DETERMINATIONS WITH APPARATUS IN WATER BATH.

Gas, Dry Oxygen.

Vol. in tubes.	Vol. in bulb.	Diff.
178.510 cc.	178.509 cc.	—0.001 cc.
	178.507	—0.003
	178.515	+0.005
	178.511	+0.001
	178.518	+0.008
	178.512	+0.002
Mean,	178.512 cc.	+0.002 cc.

Dry Hydrogen.

Vol. in tubes.	Vol. in bulb.	Diff.
178.510 cc.	178.509 cc.	—0.001 cc.
	178.514	+0.004
	178.523	+0.013
	178.518	+0.008
	178.520	+0.010
	178.518	+0.008
Mean,	178.517 cc.	+0.007 cc.

Oxygen, Saturated with Water Vapor.

Vol. in tubes.	Vol. in bulb.	Diff.
178.586 cc.	178.599 cc.	+0.013 cc.
	178.591	+0.005
	178.586	+0.000
	178.597	+0.011
	178.590	+0.004
Mean,	178.592 cc.	+0.006 cc.

Hydrogen, Saturated with Water Vapor.

Vol. in tubes.	Vol. in bulb.	Diff.
178.586 cc.	178.594 cc.	+0.008 cc.
	178.595	+0.009
	178.601	+0.015
	178.585	—0.001
	178.599	+0.013
	178.576	—0.010
	178.602	+0.016
Mean,	178.593 cc.	+0.007 cc.

Summary.

We have compared the volume occupied by a gas in a system of tubes with that which it occupies in a bulb, in an effort to explain the difference in the volumetric ratio of hydrogen to oxygen in water as determined by Morley and by Scott. We have shown that there is no difference in volume larger than one part in ten thousand, whereas the two determinations referred to differ by one part in one thousand.

URBANA, ILL.

THE DENSITY OF AQUEOUS SOLUTIONS OF COPPER SULFATE AND SULFURIC ACID.

BY H. D. HOLLER AND E. L. PEFFER.[1]

Received March 25, 1916.

I. INTRODUCTION.

In connection with an investigation on the regulation of solutions for electrodeposition, especially of acid copper sulfate solutions for electrotyping, it was found desirable to devise a simple method of determining and adjusting their composition. Since the solutions usually employed for the above purpose contain only copper sulfate and sulfuric acid, the composition of any given solution is fixed if the acid content and density at a given temperature are known. The density can be readily determined with a hydrometer, and the acidity can be ascertained with sufficient

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[1] Published by permission of the Director of the Bureau of Standards.

accuracy by titration with standard alkali, using methyl orange as indicator, as described by Wogrinz.[1] In order, therefore, to learn the content of copper sulfate, all that is required is a table showing the density of solutions containing known amounts of copper sulfate and of sulfuric acid.

Although the densities of solutions of copper sulfate and of sulfuric acid have been determined separately, no systematic study of the densities of solutions containing both could be found in the literature. Only in isolated cases were such data given concerning certain baths, such as those recommended by Pfanhauser,[2] Langbein-Brannt,[3] Steinach and Buchner,[4] and others.

The concentration of solutions containing both copper sulfate and sulfuric acid is limited by the fact that addition of sulfuric acid to copper sulfate solution causes a marked decrease in the solubility of the copper sulfate. Thus, while 395 g. of crystallized copper sulfate is contained in 1 liter of the saturated solution at 15° the addition of 100 g. per liter of sulfuric acid reduces the solubility of the copper sulfate to 215 g. per liter. Since in any practical work it is necessary to use solutions somewhat removed from the saturation point, the actual field is probably included in the range of 0 to 20% of each of the constituents. Such solutions, therefore, formed the basis of this investigation. The temperature range of 25° to 40° was selected as including the normal temperature employed in most copper plating or refining operations. Doubtless the expansion coefficients determined from such data will permit extrapolation over a moderate range above and below the temperature used.

II. METHOD OF INVESTIGATION.

1. Preparation of Solutions.

In order to avoid the influence of temperature in the preparation of the solutions, they were all made of a known composition by weight, expressed in g. of each constituent per kg. of solution. They were prepared in duplicate by mixing accurately weighed portions of water and of standardized concentrated solutions of copper sulfate and of sulfuric acid.

The stock sulfuric acid solution was prepared by diluting C. P. acid to about 12 normal with distilled water, and was standardized by the barium sulfate method with the usual precautions. It was also compared with a hydrochloric acid solution, standardized by silver chloride precipitation, through a solution of sodium hydroxide, using methyl orange as indicator.

