal copper concentrations, the diffusion current in 0.95 *F* oxalate is only about 15% larger than that in *M* potassium hydroxide[1]), one finds, as shown in Table I, that the ion-product $[Cu^{II}][OH^-]^{1.5}$ is constant in each of the various media, although it increases regularly with increasing oxalate

TABLE I

PRECIPITATION OF BASIC COPPER(II) OXALATE

$[OH^-]$, molar	i_d, arbitrary units	$[Cu^{II}]$ molar	$[Cu^{II}][OH^-]^{1.}$
	(a) 0.0905 *F* oxalate		
1 × 10^{-4}	47.0	3.02 × 10^{-3}	No precipitate
1.55	38.0	2.44	4.7 × 10^{-9}
2.00	20.5	1.32	3.7
4.57	7.0	0.45	4.4
		Mean	4.3 × 10^{-9}
	(b) 0.435 *F* oxalate		
0.50 × 10^{-3}	42.0	2.95 × 10^{-3}	No precipitate
0.71	39.9	2.80	5.3 × 10^{-8}
2.88	5.4	0.38	5.8
4.80	2.67	0.18$_6$	6.2
		Mean	5.8 × 10^{-8}
	(c) 0.450 *F* oxalate, 0.45 *F* potassium sulfate		
0.32 × 10^{-3}	70.5	4.97 × 10^{-3}	No precipitate
.58	61.6	4.35	6.1 × 10^{-8}
.68	51.3	3.62	6.4
.77	38.4	2.71	5.8
.91	32.5	2.29	6.3
1.08	25.6	1.81	6.5
1.37	17.3	1.22	6.1$_5$
2.10	7.9	0.56	5.4
		Mean	6.1 × 10^{-8}
	(d) 0.953 *F* oxalate		
2.0 × 10^{-3}	50.3[a] 47.4[b]	3.32 × 10^{-4}	No precipitate
4.03	49.4 46.6	3.26 3.27 × 10^{-4}	(4.9 4.9) × 10^{-8}
5.01	44.0 41.0	2.90 2.88	7.4 7.3$_5$
6.31	38.5 37.0	2.54 2.60	9.0 9.2
7.95	28.0 28.2	1.85 1.98	9.3 10.0
10.3$_5$	17.7 17.5	1.17 1.23	8.3 8.7
13.3	11.9 11.9	0.78$_5$ 0.83$_5$	8.3 8.8
18.0	8.5 8.2	0.56 0.57$_5$	8.6 8.8
		Mean	8.6$_5$ × 10^{-8}

[a,b] These represent two independent series of measurements.

