[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE EQUILIBRIUM BETWEEN CUPRIC ION, CUPROUS ION AND METALLIC COPPER

BY FLORENCE FENWICK[1]

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Introduction

Previous attempts to determine the constant for the equilibrium between cupric ion, cuprous ion and metallic copper have been made by Luther[2] and by Bodländer and Storbeck.[3] The results, however, are not concordant, Luther obtaining for the constant $K_1 = [Cu^{++}]/[Cu^+]^2$ the value 1.5×10^6 and Bodländer and Storbeck $1.6-2.0 \times 10^4$. The latter used a solubility method in chloride and bromide solutions, which undoubtedly contain a considerable proportion of the cuprous salt in the form of complexes, for which it was necessary to make a somewhat uncertain correction. Luther worked with sulfate solutions, titrating the cuprous salt formed, but disregarded the influence of complexes which, as Abel[4] has shown, even in sulfate solution are by no means negligible in amount. In both cases the results are calculated on the basis of ionic concentrations derived from conductivity values. Because of the disparity between the results of these authors further study of this equilibrium was undertaken, especially in perchlorate solution in which the tendency to complex formation is presumably less than in sulfate solution; and the constant calculated in terms of the ion activities.

The Determination of Total Cuprous Salt in Equilibrated Solutions of Cupric Perchlorate with Copper

Five solutions of cupric perchlorate were prepared by dissolving pure electrolytic copper in nitric acid and evaporating to dense fumes with excess of perchloric acid.[5] Copper was determined by electrolytic deposition after conversion to sulfate. Total perchlorate was determined by removing the copper electrolytically from the original solution, titrating the acid with standard alkali, and also by direct precipitation as "nitron perchlorate;"[6] excess of perchloric acid was calculated by difference.

The equilibrating tube, of about 125cc. capacity, had a capillary stopcock at one end and a ground glass stopper with a second stopcock at the other. Strips of the purest electrolytic copper procurable were introduced, the surface exposure of the metal being about 460 sq. cm., and the tube

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[1] National Research Fellow.

[2] Luther, *Z. physik. Chem.*, **36**, 385 (1901).

[3] Bodländer and Storbeck, *Z. anorg. Chem.*, **31**, 458 (1902).

[4] Abel, *Z. anorg. Chem.*, **26**, 361 (1901).

[5] 70% acid, distilled in a vacuum; obtained from the University of Illinois.

[6] Cope and Barab, THIS JOURNAL, **39**, 506 (1917).

filled with the cupric perchlorate solution. It was then placed in a sealed metal container and rotated in a water thermostat at 25° for four to five days. When equilibrium had been attained the solution was filtered quickly from contact with the copper in an atmosphere of carbon dioxide, and 100 cc. of the filtrate titrated electrometrically with 0.002 *N* (0.0004 *M*) potassium permanganate solution.[7] The electrode system used consisted of a silver chloride half-cell and a platinum electrode polarized anodically by means of an auxiliary electrode;[8] the polarization was effected by applying a potential of 0.2 volt to the two platinum electrodes through a resistance of 20,000 ohms in series. The connections were flexible to permit vigorously shaking the flask after each addition of permanganate. A constant stream of carbon dioxide was maintained but the inlet tube was not allowed to dip below the surface of the solution. The potential showed a tendency to "crawl" upward in the vicinity of the end-point, but the sudden rise was sharp, and it is believed that the end-point as shown graphically does not depart by more than 0.2 cc. of the titrating solution from the true end-point.

Table I summarizes the results obtained in perchlorate solution. Unless otherwise specified the concentrations are expressed in moles per 1000 g. of water. With Solutions 1 and 2, which must be regarded as preliminary, the period of equilibration ranged from one to three days. The filtration and titration required some skill to carry out successfully; the technique was not so well developed as in the cases of Solutions 3, 4 and 5.

Perchlorate solutions entirely free from chloride could not be prepared. A gravimetric determination of chloride on an equilibrated sample of Solution 5 gave a concentration of 18.5×10^{-2} millimoles per liter, or the equivalent of about one-fourth the total cuprous salt. The presence of the chloride is objectionable because of the increased tendency to complex formation. The assumptions made in calculating the ion activities do not take into account the proclivity of cuprous ion to enter into complexes.