The concentration of the sulfuric acid solution as determined by the barium sulfate method agreed with that obtained by comparison with the

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[1] *Chem. Ztg.*, **37**, 869 (1913).

[2] "Die Galvanoplastik," **1904**, p. 37–38.

[3] "Electrodeposition of Metals," 7th ed., **1913**, p. 574–575, 590.

[4] "Die Galvanische Metallniederschläge," **1911**, p. 160–161.

standard hydrochloric acid solution to within about 1 part in 1500. Weight burets were used, the individual titrations agreeing to within less than 1 part in 2000.

The solution of copper sulfate was prepared from recrystallized salt, which gave a perfectly clear solution. The concentration of copper sulfate ($CuSO_4.5H_2O$) was calculated from the copper content determined electrolytically, the greatest difference between any two results being 1 part in 3000. Complete removal of copper from the electrolyte was confirmed by testing with $K_4Fe(CN)_6$.

2. Density Determination.

Method of Determination.—The density measurements were made by the method of hydrostatic weighing, *i. e.*, by weighing in the sample under investigation a sinker of known mass and volume. The density[1] of the liquid is then calculated by means of the equation

$$D_t = \frac{W - \frac{(w - w_1) + (w - w_2)}{2}\left(1 - \frac{\rho}{8.4}\right)}{V_t}$$

in which

D_t = Density at temp. t

W = Mass of sinker *in vacuo*

w = Weighings with sinker off

w_1 and w_2 = Weighings with sinker on

ρ = Air density

8.4 = Assumed density of brass weights

V_t = Volume of sinker at temp. t

Apparatus Used.—The apparatus used is described in detail in Bureau publications.[2] A short description of the apparatus is given as follows:

The densimeter tube (about 45 cm. long and 2.5 cm. in diameter) containing the sample is placed in a water bath which is kept in constant circulation. This bath is surrounded by another, also in circulation, the temperature of which is regulated by means of an electric heating coil and a brine cooling coil. The temperature of the inner bath is determined by the use of two mercury thermometers. The large sinker having a length of approximately 33 cm. and diameter of 1.3 cm. is attached below a small sinker and both are suspended by means of a wire from one arm of a sensitive balance. The small sinker which is in the liquid at all times serves the purpose of keeping the suspension wire taut and in position, and thus the effect of surface tension is eliminated.

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[1] Throughout this paper the term "density" is used to denote mass per unit volume and is here expressed in grams per milliliter. The densities are therefore numerically the same as specific gravities in terms of water at 4° as unity.

[2] *Technologic Paper* No. 9 (1912) and Bureau of Standards *Bull.* 9, 371–378 (1913).

Method of Making Observations.—After sufficient time has elapsed for attaining temperature equilibrium at the desired temperature, the first weighing is made with the large sinker attached and the temperature is immediately read from each of the thermometers. Then the second weighing is made with the large sinker detached from the small sinker. In order to obviate any correction for a possible change in temperature the first weighing is repeated and the thermometers re-read. The average of the temperatures at the two weighings is taken as the true temperature. The difference between the mean of these two weighings and the second weighing is the apparent weight of the large sinker in the sample at the given temperature. After completing the observations at one point, the temperature is changed to the next and the process is repeated in the same order.

III. RESULTS OF INVESTIGATION.

The results of the density determinations and composition of the samples are shown in Table I.

TABLE I.

Density of Copper Sulfate—Sulfuric Acid Solutions.

$CuSO_4.5H_2O$, g./kg.	$CuSO_4$, g./kg.	H_2SO_4, g./kg.	Density,[1] 25°.	Mean density, 25°.	Density, 40°.	Mean density, 40°.	α.[2]
50	31.97	0	1.03014	1.03016	1.02489	1.02488	—0.00035
50	31.97	0	1.03017		1.02488		
50	31.97	50	1.06297	1.06303	1.05637	1.05638	—0.00044
50	31.97	50	1.06309		1.05639		
50	31.97	100	1.09843	1.09843	1.09060	1.09060	—0.00052
50	31.97	100	1.09843		1.09060		
50	31.97	150	1.13552	1.13549	1.12669	1.12668	—0.00059
50	31.97	150	1.13546		1.12667		
50	31.97	200	1.17421	1.17416	1.16453	1.16452	—0.00064
50	31.97	200	1.17412		1.16452		
100	63.94	0	1.06454	1.06455	1.05871	1.05872	—0.00039
100	63.94	0	1.06456		1.05874		
100	63.94	50	1.09835	1.09834	1.09097	1.09097	—0.00049
100	63.94	50	1.09833		1.09097		
100	63.94	100	1.13497	1.13498	1.12642	1.12649	—0.00057
100	63.94	100	1.13499		1.12656		
100	63.94	150	1.17367	1.17366	1.16417	1.16418	—0.00063
100	63.94	150	1.17366		1.16420		
100	63.94	200	1.21399	1.21397	1.20379	1.20375	—0.00068
100	63.94	200	1.21395		1.20371		
150	95.91	0	1.10062	1.10063	1.09428	1.09430	—0.00042
150	95.91	0	1.10064		1.09431		
150	95.91	50	1.13555	1.13554	1.12765	1.12764	—0.00053
150	95.91	50	1.13553		1.12764		

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[1] All densities here tabulated are expressed in grams per milliliter.

