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The Activity Coefficient of Copper Sulphate in Aqueous Solution

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The electromotive force of the cell Cu *two phase amalgam*/$CuSO_4$/Hg_2SO_4, Hg has been measured with solutions whose concentrations vary from 0.02 molal to saturation, and for temperatures from 15°C to 45°C. From these measurements and from freezing point and calorimetric heat of dilution data, activity coefficients have been calculated, and the value of $E°$ for the cell has been determined. The results are in reasonable agreement with those of Nielsen and Brown and of Getman, but are in definite disagreement with the results of Lebettre.

THE normal potential of the copper electrode and the activity coefficient of copper sulphate in aqueous solution have been the subject of numerous investigations dating back to the pioneer work of Lewis and Lacey.[1] The great difficulty has been the preparation of a reproducible electrode from a metal as stiff and as subject to surface strains as copper; to remove such strains, Lewis and Lacey used a spongy form of the metal, obtained by depositing it from solution with high current density, but most investigators have preferred a two phase copper amalgam.[2] A third type of electrode, the single copper crystal, has been used only by Getman. As reference electrode, the saturated mercury-mercurous sulphate electrode has usually been employed, although (owing to the appreciable solubility of mercurous sulphate) its use is restricted to fairly concentrated solutions (stronger than 0.02 molal, preferably 0.05 molal). Recently, Lebettre[3] has replaced the mercurous sulphate electrode by lead-lead sulphate in order to extend his measurements to the extremely dilute range, but his resulting activity coefficients are surprisingly small and are in complete disagreement with the freezing-point data.

We have been interested for some time in the effect of other sulphates on the thermodynamic potential of copper sulphate in aqueous solution, and in view of the considerable uncertainty that still exists as to the potential even in the absence of other salts, we have carried out the measurements recorded here on the cell Cu two phase amalgam/$CuSO_4$/Hg_2SO_4, Hg. We hope to extend this work by investigating the cell Cu amalgam/$CuSO_4$+MSO_4/$PbSO_4$, Pb.

The cells were H type of Pyrex glass; they were immersed in an oil bath electrically controlled to ±0.02° and were shielded from light; two of the four electrode chambers served for amalgam electrodes and two for mercurous sulphate electrodes. The electromotive force was measured by means of a Leeds and Northrup type K potentiometer, a galvanometer of sensitivity 2×10^{-8} amp. per mm scale deflection, and a Weston standard cell with National Bureau of Standards certificate. Temperatures were measured by means of thermometers which had been calibrated against laboratory standards.

The mercury used was purified by spraying five times through 7 percent nitric acid, and then five times through distilled water; it was then dried, and thrice fractionally distilled at 30 mm pressure, the first and last fifth of each distillation being rejected. The copper was B.D.H. analytical reagent needles, while the copper sulphate was B.D.H. analytical reagent, recrystallized once from conductivity water slightly acidified with sulphuric acid, and once from neutral conductivity water. Mercurous sulphate was prepared by the method of Hulett[4] and was stored under twice molal sulphuric acid. The copper amalgam was prepared in a cell with an anode of copper needles, the electrolyte being 0.6 m $CuSO_4$ in aqueous solution slightly acidified with sulphuric acid; the cell was fitted with a Hulett type of stirrer operating at about

[1] Lewis and Lacey, J. Am. Chem. Soc. **36**, 804 (1914).

[2] Cohen, Chattaway and Tombrock, Zeits. f. physik. Chemie **60**, 706 (1907); Oholm, Medd. Vetenskapsakad. Nobelinst. 5 N:04, 1 (1919); Obata, Proc. Phys. Math. Soc. Japan [3] **2**, 223 (1920); Nielsen and Brown, J. Am. Chem. Soc. **49**, 2423 (1927); Getman, J. Phys. Chem. **34**, 1454 (1930); Quintin, Comptes rendus **196**, 473 and 538 (1933).

[3] Lebettre, J. de Chim. phys. **31**, 348 (1934); see also Quintin and Lebettre, Comptes rendus **198**, 1140 (1934).

[4] Hulett, Phys. Rev. **22**, 321 (1906).

TABLE I.