TABLE I

THE CONCENTRATION OF TOTAL CUPROUS SALT IN EQUILIBRATED SOLUTIONS OF CUPRIC PERCHLORATE WITH COPPER AT 25°

Soln.	Concn. of $Cu(ClO_4)_2$ *M*	Concn. of $HClO_4$ *M*	$CuClO_4$ found per 100 cc. of soln. Micromoles	No. of detns.	Av. dev. from mean Micromoles	d^{25}_4	Concn. of $CuClO_4$ *M*
1	0.7837	0.0638	71.6	4	1.2	1.1406	76.1×10^{-5}
2	.2576	.0533	32.0	6	1.4	1.0496	32.7
3	.3784	.5973	39.8	6	0.8	1.0993	42.0
4	.1844	.2912	27.2	6	.6	1.0482	28.0
5	.8240	.0481	71.0	6	1.0	1.1517	75.3

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[7] Standardized against pure sodium oxalate by electrometric titration.

[8] Van Name and Fenwick, THIS JOURNAL, **47**, 19 (1925).

The Determination of Total Cuprous Salt in Equilibrated Solutions of Cupric Sulfate with Copper

For purposes of comparison with Luther's work and with our own values in perchlorate solution, equilibrium determinations were also made on three solutions of cupric sulfate. The method of preparation and analysis of the solutions was entirely analogous to that used for the perchlorate solutions. The results are given in Table II. It may be noted that the permanganate requirement of the sulfate solutions is much greater than was found by Luther,[2] which is probably due to lack of precaution on his part to prevent all oxidation of cuprous sulfate by air during the filtration and titration processes.

TABLE II

THE DETERMINATION OF TOTAL CUPROUS SALT IN EQUILIBRATED SOLUTIONS OF CUPRIC SULFATE WITH COPPER AT 25°

Soln.	Concn. of $CuSO_4$ M	Concn. of H_2SO_4 M	Cu_2SO_4 found per 100 cc. of soln. Micromoles	No. of detns.	Av. dev. from mean. Micromoles	d^{25}_4	Concn. of Cu_2SO_4 M
A	0.6666	0.7906	35.8	4	0.4	1.1411	37.1×10^{-5}
B	.3270	.3879	25.5	1	...	1.0709	26.0
C	.2176	.2584	18.4	1	...	1.0468	18.6

The Calculation of the Equilibrium Constant in Perchlorate Solution

The electromotive force at 25°, E_1, of the cell, Cu | Cu^{++} in Equilibrated Solution | Cu^+ in Equilibrated Solution | Cu, may be written

$$\begin{aligned} E_1 &= E^\circ - (0.05915/2) \log [Cu^{++}]/[Cu^+]^2 \\ &= E^\circ - 0.02958 \log K_1 \end{aligned} \qquad (1)$$

where E° is the difference between the molal electrode potential of copper to cupric ion (—0.3448 volt)[9] and that of copper to cuprous ion, and K_1 is the desired equilibrium constant. Since E_1 must be zero, K_1 may be calculated from E°, the value of which depends upon the unknown molal electrode potential of copper to cuprous ion. The latter was derived from the measurements made on the two cells described below.

The electromotive force at 25°, E_2, of the cell, Cu | Cu^+ in Equilibrated Solution | Hg_2^{++} in Equilibrated Solution | Hg, is defined by the equation

$$E_2 = E^{\circ\prime} - (0.05915/2) \log [(\gamma Cu^+)^2/(\gamma Hg_2^{++})] - (0.05915/2) \log [(m Cu^+)^2/(m Hg_2^{++})] \qquad (2)$$

where $E^{\circ\prime}$ is the difference between the molal electrode potentials of copper to cuprous ion and mercury to mercurous ion and γ represents an activity coefficient.

The electromotive force at 25°, E_3, of the cell, Hg | $Hg_2(ClO_4)_2 + HClO_4$ | $HClO_4 + AgClO_4$ | Ag, may be expressed

$$E_3 = E^{\circ\prime\prime} - (0.05915/2) \log [(\gamma Hg_2^{++})/(\gamma Ag^+)^2] - (0.05915/2) \log [(m Hg_2^{++})/(m Ag^+)^2] \qquad (3)$$

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[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 420.

where $E^{\circ\prime\prime}$ is the difference between the molal electrode potentials of mercury to mercurous ion (—0.7986 volt)[10] and silver to silver ion (—0.7995 volt).[11]

E_2 and E_3 were measured, and E° and K_1 calculated on the basis of the following assumptions: (a) that the concentration differences of the electrode solutions of the two halves of each cell are so small that the liquid potential is negligible; (b) that the ratio of the activity coefficients of mercurous and silver ions, within a small concentration range, depends only on the ionic strength of the solution; (c) that the activity coefficients of cuprous and silver ion are the same in any given solution (applied only to a few special cases).

