

# THE APPARENT ACTIVITY OF CUPRIC SULPHATE IN FEHLING'S SOLUTIONS AT 25° C.

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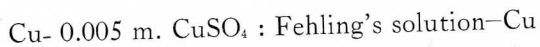
The reduction of cupric copper solutions by reducing sugars has been extensively utilized in qualitative and quantitative analyses of reducing sugars since 1841 when Trommer<sup>2</sup> first introduced alkaline cupric sulphate as a reagent to distinguish d-glucose from sucrose.

Trommer's reagent was improved by Barreswil<sup>3</sup> by the addition of potassium tartrate which prevented the precipitation of cupric hydroxide. Fehling<sup>4</sup> worked out the details of the quantitative method, giving some stoichiometrical equivalents between copper and d-glucose. He regarded the ratio of one molecule of d-glucose to five molecules of cupric sulphate as constant. It has been shown by several investigators<sup>5</sup> that the ratio varies with the total concentration of the cupric copper, with the nature and the concentration of the alkali used, and with the conditions used in the determination.

In the electrometric titration of d-glucose by means of Fehling's solution reported by Daggett, Campbell, and Whitman<sup>6</sup> attention is called to the fact that a more satisfactory end point is obtained when the concentration of the sodium hydroxide in the alkaline tartrate solution is lower than that ordinarily used.

During the course of an investigation of the electrometric titration of d-glucose with Fehling's solution it was noted that the results varied with the concentration of the sodium hydroxide and the sodium potassium tartrate. Since the active oxidizing agent in Fehling's solution is the cupric ion we thought that the measurement of the effective cupric ion concentration would be helpful in the interpretation of these results.

By the measurement of the electromotive force of a cell consisting of



the activity of the cupric sulphate in the Fehling's solution could be determined precisely if the liquid junction potential were known. It is an accepted fact that the use of a saturated potassium chloride solution as a salt bridge minimizes liquid junction potentials. Since we desired to measure the relative effects of the con-

<sup>1</sup>This paper, read before the Tennessee Academy of Science, November 30, 1928, is based upon experimental work done in the Physical Chemistry Laboratory, State University of Iowa. The author wishes to thank Dr. J. L. Whitman for his cooperation.

<sup>2</sup>Trommer. 1841. *Ann.*, 39 : 360

<sup>3</sup>Barreswil. 1844. *J. Phar.*, (3) 6 : 301

<sup>4</sup>Fehling. 1849. *Ann.*, 72 : 106; 1858. *Ann.*, 106 : 75

<sup>5</sup>Soxhlet. 1878. *J. Prakt. Chem.*, (2) 21 : 227

Kjeldahl. 1896. *J. Chem. Soc.*, 70, Abs. ii, 580

Quisumbing and Thomas. 1921. *J. Am. Chem. Soc.*, 43 : 1511

<sup>6</sup>Daggett, Campbell, and Whitman. 1923. *J. Am. Chem. Soc.*, 45 : 1043

centration of sodium hydroxide and sodium potassium tartrate upon the activity of the cupric sulphate in Fehling's solution, cells with a saturated solution of potassium chloride as a salt bridge were used.

If we neglect the liquid junction potential, the activity of cupric sulphate in Fehling's solution may be determined from the relation

$$E = \frac{RT}{nF} \ln \frac{a'_2}{a''_2} \quad (1)$$

where  $E$  is the electromotive force of a cell in which  $a'_2$  is a known activity and  $a''_2$  is an unknown activity.

Upon substitution of the values for  $R$ ,  $F$ ,  $T$  ( $25^\circ\text{C.}$ ), and  $n = 2$  and passing to Briggsian logarithms, we have for the cupric sulphate concentration cell

$$E_{25^\circ} = \frac{0.02958}{2} \log \frac{a'_2}{a''_2} \quad (2)$$

By making use of the data given by Lewis and Randall<sup>7</sup> the activity coefficient of a 0.005 molal solution of cupric sulphate

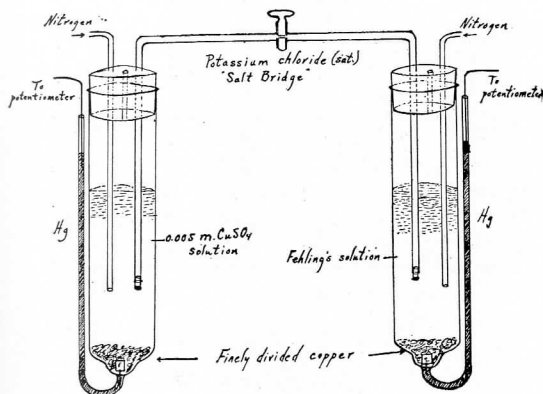


Fig. 1. The Set-up of the Cell.

is found to be 0.50, from which the activity of the cupric sulphate is found to be 0.0025. Hence we obtain for  $a''_2$ , the activity of the cupric sulphate in Fehling's solution

$$a''_2 = \log 0.0025 - \frac{E}{0.02958} \quad (3)$$

Then the electromotive force of cells of the type:

Cu-0.005 m.  $\text{CuSO}_4$  : saturated  $\text{KCl}$  : Fehling's solution-Cu will give a relative value for the activity of the cupric sulphate in Fehling's solution.