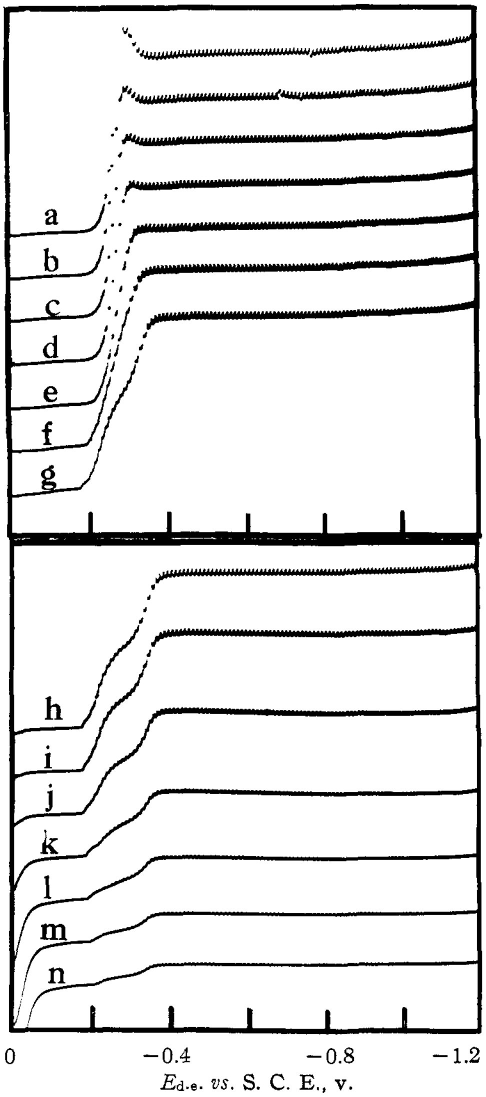

Fig. 2.—Polarograms of copper(II) in 0.953 *F* potassium oxalate at *p*H: (a) 10.06, (b) 10.29, (c) 10.47, (d) 10.72, (e) 10.96, (f) 11.20, (g) 11.45, (h) 11.60, (i) 11.80, (j) 11.80, (k) 11.90, (l) 12.01, (m) 12.13 and (n) 12.27.

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(7) R. Gane and C. K. Ingold, *J. Chem. Soc.*, 2153 (1931).

(8) Ref. 3, p. 279.

concentration. The effect of ionic strength is illustrated by parts (b) and (c) of this table: that it is small is probably due to a compensation of much larger effects on the activity coefficients of the ions involved in the equilibrium.

Now the most obvious reaction involving this relationship is

$$4Cu(C_2O_4)_2^{=} + 6OH^- \longrightarrow Cu_4(OH)_6(C_2O_4) + 7C_2O_4^{=} \quad (5)$$

Using the values of $[Cu^{II}][OH^-]^{1.5}$ from Table I, one finds for the equilibrium constant of this reaction 1.45 × 10^{26} in 0.0905 *F* oxalate, 2.5 × 10^{26} in 0.435 *F* oxalate and 1.3 × 10^{26} in 0.953 *F* oxalate. These values are quite satisfactorily concordant, and from their mean, giving the double series in 0.953 *M* oxalate twice the weight of each of the others, we calculate

$$K = [C_2O^-]^7/[Cu(C_2O_4)_2^{=}]^4[OH^-]^6 = 1.6\ (\pm 0.4) \times 10^{26} \quad (6)$$

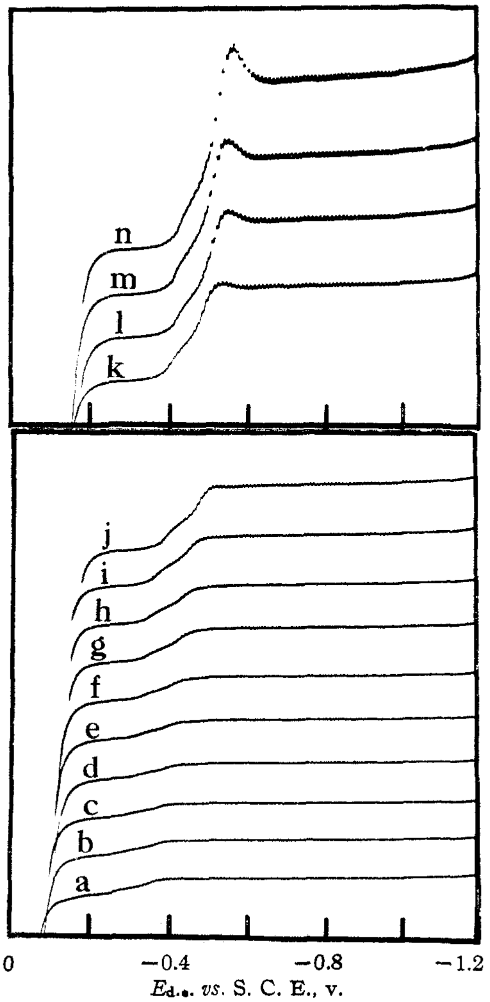

Fig. 3.—Polarograms of 0.98 *F* potassium oxalate saturated with basic copper(II) oxalate and containing: (a) 0.095, (b) 0.135, (c) 0.20, (d) 0.34, (e) 0.446, (f) 0.59, (g) 0.805, (h) 1.01, (i) 1.43, (j) 1.82, (k) 2.24, (l) 2.57, (m) 3.16 and (n) 3.72 *M* potassium hydroxide.