The Measured Electromotive Force of the Cell

$$Hg \mid Hg_2(ClO_4)_2 + HClO_4 \mid HClO_4 + AgClO_4 \mid Ag, \text{ at } 25^\circ$$

Preparation of Solutions.—The stock solution of mercurous perchlorate was prepared by dissolving pure mercuric oxide in perchloric acid, filtering and heating with distilled mercury. The solution was diluted to about 0.07 *M*, sufficient excess of acid being present to prevent the formation of an insoluble basic salt, stored over pure mercury and analyzed at frequent intervals. A sharp and reproducible end-point was obtained by titrating the total mercurous salt electrometrically; the electrode system used consisted of a Ag | AgCl, KNO_3 half-cell and a freshly ignited platinum wire.[12] Total perchlorate was determined by precipitation as "nitron perchlorate" and the free acid calculated by difference. This last determination was checked by removing the mercurous salt by precipitation with sodium chloride and titrating the filtrate with standard alkali.

A stock solution of 0.1 *M* silver perchlorate was prepared by treating perchloric acid with an excess of pure silver oxide, warming gently, filtering and diluting; the resulting solution contained practically no excess of acid. The silver content was determined gravimetrically, weighing as silver chloride.

Electrodes.—The electrode vessels used were the ordinary type of half-cell with stopcocks in the siphon arms and glass stoppers.

In making up the mercury electrodes pure distilled mercury was introduced into the cell in sufficient quantity to cover the platinum wire before the vessel was filled with the mercurous perchlorate-perchloric acid mixture.

Finely divided metallic silver was used for the silver electrodes. It was prepared electrolytically by deposition at a fine platinum point cathode,[13] the carefully washed metal kept under dilute perchloric acid and washed repeatedly, before use, with portions of the solution to be investigated. All silver solutions were kept in the dark and all measurements made in artificial light.

The electrodes were kept at 25° in an air thermostat, which was found very convenient and satisfactory for the purpose. The potential measurements were made with a Leeds and Northrup Type K potentiometer.

The mercury and silver electrodes were made up together and placed in

[10] Ref. 9, p. 417.

[11] Ref. 9, p. 414.

[12] The titration is very similar to the corresponding silver titration already described, Ref. 8.

[13] Lewis, This Journal, **28**, 158 (1906). Linhart, *ibid.*, **41**, 1175 (1919).

the thermostat. The potential became constant in one to two hours and, except with the most acid solutions, remained constant for at least five or six hours. When the cell had stood for 15 hours, or more, a decrease in the potential difference, 0.1–0.3 millivolt, was observed in some cases, believed to be due to the slight solvent action of the acid on the finely divided silver.

Table III gives the experimental observations. The potential E_3 is the average of the values found by measuring the potential difference between each of the three mercury electrodes against each of the four silver electrodes in turn; the average deviation from the mean of the silver range was from 0.03 to 0.11 mv., of the mercury from 0.01 to 0.07 mv. With the most concentrated solution, Solution VII, the potential fell rapidly with time, about a millivolt during the first hour; the value recorded is the average limiting value given by graphic extrapolation of the curve obtained by plotting the potentials read over a period of nine hours. The two electrode solutions for each cell are indicated by X Hg and X Ag, respectively, in the first column of the table; μ is the ionic strength. The last column of the table contains the ratio of the activity coefficient of mercurous ion to the square of the activity coefficient of silver ion, as derived from Equation 3.