#### EXPERIMENTAL

A stock solution of cupric sulphate was prepared from hydrated cupric sulphate which had been recrystallized three times from

<sup>7</sup>Lewis and Randall, 1923, Thermodynamics, McGraw-Hill Book Co., Table 12, p. 362

distilled water. This solution was standardized and used in the preparation of the Fehling's solutions.

A 0.005 molal solution of cupric sulphate was prepared and used as the standard for the cells.

Stock solutions of carbonate free sodium hydroxide and of sodium potassium tartrate were prepared and standardized. The sodium hydroxide solution was standardized against benzoic acid obtained from the Bureau of Standards. The sodium potassium tartrate solution was standardized by evaporating a known volume, igniting the residue, converting the residue to chlorides, and weighing the combined chlorides of sodium and potassium.

The copper for the electrodes was prepared by the electrolysis of a molar solution of cupric sulphate, using a copper anode within

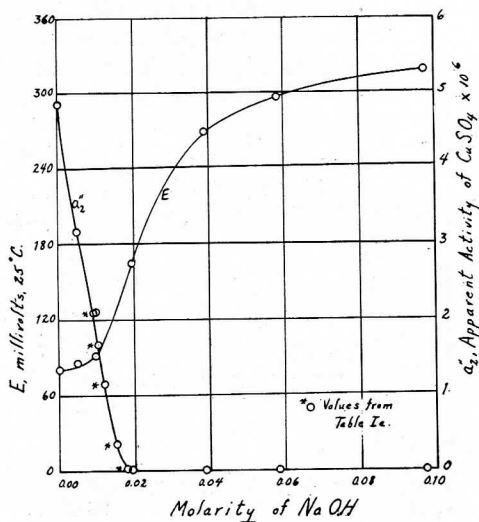


Fig. 2. Relation of Apparent Activity of Cupric Sulphate to the Concentration of Sodium Hydroxide.

a porous cup and a short platinum wire cathode. The current density was made high so that the copper was precipitated in a finely divided, spongy form as recommended by Lewis and Lacey<sup>8</sup> in their determination of the normal electrode potential of copper.

The cells consisted of large test tubes with platinum foil electrodes sealed into the bottom of the tubes. They were closed at the top with three holed rubber stoppers that had been treated with a boiling solution of sodium hydroxide. The half-cells were connected by means of a saturated potassium chloride salt bridge containing a stop-cock and having small ground glass stoppers

at the ends. The ground glass stoppers gave an excellent and a reproducible junction and prevented diffusion into the bridge. The set-up is shown in Figure 1.

After placing the finely divided copper in the half-cells the solutions were carefully introduced. The cells were then placed in an oil bath thermally regulated at  $25^{\circ}\text{C.} \pm 0.03^{\circ}$ . A gentle stream of purified nitrogen was then passed through the solutions to carry out any dissolved oxygen. The tubes were then closed, the stop-cock of the salt bridge was opened, and the electromotive force of the cell measured.

The electromotive force measurements were made with a Leeds and Northrup Student Potentiometer. An unsaturated cadmium

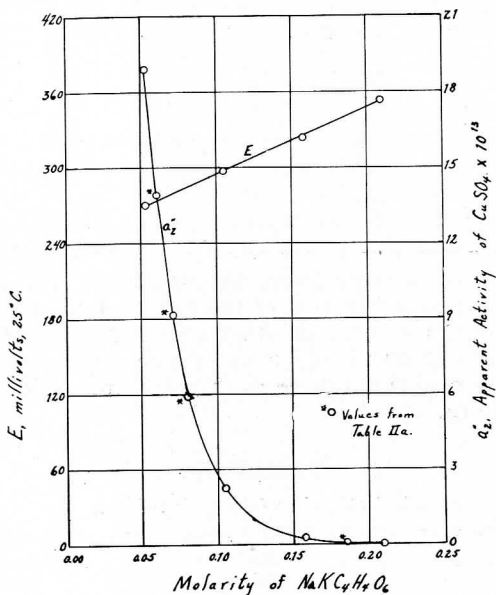


Fig. 3. Apparent Activity of Cupric Sulphate with Variable Concentration of Sodium Potassium Tartrate.

cell that had been standardized against a certified Standard Cell was used for the primary standard.

Measurements were made in which the concentration of the sodium hydroxide was varied, while the concentrations of the cupric sulphate and the sodium potassium tartrate were kept constant. The results are given in Table I.