Combining equations (3) and (6), we then find for the solubility product of the precipitate

$$K = [Cu^{++}]^4[OH^-]^6[C_2O_4^{=}] = 2.6 \times 10^{-68} \quad (7)$$

and, for its standard free energy of formation, −413.1 kcal.

Attempts to separate the precipitate from its mother liquor so that it could be identified by other methods have been uniformly unsuccessful. Under alkaline solutions containing 1 *F* oxalate, it can be kept for some hours, but it is much less stable in dilute oxalate solutions and on washing decomposes fairly rapidly, probably losing oxalate, to a dark grayish-green gelatinous substance which was not further studied. An authentic specimen of hydrous copper(II) oxide did not decompose under these conditions.

As the *p*H is still further increased, the precipitate redissolves (Fig. 3), giving a very deep blue solution. Table II shows the effect of hydroxyl ion concentration on the solubility of the precipitate in 0.1 *F* and 1 *F* oxalate. The concentrations of dissolved copper were computed on the assumption that its effective diffusion coefficient is equal to that of the $Cu(C_2O_4)_2^{=}$ ion.

TABLE II

SOLUBILITY OF BASIC COPPER OXALATE IN EXCESS ALKALI

$[OH^-]$, molar	i_d, arbitrary units	$[Cu^{II}]$, molar	$[Cu^{II}]/[OH^-]$
	(a) 0.097 *F* oxalate		
10^{-4}	106.0	3.22×10^{-3}	....
0.72	11.0	3.3×10^{-4}	4.7×10^{-4}
0.99	15.8	4.8	4.85
1.27	22.5	6.85	5.4
1.91	32.6	9.9	5.2
2.54	45.6	1.39×10^{-3}	5.5
3.16	53.1	1.62	5.1
		Mean	5.1×10^{-4}
	(b) 0.98 *F* oxalate		
10^{-3}	106.1	3.32×10^{-3}	....
0.446	4.8	1.72×10^{-4}	3.9×10^{-4}
0.59	5.8	2.0	3.5
0.805	9.0	3.2	3.9
1.01	10.4	3.6	3.6
1.43	13.3	4.65	3.3
1.82	17.0	5.95	3.3
2.24	25.0	8.75	3.9
2.57	31.6	1.11×10^{-3}	4.3
3.16	36.5	1.3	4.0
3.72	43.4	1.5	4.1
		Mean	3.8×10^{-4}

The values for the ratio $[Cu^{II}]/[OH^-]$ in the two media are equal within the probable uncertainty introduced by the assumptions made, so that we take

$$K = [Cu^{II}]/[OH^-] = 4.5 \times 10^{-4} \quad (8)$$

Since the oxalate concentration does not appreciably affect the solubility as expressed by equation (8), the oxalate ion contained in the precipitate is presumably not liberated in the reaction. The predominant product of the reaction is presumably a cuprate species, but the manner in which the single oxalate ion is bound is not clear. Although there is a marked similarity between the polarograms of Fig. 3 and those found previously[1] for the reduction of $Cu(OH)_4^=$, the former occur at slightly less negative potentials, the separation of the two waves is decidedly less marked, and the maximum is somewhat less pronounced. That the reaction under consideration here is not simply $Cu(OH)_2 + 2\ OH^- \rightarrow Cu(OH)_4^=$ is also shown by the fact that the solubility (2.18×10^{-3} *F*) of the hydrous oxide in *F* alkali is over four times that for the present precipitate.

In ammonium oxalate solutions of *p*H less than 9, only a single wave is observed. Its half-wave potential (*e. g.*, −0.223 ± 0.004 v. in 0.25 *F* ammonium oxalate) is in agreement with that calculated from equation (1) and the measured half-wave potentials in solutions of potassium oxalate. The variation of the half-wave potentials with *p*H is depicted in Fig. 4; at *p*H values above 8.9, two waves, of which the first is reversible, but the second is not, appear. These waves are equal in height and therefore represent reduction of the copper(II) complex to the metal *via* the +1 state.