TABLE III

THE MEASURED ELECTROMOTIVE FORCE OF THE CELL

$Hg \mid Hg_2(ClO_4)_2 + HClO_4 \mid HClO_4 + AgClO_4 \mid Ag$, at 25°

Soln.	Concn. of $HClO_4$ M	Concn. of $Hg_2(ClO_4)_2$ M	Concn. of $AgClO_4$ M	μ	E_3 Volts	$(\gamma Hg_2^{++})/(\gamma Ag^+)^2$
I Hg	0.1482	0.005350	......	0.164	−0.05729	0.4425
I Ag	.1470	......	0.005051	.152		
II Hg	.2493	.005350	......	.265	− .05584	.3988
II Ag	.2480	......	.005073	.253		
III Hg	.5029	.005393	......	.519	− .05386	.3465
III Ag	.5014	......	.005128	.507		
IV Hg	.7623	.005459	......	.779	− .05287	.3242
IV Ag	.7608	......	.005187	.766		
V Hg	1.0271	.005522	......	1.044	− .05208	.3081
V Ag	1.0255	......	.005244	1.031		
VI Hg	1.0535	.005588	......	1.070	− .05235	.3117
VI Ag	1.0511	......	.005251	1.056		
VII Hg	2.2093	.005863	......	2.227	− .0503	.2789
VII Ag	2.2074	......	.005511	2.213		

The Measured Electromotive Force of the Cell

H_2 | $HClO_4$ | $HClO_4$ + $Hg_2(ClO_4)_2$ | Hg, at 25°

Although unnecessary for the calculation of the equilibrium constant under investigation, the electromotive force of the cell, H_2 | $HClO_4$ | $HClO_4$ + $Hg_2(ClO_4)_2$ | Hg, was measured over a much greater range in acid concentration than was used by Linhart[14] in his determination of the molal electrode potential of mercury to mercurous ion; and the ratio of the square of the activity coefficient of hydrogen ion to the activity coefficient of mercurous ion was calculated. From the ratios of the ion activities it may be possible to derive the individual ion activities concerned in the present study when the behavior of mixed electrolytes may be better postulated.

Preparation of Electrodes.—The mercury electrodes were prepared as described for the preceding cell.

The hydrogen electrode vessel used was the type described by Lewis, Brighton and Sebastian.[15] The electrode proper consisted of a piece of thin, platinized platinum foil about 12 × 24 mm. Commercial electrolytic tank hydrogen, purified by being passed over phosphorus pentoxide and then through two tungsten lamp bulbs, such as described by Clark,[16] was bubbled through a solution of the same composition as that contained in the hydrogen electrode vessel before it reached the bubbler forming part of the electrode.

The gas was bubbled through the hydrogen electrodes, arranged in parallel, at the rate of 4 or 5 bubbles per minute for one to two hours, to insure displacement of air, before the lamp bulbs were lighted. The potential became constant about an hour thereafter, and remained constant for at least six hours. The values obtained during this period, usually four or five hours after the flow of gas had been started, were ac-

TABLE IV

THE MEASURED ELECTROMOTIVE FORCE OF THE CELL

H_2 | $HClO_4$ | $HClO_4$ + $Hg_2(ClO_4)_2$ | Hg, at 25°

Soln.	Concn. of $HClO_4$ *M*	Concn. of $Hg_2(ClO_4)_2$ *M*	μ	E_4 Volts	$(\gamma H^+)^2/(\gamma Hg_2^{++})$
I	0.1585		0.159		
Ia	.1598	0.005286	.176	0.76681	2.50
Ib	.1591	.002641	.167	.75825	2.43
II	.4948		.495		
IIa	.4965	.005317	.513	.73391	3.35
IIb	.4956	.002656	.504	.72500	3.35
III	.5359		.536		
IIIa	.5375	.005378	.554	.73150	3.48
IIIb	.5367	.002686	.545	.72270	3.45

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[14] Linhart, THIS JOURNAL, **38**, 2356 (1916).

[15] Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).

[16] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, **1922**, p. 228.

TABLE IV (*Concluded*)

Soln.	Concn. of $HClO_4$ *M*	Concn. of $Hg_2(ClO_4)_2$ *M*	μ	E_4 Volts	$(\gamma H^+)^2/(\gamma Hg_2^{++})$
IV	.7665		.767		
IVa	.7684	.005303	.784	.72058	3.92
IVb	.7674	.002662	.775	.71177	3.91
V	1.0859		1.086		
Va	1.0876	.005511	1.104	.70966	4.75
Vb	1.0867	.002753	1.095	.70068	4.78
VI	1.7783		1.778		
VIa	1.7806	.005594	1.797	.69232	6.94
VII	2.7651		2.765		
VIIa	2.7680	.005803	2.785	.67567	10.9
VIIb	2.7666	.002917	2.775	.66684	10.9
VIII	4.1661		4.166		
VIIIa	4.1703	.006226	4.189	.65653	22.8
VIIIb	4.1685	.003111	4.178	.64752	23.0

cepted. With prolonged bubbling, 10–15 hours, the potential difference sometimes decreased as much as 0.1–0.2 mv.