[2] Change in density per degree rise in temperature.

TABLE I (*continued*).

$CuSO_4.5H_2O$, g./kg.	$CuSO_4$, g./kg.	H_2SO_4, g./kg.	Density, 25°.	Mean density, 25°.	Density, 40°.	Mean density, 40°.	α.
150	95.91	100	1.17366	1.17364	1.16457	1.16455	—0.00061
150	95.91	100	1.17361		1.16453		
150	95.91	150	1.21392	1.21393	1.20391	1.20394	—0.00067
150	95.91	150	1.21394		1.20396		
150	95.91	200	...	...	1.24528	1.24523	...
150	95.91	200	[1]		1.24518		
200	127.9	0	1.13833	1.13834	1.13152	1.13153	—0.00045
200	127.9	0	1.13835		1.13154		
200	127.9	50	[2]	1.17485	...	1.16638	—0.00056
200	127.9	50	1.17485		1.16638		
200	127.9	100	1.21449	1.21448	1.20476	1.20476	—0.00065
200	127.9	100	1.21447		1.20475		
200	127.9	150	...	...	1.24579	1.24575	...
200	127.9	150	[1]		1.24571		

In Table I the composition of the solutions is expressed in g. of $CuSO_4.5H_2O$ per kg. of solution. The concentration in g. per liter may be readily

TABLE II.

Showing the Relation Between Total Concentration and Density.

Total concentration, g./kg.	$CuSO_4.5H_2O$, g./kg.	H_2SO_4, g./kg.	Density, 25°.
50	0	50	1.0300
	50	0	1.0302
100	0	100	1.0640
	50	50	1.0630
	100	0	1.0646
150	0	150	1.0994
	50	100	1.0984
	100	50	1.0983
	150	0	1.1006
200	0	200	1.1365
	50	150	1.1355
	100	100	1.1350
	150	50	1.1355
	200	0	1.1383
250	0	250	1.1751
	50	200	1.1742
	100	150	1.1737
	150	100	1.1736
	200	50	1.1749
300	0	300	1.2150
	100	200	1.2140
	150	150	1.2139
	200	100	1.2145

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[1] Solutions of these compositions do not exist at 25°.

[2] Sample lost by breakage of the container.

obtained by multiplying the above concentrations in g. per kg. by the corresponding densities. In each case density determinations were made upon duplicate solutions, and these results are seen to agree in most cases to somewhat better than 1 in the fourth decimal place. From the density data for 25° and 40°, respectively, the thermal density coefficient α has been calculated, which may be defined as the change in density (always negative) for an increase in temperature of 1°.