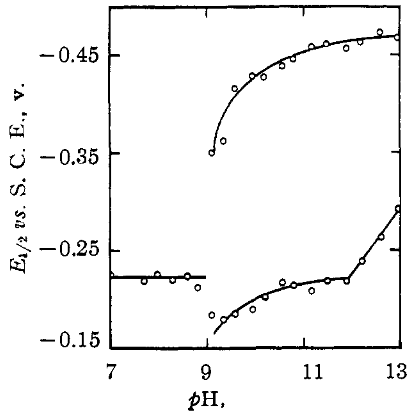

Fig. 4.—Half-wave potentials of 3.2 millimolar copper(II) in 0.25 *F* ammonium oxalate.

Figure 5 shows the dependence of these half-wave potentials on the logarithm of the concentration of ammonia. The $E_{1/2}$ values used were interpolated from Fig. 4, and the dissociation constant of ammonia was taken as 1.8×10^{-5}. For the first wave $\Delta E_{1/2}/\Delta \log [NH_3]$ is −105 mv., which gives *x* (equation (1)) as 1.8. Therefore we write

$$Cu(NH_3)_a(C_2O_4)_y^{2-2y} + e \longrightarrow$$
$$Cu(NH_3)_{a-2}(C_2O_4)_z^{1-2z} + 2NH_3 + (y - z)C_2O_4^= \quad (9)$$

For the second wave, however, $\Delta E_{1/2}/\Delta \log [NH_3]$ is −310 mv., which would give *a* in equation (9) as 7.2: this absurd value is a direct consequence of the irreversibility of this wave.

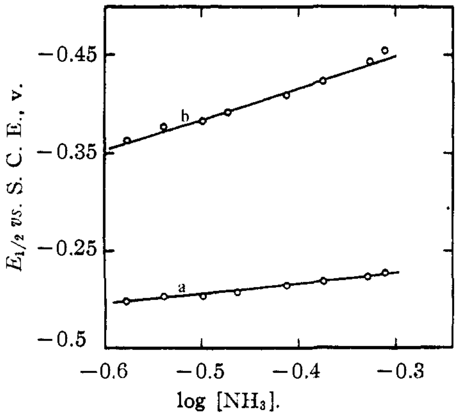

Fig. 5.—Effects of ammonia concentration on the half-wave potentials for the reduction of copper(II) from 0.25 *F* ammonium oxalate solutions: (a) reduction to copper(I); (b) reduction of copper(I) to the metal.

In 0.25 *F* ammonium oxalate the half-wave potential of the first wave is −0.222 v. at *p*H values sufficiently high (11–12) that most of the ammonium ion originally present is converted to free ammonia (0.5 *F*); in the same *p*H range in 0.1 *F* ammonium oxalate (*i. e.*, 0.2 *F* ammonia and 0.1 *F* oxalate) it is −0.177 v. The stability of the ammino-copper(II) complex is such that the basic oxalate formed in ammonia-free solutions does not appear. Correcting the latter figure for the difference in the ammonia concentrations, using equations (1) and (9), it becomes −0.224 v. in 0.5 *F* ammonia and 0.1 *F* oxalate. This shows that $(y - z)$ in equation (9) is equal to zero, so that the electrode reaction must be

$$Cu(NH_3)_a(C_2O_4)_y^{2-2y} + e \longrightarrow$$
$$Cu(NH_3)_{a-2}(C_2O_4)_y^{1-2y} + 2NH;$$
$$E^0 = -0.01 \text{ v. (N.H.E.)} \quad (10)$$

where the E^0 value is computed by correcting the observed potentials to 1 *F* ammonia with the aid of equation (1). The irreversibility of the second wave, as contrasted with the reversibility of the reduction of the simple ammino-copper(I) ion at the dropping electrode suggests (but does not prove) that *y* in equation (10) is not zero.