TIME	1.8	3.6	4.1	5.8	27.9
A−1	0.37248	0.37247	0.37249	0.37249	0.37245
B−1	.37247	.37244	.37244	.37243	.37240
A−2	.37246	.37246	.37248	.37251	.37252
B−2	.37246	.37244	.37244	.27245	.37247

TABLE II. $T = 25.00°C$; $E° = 0.2702$ volt.

m	E	$-\log \gamma$	m	E	$-\log \gamma$
0.02024	0.4011	0.520	0.1719	0.3728	0.970
0.02735	0.3968	0.577	0.3162	0.3651	1.104
0.03162	0.3945	0.601	0.3518	0.3640	1.132
0.05000	0.3876	0.684	0.5000	0.3596	1.210
0.0883	0.3802	0.806	0.9990	0.3518	1.379
0.0993	0.3787	0.831			

TABLE III. $T = 25.00°C$.

$m^{1/2}$	$-\log \gamma$	$m^{1/2}$	$-\log \gamma$	$m^{1/2}$	$-\log \gamma$
0.100	0.390	0.25	0.730	0.6	1.135
.125	.468	.30	.808	.7	1.205
.150	.543	.35	.880	.8	1.263
.175	.598	.40	0.948	0.9	1.321
0.200	0.642	0.50	1.052	1.0	1.379

80 r.p.m., and the current density used in forming the amalgam was 3 amp./sq. dcm; after preparation, the product, containing 4 to 5 percent copper, was stored under the electrolyte. The copper sulphate solutions were made by gravimetric dilution of stock solutions (about 1 m in copper sulphate) which had been analyzed electrolytically for copper; a good grade of conductivity water was used in making all solutions. The nitrogen was purified by passing through a tower containing copper turnings in ammonia plus ammonium carbonate solution, then through water, then through sulphuric acid, and finally through a copper sulphate solution identical with that to be used in the cells.

In carrying out a measurement, the mercurous sulphate was washed five times with the electrolyte in a filtering crucible, and the copper amalgam was also washed thoroughly with the electrolyte and then dried with filter paper. The mercury, mercurous sulphate and amalgam were introduced into the cell, and the cell and the electrolyte in its reservoir in the thermostat were evacuated and flushed several times with nitrogen; the electrolyte was then forced over into the cell by nitrogen pressure.

In general a steady e.m.f. was obtained in a few hours, although this was not always the case (see below). Readings were made over a period of from 12 to 24 hours except in the high temperature runs, when the period was usually somewhat shorter. The history of one cell, 0.2176 m at 15.06°C, is summarized in Table I; A and B are the amalgam electrodes, and 1 and 2 are the mercurous sulphate electrodes. Times are in hours after the cell was formed. The mean value for the e.m.f. is thus 0.37246±0.00006 volt. It is evident from the table that the mercurous sulphate electrodes (except for the last measurements) are in agreement within two-hundredths of a millivolt, and this was generally found to be the case; the deviation between the amalgam electrodes, on the other hand, is somewhat larger, and for this reason, the e.m.f. in Tables II and IV are recorded only to the nearest tenth of a millivolt, which is the reproducibility of the measurements.

While Table I is typical of the behavior of the great majority of the cells, occasionally a cell would behave somewhat erratically. For example, in one experiment with 0.9990 m solution at 25°, amalgam electrode B reached a steady state seven hours after the cell was formed, and showed an e.m.f. against either mercurous

TABLE IV.

(a) $T = 15.06°C$				(b) $T = 35.00°C$				(c) $T = 44.95°C$			
m	E	$-\log \gamma$	$E°$	m	E	$-\log \gamma$	$E°$	m	E	$-\log \gamma$	$E°$
0.02850	0.3986	0.571	0.2776	0.02735	0.3943	0.593	0.2625	0.02735	0.3915	0.606	0.2546
0.0883	0.3823	0.786	(0.2769)	0.0878	0.3771	0.820	0.2624	0.2176	0.3623	1.054	(0.2540)
0.2176	0.3725	1.001	0.2774	0.2892	0.3628	1.104	0.2624	0.2892	0.3594	1.121	0.2546
0.2892	0.3694	1.066	0.2776	1.0000	0.3481	1.400	0.2625	0.7823	0.3467	1.349	0.2548
0.7823	0.3576	1.288	0.2778			Mean	0.2625	1.0000	0.3442	1.420	0.2546
1.0000	0.3551	1.356	0.2776							Mean	0.2546
		Mean	0.2776								

sulphate electrode of 0.35183 ± 0.00003 volt for over five days, a result that agreed within a few hundredths of a millivolt with the result of a previous experiment with the same solution. Amalgam electrode A, however, after seven hours, maintained a steady e.m.f. of 0.35165 ± 0.00004 volt for the next 30 hours; then, in the next 12 hours, the e.m.f. rose and remained steady at 0.35187 ± 0.00004 volt for the remainder of the run.