The above results are shown graphically in Fig. 1, which illustrates the

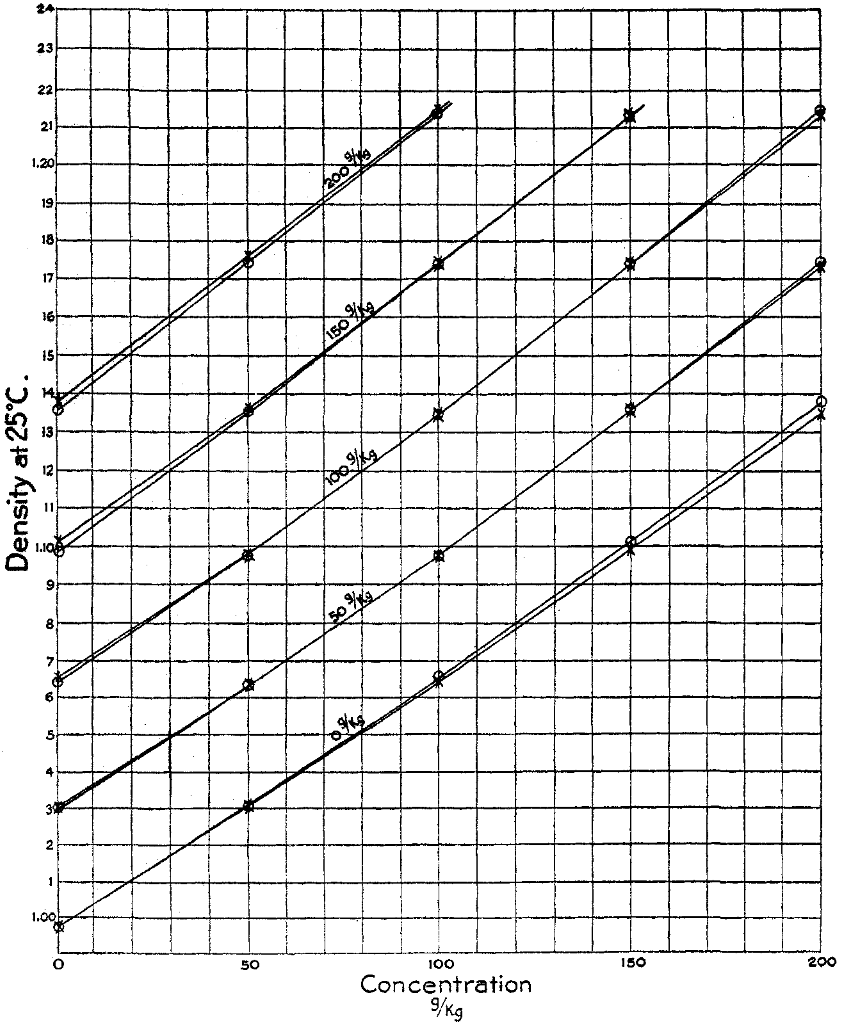

Fig. 1.—Density of copper sulphate-sulphuric acid solutions.
O — sulphuric acid constant.
× — copper sulphate constant.

effect upon the density of additions of copper sulfate to sulfuric acid solutions and of sulfuric acid to copper sulfate solutions. The curves for sulfuric acid solutions are derived from the data of Donke as given in Landolt and Börnstein, fourth edition (1912). The close agreement between the densities of solutions of the same total concentration, shown in Table II is illustrated in Fig. 1. The curves passing through the circles show the change in density produced by the addition of copper sulfate to solutions containing a definite amount of sulfuric acid per kg. of solution. Those through the crosses show the change in density produced by the addition of sulfuric acid to solutions containing a definite amount of copper sulfate per kg. of solution, the total concentration in each case being the same as for the corresponding curve through the circles.

Example.—In the case of the curves marked 50 g./kg., the one passing through the circles shows the change in density produced by the addition of definite amounts (50, 100, 150, 200 g.) of copper sulfate to a solution containing 50 g. of sulfuric acid per kg. of solution, and the one passing

TABLE III.

Total Concentration of Solutions of Given Density.

25° C.		40° C.	
Density.	$CuSO_4.5H_2O + H_2SO_4$, g./l.	Density.	$CuSO_4.5H_2O + H_2SO_4$, g./l.
1.01	20	1.01	26
1.02	36	1.02	43
1.03	52	1.03	60
1.04	68	1.04	76
1.05	84	1.05	93
1.06	100	1.06	110
1.07	117	1.07	127
1.08	133	1.08	144
1.09	150	1.09	161
1.10	166	1.10	178
1.11	183	1.11	195
1.12	200	1.12	212
1.13	217	1.13	229
1.14	234	1.14	247
1.15	251	1.15	265
1.16	268	1.16	282
1.17	286	1.17	300
1.18	303	1.18	318
1.19	321	1.19	336
1.20	339	1.20	354
1.21	357	1.21	372
1.22	375	1.22	390
1.23	393	1.23	408
		1.24	427

through the crosses shows the change in density produced by the addition of the same definite amounts of sulfuric acid to a solution containing 50 g. of copper sulfate per kg. of solution.

From the above tables and curves it may be seen that:

1. Within the range studied, the density of copper sulfate-sulfuric acid solutions is approximately a linear function of the concentration.

2. The density of solutions of equal (not equivalent) concentrations of copper sulfate ($CuSO_4.5H_2O$) and of sulfuric acid is nearly identical.