Table IV contains the experimental observations. The potential, E_4, which in each case is corrected to one atmosphere partial pressure of hydrogen, is the average of the values found by measuring the potential difference between each of the two hydrogen electrodes in pure acid, Solution X, against each of the two or three mercury electrodes in a mixture of perchloric acid and mercurous perchlorate, Solution Xa or Xb. The average deviation from the mean of the hydrogen and of the mercury electrodes was 0.03 mv.

The Measured Electromotive Force of the Cell

Cu | Cu^+ in Equilibrated Solution | Hg_2^{++} in Equilibrated Solution | Hg, at 25°

Preparation of Electrodes.—The solutions in contact with the copper were the same as those on which the equilibrium determinations were made. Finely divided metallic copper was prepared,[17] several grams placed in a glass tube of about 35cc. capacity, washed repeatedly with portions of the solution to be measured, the tube filled, a ground glass stopper sealed in with paraffin, and the tube rotated for two to three days in an air thermostat at 25°. It was then opened and a rubber stopper carrying a siphon arm with (ungreased) stopcock, air inlet tube and copper plated platinum point electrode quickly sealed in so that the plated wire was entirely surrounded with the finely divided copper.

The mercury electrodes were made up as described for the mercury-silver cell, using solutions identical with those in contact with the copper with respect to cupric perchlorate and perchloric acid but containing in addition a little mercurous perchlorate. With the weakly acid solutions, 1, 2 and 5, a basic mercurous salt slowly settled out after the addition of the mercurous perchlorate; this was filtered off and the mercurous per-

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[17] Lewis and Lacey, THIS JOURNAL, **36**, 805 (1914).

chlorate in the filtrate determined by electrometric titration with 0.01 *M* potassium chloride.

The observed potential difference decreased slowly with time, but the change in 24 hours was usually less than 0.5 mv. It is believed that this was due to the oxidation of some cuprous salt, equilibrium being restored too slowly to maintain a constant potential. The value adopted for the cell potential was the reading obtained two to four hours after the cells were set up. Four copper and two mercury electrodes were made with each solution; the average deviation from the mean ranged from 0.03 to 0.13 mv.

TABLE V

THE MEASURED ELECTROMOTIVE FORCE OF THE CELL

Cu $\mid$ Cu^+ in Equilibrated Solution $\mid$ Hg_2^{++} in Equilibrated Solution $\mid$ Hg, at 25°

Equil. soln.	Concn. of $Hg_2(ClO_4)_2$ *M*	μ	E_2 Volts	$(\gamma Cu^+)^2/(\gamma Hg_2^{++})$	$\overset{\circ}{E}_{Cu, Cu^+}$ Volts	$\overset{\circ}{E}_{Cu^+, Cu^{++}}$ Volts	K_1
1	0.000302	2.415	0.34603	3.61	−0.5165	−0.1731	6.4×10^5
2	.000449	0.827	.36944	3.14	− .5216	− .1780	9.5
3	.005295	1.748	.39083	3.49	− .5241	− .1655	11.5
4	.005162	0.860	.40430	3.16	− .5220	− .1676	9.8
5	.002209	2.526	.36797	3.62	− .5203	− .1693	8.6
				Av., 3, 4, 5	− .5221	− .1675	10.0×10^5
				Av. dev. from mean	.0013	.0013	1.0×10^5
							% Dev., 10

The molalities of cupric perchlorate, cuprous perchlorate and perchloric acid for the five perchlorate solutions are stated in Table I. Col. 4 of Table V contains the measured electromotive force of the copper-mercury cell, E_2. By graphic extrapolation of the values in the last column of Table III, $(\gamma Cu^+)^2/(\gamma Hg_2^{++})$ was derived on the basis of the previously stated assumptions (b) and (c). The molal electrode potential of copper to cuprous ion and the equilibrium constant, K_1, were computed as described. Because of the preliminary character of the equilibrium determinations made on the first two perchlorate solutions they are not considered in the final average value for the equilibrium constant. The calculated molal electrode potential of cuprous ion to cupric ion, $2\overset{\circ}{E}_{Cu, Cu^{++}} - \overset{\circ}{E}_{Cu, Cu^+} = \overset{\circ}{E}_{Cu^+, Cu^{++}}$, is included in the table.