In ammonium oxalate solutions of *p*H higher than about 12.2, the half-wave potential of the first wave shifts to more negative values ($(\Delta E_{1/2}/\Delta pH) = -70$ mv.), while that of the second wave remains approximately constant (Fig. 4). This is the expected effect of *p*H on the half-wave potential corresponding to the reaction

$$Cu(OH)(NH_3)_b(C_2O_4)_m^{1-2m} + e \longrightarrow$$
$$Cu(NH_3)_c(C_2O_4)_n^{1-2n} + OH^- + (b - c)NH_3 +$$
$$(m - n)C_2O_4^= \quad (11)$$

Increasing the ammonia concentration from 0.2 *F* to 0.5 *F* shifts the half-wave potential of this wave to more negative values by 42 mv., while the effect calculated on the assumption that $(b - c) = 2$ is 47 mv. An increase in the oxalate concentration, on the other hand, produces no detectable change, so that, correcting to *p*H 14.0 and 1.0 *F* ammonia

$$\mathrm{Cu(OH)(NH_3)_b(C_2O_4)_m^{1-2m} + e \longrightarrow}$$
$$\mathrm{Cu(NH_3)_{b-2}(C_2O_4)_m^{1-2m} + OH^- + 2NH_3;}$$
$$E^0 = -0.15 \text{ v. (N.H.E.)} \quad (12)$$

Polarography of Cu(II) in Carbonate Media.—Addition of copper(II) to a potassium bicarbonate solution gives a light blue precipitate becoming finely crystalline on long standing. With sodium bicarbonate, according to Pickering,[9] the compound formed is $5CuO \cdot 3CO_2$, but the amperometric titration data of Fig. 6 show that we are, more probably, dealing with $K_2Cu(HCO_3)_4$, which has not been reported previously.

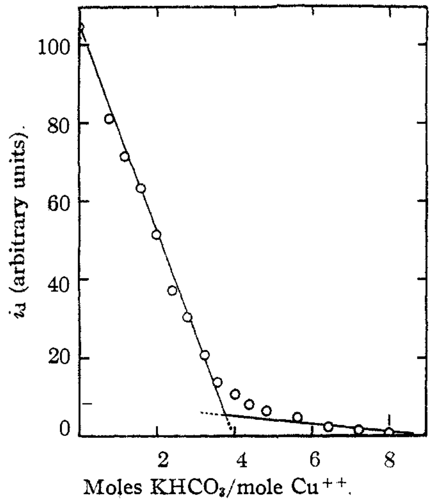

Fig. 6.—Titration of 11.1 m*M* Cu^{++} in 1.0 *F* potassium nitrate with 1.00 *F* potassium bicarbonate: $E_{d.e.} = -0.60$ v. *vs.* S. C. E.

From measurements of the diffusion current at and slightly after the equivalence point, one computes values for the solubility product of the precipitate varying erratically between 3×10^{-13} and 2×10^{-11}; in mean

$$K = [K^+]^2[Cu^{++}][HCO_3^-]^4 = 3(\pm 2.5) \times 10^{-12} \quad (13)$$

It is soluble in excess bicarbonate, and in 1.0 *M* potassium nitrate the quotient $[Cu^{II}]/[HCO_3^-]$ is substantially constant (±3%) from 0.02 to 0.3 *M* bicarbonate. From ten measurements of this ratio, at $\mu = 1.0$

$$\mathrm{K_2Cu(HCO_3)_4 + HCO_3^- \longrightarrow}$$
$$\mathrm{Cu(HCO_3)_5^{\equiv} + 2K^+;}\ K = 0.0105 \quad (14)$$

In *M* bicarbonate this complex is reduced directly to the metal and $E_{1/2} = -0.144$ v.: the wave at *p*H values between 8 and 10 has a small maximum which renders this half-wave potential value somewhat tentative. In 0.25 *F* carbonate (Fig. 7) there are two waves, only about 70 mv. apart.

As the *p*H of a carbonate solution of copper(II) is increased, its blue color becomes more intense and the waves move to slightly more negative potentials. Thus, in 0.91 *F* carbonate, *p*H 9.5–11, $E_{1/2} = -0.201 \pm 0.004$ v. In 0.24 *F* carbonate the half-wave potentials in this *p*H range are, approximately, −0.165 and −0.24 v. The effect of carbonate concentration on the wave form at *p*H 10.5 is shown in Fig. 8. The waves are unfortunately too close together to permit half-wave potential measurements accurate enough to identify the ionic species present in this *p*H range. The double waves seem to be roughly equal in height, and their ratio is not sensibly affected by carbonate concentration or *p*H. It is difficult to see how these facts could be explained by the assumption of two co-existing