The measurements at 25.00°C are recorded in Table II, the first column giving the molality, and the second the observed e.m.f. At the lowest concentration of the table, the correction due to the solubility of the mercurous sulphate is probably not greater than 0.1 mv, which is the limit of error of the measurements, and so can be disregarded.

Hovorka and Rodebush[5] have determined the freezing point of dilute solutions of copper sulphate, and their measurements for 0.001, 0.005 and 0.01 molal can be represented within their limits of error by means of a Lewis and Randall[6] j-function with $j = 1.718\,m^{0.423}$; this gives for these concentrations at the freezing point, $\log \gamma = \bar{1}.865, \bar{1}.733$ and $\bar{1}.642$, respectively. If it be assumed that this j-equation is also valid for $0.02024\,m$ solution, $\log \gamma$ for the weakest solution of Table II, at the freezing point, will be $\bar{1}.518$. Lange, Monheim and Robinson[7] have determined calorimetrically $\bar{L}_2$ for copper sulphate solutions, and since $(\bar{C}_{P_2} - \bar{C}_{P_2}°)$ is negligibly small,[8] $\log \gamma$ for these solutions at 298.2°K may be obtained at once. The resulting values for Hovorka and Rodebush's three solutions $(\bar{L}_2 = 448, 813$ and 965 cal., respectively) are $\bar{1}.850, \bar{1}.706$ and $\bar{1}.610$. The corresponding $\log \gamma$ for $0.02024\,m$ $(\bar{L}_2 = 1127$ cal.) is $\bar{1}.480$, the uppermost entry in the third column of Table II. $E°$, defined by $E = E° - (2RT/nF) \cdot \ln \gamma m$, is thus 0.2702 volt; this corresponds to a normal potential for the copper amalgam electrode of -0.3450 volt if the normal potential of the mercury-mercurous sulphate electrode[9] be taken

[5] Hovorka and Rodebush, J. Am. Chem. Soc. **47**, 1614 (1925).
[6] Lewis and Randall, *Thermodynamics*, p. 286 (1923).
[7] Lange, Monheim and Robinson, J. Am. Chem. Soc. **55**, 4733 (1933).
[8] *International Critical Tables*, Vol. V, p. 122.
[9] Harned and Hamer, J. Am. Chem. Soc. **57**, 27 (1935).

TABLE V. *Cell Cu amalgam/$CuSO_4$ sat./Hg_2SO_4, Hg.*

T°C	15.06	25.0	35.00	44.95
E	0.3530	0.3468	0.3399	0.3329

as -0.6152 volt. The other entries in the third column follow at once from the observed e.m.f. and the value just obtained for $E°$.

From a large scale plot of the entries in the third column, values of the logarithm of the activity coefficient for rounded values of $m^{\frac{1}{3}}$ were obtained, and are entered in Table III; interpolation in this table yields values of $\log \gamma$ agreeing in general with those in Table II within ± 0.002. The entries in Table III and the corresponding $E°$ are of course uncertain to the extent of a small additive constant owing to the extrapolation of the freezing point equation from 0.01 m to 0.02 m, but they can be revised if necessary without difficulty when further data for more dilute solutions appear.

Table IV gives the results of measurements at other temperatures; the first column gives the molality, the second the observed e.m.f., the third the value of $\log \gamma$ obtained from Table II and Lange, Monheim and Robinson's values of $\bar{L}_2$, the fourth the resulting $E°$; bracketed values were not used in obtaining the final mean. It is evident from the table that $\partial E°/\partial T$ at 25°C is about -7.6×10^{-5} volt per degree. Table V gives for the various temperatures the results for the cell Cu amalgam/$CuSO_4$ sat./Hg_2SO_4, Hg.