TABLE I

*Experimental values for cupric sulphate with variable sodium hydroxide  
CuSO<sub>4</sub>, 0.01374 M.; NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, 0.1045 M.*

CONC. NaOH M.	E <sub>25</sub> °C. VOLTS		APPARENT ACTIVITY OF CuSO <sub>4</sub>
	MEASURED	MEAN	
0.0000	0.0801 0.0802	0.08015	4.85 x 10 <sup>-6</sup>
0.00487	0.0858 0.0856	0.0857	3.17 x 10 <sup>-6</sup>
0.00975	0.0911 0.0912 0.0908	0.0910	2.10 x 10 <sup>-6</sup>
0.0195	0.1658 0.1649	0.1653	6.45 x 10 <sup>-9</sup>
0.0390	0.2688 0.2690	0.2689	2.03 x 10 <sup>-12</sup>
0.0585	0.2965 0.2966	0.2965	2.37 x 10 <sup>-13</sup>
0.0975	0.3175 0.3180	0.3178	4.54 x 10 <sup>-14</sup>

By plotting, on a large scale, the values for the electromotive force against the concentration of the sodium hydroxide, the values for the electromotive force at other concentrations of the sodium hydroxide were determined, from which other values for the activity of the cupric sulphate were calculated. These values are given in Table Ia.

TABLE Ia.

*Calculated values for cupric sulphate*

CONC. NaOH M.	E <sub>25</sub> ° VOLTS	APPARENT ACTIVITY OF CuSO <sub>4</sub>
0.0090	0.0910	2.10 x 10 <sup>-6</sup>
0.0102	0.0938	1.68 x 10 <sup>-6</sup>
0.0120	0.0987	1.15 x 10 <sup>-6</sup>
0.0153	0.1179	3.17 x 10 <sup>-7</sup>
0.0180	0.1470	2.68 x 10 <sup>-8</sup>

When the values for the apparent activity of the cupric sulphate are plotted against the concentration of the sodium hydroxide, a smooth curve, within the limits of experimental error, is obtained. The curves are given in Fig. 2.

Measurements also were made in which the concentration of the sodium potassium tartrate was varied, while the concentrations of the sodium hydroxide and the cupric sulphate were kept constant. The results are given in Table II.

TABLE II.

Experimental values of cupric sulphate with variable sodium potassium tartrate.  
 $\text{CuSO}_4$ , 0.01374 M.;  $\text{NaOH}$ , 0.0585 M.

CONC. $\text{NaKC}_4\text{H}_4\text{O}_6$ M.	$E_{25}^\circ$ VOLTS		APPARENT ACTIVITY OF $\text{CuSO}_4$
	MEASURED	MEAN	
0.0522	0.2694 0.2702	0.2698	$1.89 \times 10^{-12}$
0.1044	0.2968 0.2970	0.2969	$2.30 \times 10^{-13}$
0.1566	0.3243 0.3233	0.3238	$2.81 \times 10^{-14}$
0.2088	0.3540 0.3545	0.3543	$3.34 \times 10^{-15}$

When the values for the electromotive force are plotted against the concentration of the sodium potassium tartrate the curve is almost a straight line, from which it is easy to read other values and hence, to calculate the apparent activity for other concentrations of sodium potassium tartrate. These values are given in table IIa.

TABLE IIa.

Calculated values for cupric sulphate

CONC. $\text{NaKC}_4\text{H}_4\text{O}_6$ M.	$E_{25}^\circ$ VOLTS	APPARENT ACTIVITY OF $\text{CuSO}_4$
0.0600	0.2738	$1.39 \times 10^{-12}$
0.0700	0.2791	$9.17 \times 10^{-13}$
0.0800	0.2843	$5.92 \times 10^{-13}$
0.1850	0.3400	$8.08 \times 10^{-15}$

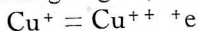
When the values for the apparent activity of the cupric sulphate are plotted against the concentration of the sodium potassium tartrate, a smooth curve is obtained. The curves are given in Fig. 3.

## DISCUSSION

The results show that the activity of the cupric sulphate is decreased by an increase in the concentration either of the sodium hydroxide or of the sodium potassium tartrate. A change in concentration of sodium hydroxide effects the activity to a greater extent than a change in concentration of sodium potassium tartrate. This is to be expected, since an increase in the hydroxyl ion concentration should tend to increase the ionization of the alcoholic group of the tartrate ion, and therefore favor the formation of

the cupryl tartrate ion. The results show that the cupryl tartrate ion is very stable and is only very slightly ionized.

If we consider the equilibrium that exists in Fehling's solution during its reduction by reducing sugars, namely



we would expect that as the activity of the cupric ion is decreased there would be less tendency for it to be reduced to the cuprous ion. Then it would take a higher concentration of reducing sugar to give the end point when the activity of the cupric ion is decreased. This is precisely in accordance with the facts as observed during the investigation of the electrometric titration of d-glucose by means of Fehling's solution. It must be pointed out that the electrometric end point is apparently caused by an abrupt decrease in the concentration of the cupric ion. The activity measurements were made at 25° C., while the electrometric titrations were made at temperatures near 100° C.

While the electromotive force measurements are not precise, it seems that they are of the right order of magnitude.

#### SUMMARY

1. The effective cupric ion concentration or the apparent activity of cupric sulphate in Fehling's solutions has been measured at 25° C.

2. The measurements were made in the absence of oxygen, which has been shown by others to have a considerable effect upon electromotive force measurements of this type.