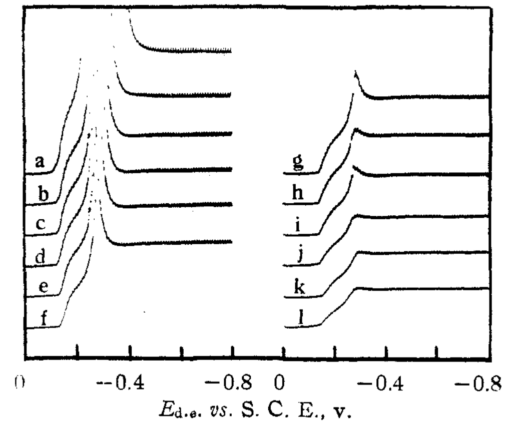

Fig. 7.—Polarograms of copper(II) in 0.24 *F* potassium carbonate at *p*H: (a) 9.41, (b) 9.90, (c) 10.12, (d) 10.23, (e) 10.30, (f) 10.41, (g) 10.50, (h) 10.61, (i) 10.72, (j) 10.88, (k) 10.97 and (l) 11.12.

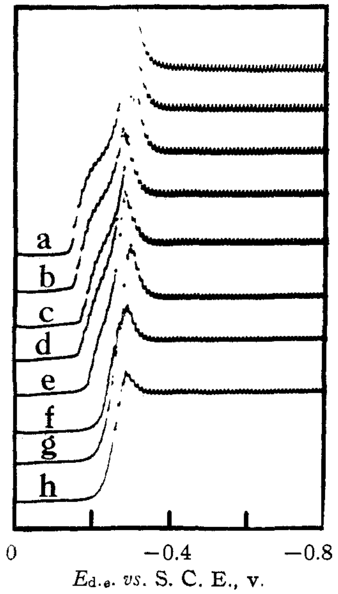

Fig. 8.—Polarograms of copper(II) in solutions of *p*H *ca.* 10.5 containing: (a) 0.327, (b) 0.372, (c) 0.456, (d) 0.537, (e) 0.683, (f) 0.870, (g) 1.030 and (h) 1.212 *F* carbonate.

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(9) S. V. Pickering, *J. Chem. Soc.*, **95**, 1409 (1909).

species, and one is tempted to conclude that the copper(II) complex is being reduced *via* the +1 state.

At *p*H 11.5 in 0.24 *F* carbonate, or *p*H 11.0 in 0.91 *F* carbonate, a gelatinous blue precipitate begins to separate out (Fig. 7). A portion of this precipitate, filtered on a sintered Pyrex Buchner-type funnel, washed with water and acetone, and air-dried overnight, lost 32.0% at 100°. The material thus dried was ignited to cupric oxide; it contained 80.0% (calcd. for $Cu(OH)_2 \cdot 2.25\ H_2O$: 31.6% H_2O, 81.5% CuO).

According to Pickering,[9] solutions of copper(II) in excess sodium carbonate contain "α-cupricarbonate," which he represented as $Na_2Cu(CO_3)_2 \cdot Na_2CO_3$. Assuming that the copper is actually present as the $Cu(CO_3)_3^{-4}$ ion, we have

$$Cu(CO_3)_3^{-4} + 2OH^- \longrightarrow Cu(OH)_2 + 3CO_3^=$$

$$K = [CO_3^=]^4/[Cu(CO_3)_3^{-4}[OH^-]^2 \quad (15)$$

But the carbonate concentration also depends on *p*H: letting $[CO_3^=] + [HCO_3^-] = C$

$$K = C^3[OH^-]/[Cu(CO_3)^{-4}]([OH^-] + K_W/K_2)^3 \quad (16)$$

In 0.915 *F* carbonate the calculated value of K is (1.15 ± 0.2) × 10^7, and in 0.240 *F* carbonate it is (1.85 ± 0.3) × 10^7. In mean, therefore, $K = (1.5 \pm 0.4) \times 10^7$.