The Measured Electromotive Force of the Cell

Cu $\mid$ Cu^+ in Equilibrated Solution $\mid$ Hg_2^{++} in Equilibrated Solution $\mid$
$Hg_2(SO_4)(s)$ $\mid$ Hg, at 25°

The electrodes for the copper-mercury cell containing the equilibrated sulfate solutions were made up like those for the cells containing the perchlorate solutions except that the solution in contact with the mercury was saturated with pure mercurous sulfate and the mercury covered with a layer of mercurous sulfate before the electrolyte was introduced. Two mercury and four copper electrodes were prepared with each solution; the average deviation from the mean of the difference was 0.12 mv. The average values for the electromotive force of the three cells E_2' are given in the third column of Table VI. The molalities of cupric sulfate, cuprous sulfate and sulfuric acid in the solutions used have already been stated in Table II.

TABLE VI

THE MEASURED ELECTROMOTIVE FORCE OF THE CELL

$Cu \mid Cu^+$ in Equilibrated Solution $\mid Hg_2^{++}$ in Equilibrated Solution $\mid Hg_2(SO_4)(s) \mid Hg$, at 25°

Equil. soln.	μ	E_2' Volts	$(\gamma Cu^+)^2/(\gamma Hg_2^{++})$	E°_{Cu, Cu^+} Volts	$E^\circ_{Cu^+, Cu^{++}}$ Volts	K_1
A	5.048	0.35913	3.71	−0.5224	−0.1672	10.1×10^5
B	2.477	.37026	3.61	− .5207	− .1689	8.9
C	1.646	.37581	3.42	− .5245	− .1651	11.9
			Av.	− .5225	− .1671	10.3×10^5
		Av. dev. from mean		.0013	.0013	1.1×10^5
					% Dev., 11	

The method of calculation of the equilibrium constant in sulfate solution does not differ from that used for the perchlorate. Assuming a molality of mercurous sulfate in the three solutions used equal to its solubility in pure water,[18] 13×10^{-4}, as seems reasonable from solubility determinations made in mixtures of various sulfates, the last term in Equation 2 was calculated. The first logarithmic term was obtained exactly as before, although the assumption that the value of $(\gamma Hg_2^{++})/(\gamma Ag^+)^2$ depends only on the ionic strength is undoubtedly less probable than in the former case.

The Calculation of the Equilibrium Constant on the Basis of the Divalent Cuprous Ion

The authors of earlier studies of this equilibrium believed they had established the univalence of the cuprous ion. For purposes of comparison, however, the constant $K_2 = [Cu^{++}]/[Cu_2^{++}]$ was calculated.

If the equation for the electromotive force of the copper-mercury cell is written

$$E_2'' = E^{\circ\prime\prime\prime} - (0.05915/2) \log [(\gamma Cu_2^{++})/(\gamma Hg_2^{++})] - (0.05915/2) \log [(m Cu_2^{++})/(m Hg_2^{++})]$$

the first logarithmic term drops out if the assumption is made that in any given solution the activity coefficients of the similarly divalent mercurous and cuprous ions are the same within a small concentration range. Since $m Cu_2^{++} = {}^1/_2 m Cu^+$ the difference between the molal electrode potentials of copper to the divalent cuprous ion and mercury to mercurous ion, $E^{\circ\prime\prime\prime}$, may be obtained.

The two molal electrode potentials involving the divalent cuprous

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[18] Horsch, THIS JOURNAL, **41**, 1787 (1919).

ion and the corresponding values for K_2 for both the perchlorate and sulfate solutions are given in Table VII.