It is of interest to compare our results with those of other investigators who have used the same cell. Nielsen and Brown[2] with 0.05, 0.1, 0.2 and 0.5 molal solutions obtained at 25°C 0.3874, 0.3784, 0.3697 and 0.3592 volt, respectively; if our value of $E°$ and the data of Table III (log $\gamma = \bar{1}.315, \bar{1}.168, \bar{2}.999$ and $\bar{2}.791$ for their concentrations) be assumed, the calculated values of E would be 0.3877, 0.3786, 0.3707 and 0.3595 volt, respectively, which with one exception are about 0.3 mv greater than their results. Getman[2] found for 25°C and $m = 0.02098$, 0.04193, 0.10488 and 0.20984, $E = 0.4007, 0.3905$, 0.3785 and 0.3701 volt, respectively; the values calculated from Table III with $E° = 0.2702$, are 0.4007, 0.3902, 0.3780 and 0.3702 volt. Thus Nielsen and Brown's results lie somewhat below

ours and Getman's on the whole somewhat above. Quintin's measurements, on the other hand, show a definite drift when compared with our data, her e.m.f. being smaller at lower concentrations and greater at high concentrations. The entry for 25°C in Table V is in agreement with the mean of the previous results for the saturated cell.

As we have mentioned above, Lebettre[3] on the basis of his results for the cell Cu amalgam/CuSO$_4$/PbSO$_4$, Pb, has computed activity coefficients from measurements extending down to solutions as dilute as 0.001 molal; his coefficients are in complete disagreement with those listed in Tables II and III and with the freezing point data, and, moreover, correspond to a La Mer

"a" parameter[10] of only 2.4A—an extraordinarily small value. It seems to us that the most probable explanation of his results is that the copper sulphate in his most dilute solutions was partially hydrolyzed and that as a result his effective cupric ion concentrations were less than he supposed. The entry in Table III for 0.01 m, computed from freezing point and heat of dilution data, corresponds to an "a" of 3.9A—a more reasonable value in view of the results that have been obtained for other bivalent sulphates.[11]

[10] Gronwall, La Mer and Sandved, Physik. Zeits. 29, 358 (1928).

[11] See, for example, La Mer and Parks, J. Am. Chem. Soc. 53, 2040 (1931), Cowperthwaite and La Mer, J. Am. Chem. Soc. 53, 4333 (1931), and reference 10.

The Relaxation Time and Dipole Moment of Gliadin

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THE dielectric constant of a medium depends not only on the temperature and concentration but also on the frequency. This is due to the fact that the molecules cannot orient themselves instantaneously with their electrical charges against the field when the latter changes rapidly. Accordingly Debye[1] writes the Clausius-Mosotti formula in the following manner:

$$\frac{\epsilon-1}{\epsilon+2}\frac{M}{d}=\frac{4\pi N}{3}\left(\alpha_0+\frac{1}{3kT}\cdot\frac{\mu^2}{1+i\omega\tau}\right). \quad (1)$$

In this equation $\epsilon=\epsilon'-i\epsilon''$ (ϵ' being the real part of the dielectric constant or that which is measured and ϵ'' the imaginary part which cannot be measured by capacity methods), M is the molecular weight, d is the density of the medium, N is the Avogadro number, α_0 is the optical polarisation, μ is the dipole moment, $\omega=2\pi\nu$ is the frequency, τ is the relaxation time, T is the absolute temperature and k is the Boltzmann constant.

If the frequency is of the order of that of light formula (1) reduces to

$$\frac{\epsilon_0-1}{\epsilon_0+2}=\frac{4\pi N\alpha_0}{3}, \quad (2)$$

and if the frequency is (small or) zero (direct current field) the formula reduces to the following

$$\frac{\epsilon_\infty-1}{\epsilon_\infty+2}=\frac{4\pi N}{3}\left(\alpha_0+\frac{\mu^2}{3kT}\right). \quad (3)$$

By combining formulas 1, 2, and 3 and solving for the real part of ϵ we obtain

$$\epsilon'=\epsilon_0+(\epsilon_\infty-\epsilon_0)\Big/\left(1+\left(\frac{\epsilon_\infty+2}{\epsilon_0+2}\right)^2\omega^2\tau^2\right). \quad (4)$$

By remembering that it is necessary to exert a torque to rotate a spherical molecule against the inner friction of the medium in which it is suspended the time of relaxation of such a molecule may be expressed in terms of its radius to give the following important result[8]

$$\tau=\frac{4\pi\eta r^3}{kT}=\frac{\epsilon_0+2}{\epsilon_\infty+2}\cdot\frac{1}{2\pi\nu_c}. \quad (5)$$

The frequency ν_c is that frequency for which $\epsilon=(\epsilon_\infty+\epsilon_0)/2$.

But if the molecule is a rotation ellipsoid with its long axis equal to a, and the short axis to b,