As the *p*H is raised to still higher values, the hydrous oxide redissolves, giving waves identical with those found in the absence of carbonate,[1] and hence presumably due to the $Cu(OH)_4^=$ ion.

Summary

The following new thermodynamic data have been derived from polarographic measurements.

$Cu(C_2O_4)_2^= \longrightarrow Cu^{++} + 2C_2O_4^=$	$K = 4.8 \times 10^{-11}$
$Cu(C_2O_4)_2^=$	$F^0 = -315.5$ kcal.
$Cu + 2C_2O_4^= \longrightarrow Cu(C_2O_4)_2^= + 2e$	$E^0 = -0.04$ v.
$Cu_4(OH)_6(C_2O_4) \longrightarrow 4Cu^{++} + 6OH^- + C_2O_4^=$	$K = 2.6 \times 10^{-68}$
$Cu_4(OH)_6(C_2O_4)$	$F^0 = -413.1$ kcal.
$Cu_4(OH)_6(C_2O_4) + 4OH^- \longrightarrow 4Cu^{II}$	$K = 4.5 \times 10^{-4}$
$Cu(NH_3)_{a-2}(C_2O_4)_y^{1-2y} + 2NH_3 \longrightarrow Cu(NH_3)_a(C_2O_4)_y^{2-2y} + 2e$	$E^0 = +0.01$ v.
$Cu(NH_3)_{b-2}(C_2O_4)_m^{1-2m} + OH^- + 2NH_3 \longrightarrow Cu(OH)(NH_3)_b(C_2O_4)_m^{1-2m} + e$	$E^0 = +0.15$ v.
$K_2Cu(HCO_3)_4 \longrightarrow 2K^+ + Cu^{++} + 4HCO_3^-$	$K = 0.3 \times 10^{-11}$
$K_2Cu(HCO_3)_4 + HCO_3^- \longrightarrow 2K^+ + Cu(HCO_3)_5^-$	$K = 0.0105$
$Cu(CO_3)_3^{-4} + 2OH^- \longrightarrow Cu(OH)_2 + 3CO_3$	$K = 1.5 \times 10^7$

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Polarography of Chromium(II)

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The anodic wave of chromous ion in sulfuric acid has been used for the determination of chromium in steel,[1] and the reversible behavior at the dropping mercury electrode of the chromo–chromicyanide couple has been studied by Hume and Kolthoff.[2] These are the only data available concerning the polarography of +2 chromium.

In the present paper, the results of a systematic investigation of the anodic wave produced by the oxidation of +2 chromium to the +3-state in various supporting electrolytes are reported.

Experimental

Apparatus.—Earlier measurements were made with a manual instrument based on a circuit previously described.[3] Later measurements, including most of those described herein, were made with a modified Fisher Elecdropode. Since this instrument is not suitable for measuring anodic currents, a reversing switch was placed across the galvanometer terminals and the damping condenser was removed. An auxiliary variable resistance was placed across the galvanometer terminals so that the galvanometer sensitivity could be adjusted to correspond to convenient multiples of microamperes. This resistance was correctly adjusted for each shunt value by measuring the potential drop across a precision resistance with a potentiometer and applying Ohm's law. The polarizing slide wire was calibrated with a potentiometer.

All measurements were made in an H-cell with a saturated calomel electrode at 25.0 ± 0.1°. The drop time of the capillary was 5 sec. on open circuit and 3.5 sec. at an applied potential of 1.7 volts. The rate of flow of mercury was measured automatically.[4] Purified nitrogen was used to remove dissolved oxygen from the test solutions. Residual currents were measured and the proper corrections have been made for all diffusion current constants reported.

The *p*H of the solutions was measured with a glass electrode.

All potentials were measured against the saturated calomel electrode (S. C. E.).

Reagents.—Standard solutions of chromous sulfate were prepared as previously described.[5] This method introduces zinc into the solution which is reduced at a more positive potential than the anodic wave of chromous ion in many supporting electrolytes and thus interferes. Although zinc can be separated by precipitating the chromium as chromous acetate,[6] other methods of reduction were investigated. Reduction by pure aluminum metal

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