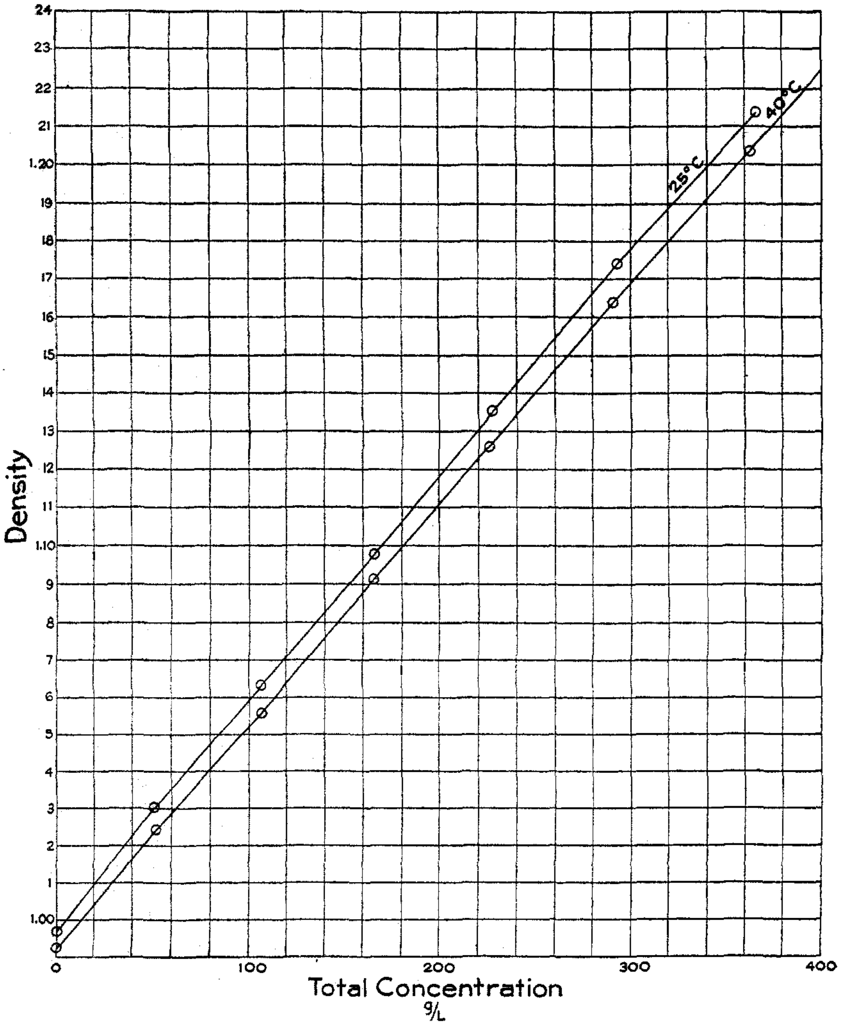

Fig. 2.—Density of solutions of total concentration of copper sulphate plus sulphuric acid.

3. As a natural consequence of the conclusions noted in (1) and (2), a curious relation was found to exist, *i. e.*, that the density of solutions containing appreciable amounts of each constituent is dependent principally upon the total concentration of the two solutes, and is almost independent of their proportion. (See Table II.) Thus, a solution containing 50 g. per kg. of copper sulfate and 150 of sulfuric acid has practically the same density (1.1355) as has a solution containing 100 g. per kg. of copper sulfate and 100 of sulfuric acid (1.1350). This simple relation, which is apparently only a mathematical coincidence, has been used as the basis for the curve shown in Fig. 2 in which the total concentration, in g. per liter,[1] of copper sulfate plus sulfuric acid is plotted against the density, yielding an almost straight line. The application of such a curve, or of the table derived from it (Table III) in determining the composition of unknown solutions, is obvious, involving only a determination of the density and acidity, the latter then being deduced from the total concentration corresponding to the observed density, to obtain the copper sulfate concentration.

Details of the application of this table in the regulation of electrolytic copper baths will be given in the second edition of Bureau of Standards *Circular* **52**.

In conclusion, the authors desire to acknowledge their indebtedness to Dr. William Blum and Mr. H. W. Bearce under whose direction this investigation was made.

WASHINGTON, November 27, 1915.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN.]

THE RELATION OF OSMOSE OF SOLUTIONS OF ELECTROLYTES TO MEMBRANE POTENTIALS. THEORETICAL.

BY F. E. BARTELL AND C. D. HOCKER.

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The fact that the osmose of solutions of electrolytes shows a close relationship to the differences of potential, which have been found to exist between the two faces of membranes separating such solutions from water, lends support to the theory that the osmose of such solutions is largely dependent upon the electrical condition of the membrane in question. In attempting to explain the osmose of salt solutions by an electrical theory similar to that used to account for electric osmose, two determining factors must be considered: (1) the electric charge of the membrane ma-

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[1] Obviously, the above relation exists whether the concentration is expressed in g. per kg. or g. per liter. The data shown in Fig. 2 and Table III have been calculated to g. per liter since the results of the analysis of solutions are usually expressed in that form.