TABLE VII

THE CALCULATION OF THE EQUILIBRIUM CONSTANT ON THE BASIS OF THE DIVALENT CUPROUS ION

Equil. soln.	$E^\circ_{Cu, Cu_2^{++}}$ Volts	$E^\circ_{Cu_2^{++}, Cu^{++}}$ Volts	K_2
1	−0.4496	−0.2400	35×10^2
2	− .4431	− .2465	21
3	− .4492	− .2404	34
4	− .4406	− .2490	17
5	− .4533	− .2363	47
Av. 3, 4, 5	− .4477	− .2419	33×10^2
Av. dev. from mean	.0047	.0047	10×10^2
			% Dev., 30
A	− .4556	− .2340	56×10^2
B	− .4490	− .2406	33
C	− .4498	− .2398	36
Av.	− .4515	− .2381	42×10^2
Av. dev. from mean	.0028	.0028	10×10^2
			% Dev., 24

Comparison of Results

K_1 in Tables V and VI is more "constant" than K_2 in Tables VII, thus supporting the belief in the univalence of the cuprous ion. The difference between the average values of K_1 for the sulfate and perchlorate solutions is well within the limit of error, a fact which is strong evidence for the validity of the activity assumptions made throughout. However, since the assumptions made in the calculations for the sulfate solutions were the more doubtful, the average value of K_1 and the corresponding values for the molal electrode potentials obtained for the perchlorate solutions are stressed.

As regards a comparison of the value of K_1 of 1×10^6 with earlier data, not much can be said because of the totally different methods of experiment and interpretation of the problem. The great difficulty lies in the proper evaluation of the ion activities in the concentrated solutions with which it is necessary to work on account of the relatively very small amounts of cuprous ion present at equilibrium. While the calculation offered here is based on assumptions which are open to some question it must be more nearly correct than those of former authors which, in the light of recent work on activity, are certainly wrong.

In conclusion I wish to express my thanks to Professor R. G. Van Name for the suggestions and assistance he has given.

Summary

1. The total amounts of cupric and cuprous salt in equilibrium with metallic copper at 25° were determined both in perchlorate and sulfate

solutions over a range in concentration of 0.18–0.82 *M* cupric salt in the first group of solutions and 0.22–0.67 *M* in the second.

2. By means of an electromotive-force method for the determination of the necessary ion activities, evidence for the univalence of the cuprous ion was found and the following molal electrode potentials at 25° were calculated: Cu, Cu^+, —0.522 volt; and Cu^+, Cu^{++}, —0.167 volt.

3. From the foregoing data the equilibrium constant $K_1 = [Cu^{++}]/[Cu^+]^2$ was found to be 1×10^6, with a mean deviation of 10%.

4. The electromotive force of the cell, $H_2 \mid HClO_4 \mid HClO_4 + Hg_2(ClO_4)_2 \mid Hg$, was measured and the ratio of the square of the activity coefficient of hydrogen ion to the activity coefficient of mercurous ion calculated over a range in ionic strength of 0.16–4.17.

New Haven, Connecticut

[Contribution from the Nela Research Laboratory]

A SIMPLE RELATION BETWEEN COMPOSITION AND BOILING POINT[1]

By Elliot Q. Adams

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Of the equations for the approximate calculation of boiling points of normal organic liquids, perhaps the best known is that of Longuinesu[2]

$$T/(D\sqrt{n}) \underset{\cdot}{=} 100 \qquad (1)$$

in which *T* is the absolute boiling point (°K.); *D*, the density of the liquid, and *n*, the number of atoms in the molecule.

It seems worth while to call attention to an even simpler expression

$$T \underset{\cdot}{=} \sqrt{20{,}000\, m} \qquad (2)$$

which holds within a fraction of a unit in m for most normal[3] *organic* liquids and many inorganic non-electrolytes.

T is, as before, the absolute boiling point at 760 mm. pressure; *m* is, in the case of hydrocarbons, the number of carbon atoms in the molecule. For other elements, the number of atoms is to be multiplied by one less than the number of the row in the periodic system,[4] Fig. 1, in which the

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society at Washington, April, 1924. Equation 3 has been added in the rewriting.

[2] Longuinesu, *J. chim. phys.*, **1**, 288, 296, 391 (1903); **6**, 552 (1908).

[3] Compare J. H. Hildebrand, "Solubility," Chemical Catalog Co., New York, **1924**, pp. 84, 91, 94. Normal organic liquids may be defined as those which do not contain hydrogen (or metallic elements) directly united to any element except carbon, which do not have intramolecular ionization (as in betaine), and which do not contain multiple bonds except between carbon atoms. This definition excludes esters, most of which appear to be normal.

[4] *J. H. Hildebrand, "Principles of Chemistry," The MacMillan Co., New York,* **1918**, p. 257. He credits the form of the table to J. Thomsen [*Z. anorg. Chem.*, **9**, 190–3 (1895)], although it has not a single feature that was original with Thomsen. Com-