TABLE I

DISTRIBUTION OF PHENOL BETWEEN PENTACHLOROETHANE AND WATER

$k = 1.085$, $\alpha = 0.83$, $\beta = 0$

Q	$D_{\text{obsd.}}$	$D_{\text{calcd.}}$
0.0495	1.18	1.17
.110	1.27	1.28
.226	1.51	1.51
.432	1.94	1.92
.708	2.53	2.56
1.170	3.51	3.50

I wish to thank Professor Linus Pauling for suggesting this problem, and for his help and encouragement throughout the work. I wish also to thank Professor Roscoe G. Dickinson for the many helpful discussions we have had.

Summary

1. A method of calculating equilibrium constants of polymerization reactions from freezing point, boiling point, and distribution data is described.

2. The method is applied to various compounds and it is shown that the data are often fitted by the empirical relation $n = 1 + \alpha Q + \beta N$.

3. The distribution of phenol between pentachloroethane and water is accurately accounted for by the same type of equation as accounts for freezing point lowering data.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NEBRASKA]

The Standard State of Copper. A Study of the Copper–Cupric Electrode

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Electrodes composed of all but the softer metals have the tendency to show irregularities of potential which seem to depend somewhat on the previous treatment of the metal. Many methods have been tried for eliminating these irregularities. In 1914, Lewis and Lacey[1] devised an electrolytic method. They claim that a metal that has been plated upon platinum under high current densities from a solution of its salt will be strainless. In the case of copper, an acidified solution of copper sulfate was used. Copper prepared in this manner has a higher reducing potential than that of the copper amalgam. From theoretical considerations, a two-phase amalgam should be strainless and will give the potential of the standard state if there is no compound formation and if the mercury is not appreciably soluble in the metal. The solubility of mercury in copper is unknown, but if we assume that there is no compound formation, the value obtained by Lewis and Lacey would indicate an enormous solubility of mercury in copper which does not seem reasonable. So any large difference would indicate compound formation between copper and mercury. There are such compounds reported in the literature.

In this work, an application of von Weimarn's law was used in the preparation of the copper crystals at 25°. Copper sulfate in silica gels was reduced by organic reducing agents. The gel prevented the mechanical mixing of the copper sulfate with the reducing agent so that the rate of diffusion controlled the rate of reduction of the $CuSO_4$. By this method, it was hoped to secure the standard state of metallic copper.

Materials and Apparatus

The copper amalgam used was prepared by electrolysis of a half molal solution of cupric sulfate, slightly acidified, using about five amperes per sq. dm. of mercury surface and a copper anode. The amalgam was kept under this solution after preparation. Mercurous sulfate was prepared by electrolysis according to the method of Hulett.[2] The cupric sulfate used had been recrystallized from an acidified solution of the C. P. crystals. Conductivity water and distilled mercury were used in preparing the reagents. Silica gels were prepared by mixing equal volumes of N acetic acid and sodium silicate solution (sp. gr., 1.06). Before the mixture gelled, it was made 0.04 N with cupric sulfate. After the mixture gelled, a 2% solution of semicarbazide hydrochloride was poured on top of the gel and placed in an air-bath maintained at 25 ± 0.1°. In about a month, the gel was removed with concentrated sodium hydroxide solution, and the resulting crystals of copper removed and washed with water. Finely divided copper was obtained by pouring an ammoniacal solution of cuprous sulfate into an excess of dilute sulfuric acid. This was always prepared fresh. Measurements were made on a Leeds and Northrup "Type K" potentiometer, using a Weston cell with a Bureau of Standards certificate. The thermostat consisted of a bath of distilled water maintained at 25 ± 0.05°.

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[1] Lewis and Lacey, THIS JOURNAL, **36**, 804 (1914).

[2] Hulett, *Phys. Rev.*, **32**, 32 (1900).

Procedure

A "nest" of six cells was used. The cells were filled with approximately half molar cupric sulfate solution containing a drop of 0.1 *N* sulfuric acid per liter of solution to prevent hydrolysis. Purified nitrogen was then bubbled through the liquid for five minutes to remove the oxygen.

Copper amalgam was washed several times with cupric sulfate solution of the same strength as that used in the cells and then poured into the cells. The amalgams were checked against one another.

Crystals of copper were washed with *N* nitric or sulfuric acid followed by cupric sulfate solution and then dropped onto one of the amalgams. The electromotive force of the crystals against the amalgam was determined.

To check the method, cells were made so that some of the crystals could be dropped on platinum wire and their electromotive force determined against the copper amalgam. Another check on the method was made by determining the electromotive force of a copper wire suspended into the solution, and then dropping the wire onto an amalgam and again determining the electromotive force. Both of the above proved that the method used was all right. If the crystals were dropped onto the amalgam so that they would pile up, the potential of the resulting cell remained constant for as long as forty-eight hours.

From time to time the cell Cu amalgam/$CuSO_4$ (satd.)/Hg_2SO_4/Hg was prepared as a check on the amalgam.

Results

The finely divided copper was a better reducer than the amalgam by 5.0 mv. while the copper crystals were better by 3.0 mv. If oxidation potentials are used, the normal electrode potential for the amalgam as obtained by Nielsen and Brown[3] is 0.3502 v. From this the normal electrode potential of finely divided copper will be 0.3452 v. and for the crystals, 0.3472 v. These values are correct within 0.2 mv.

Discussion

If a large particle of a given mass be subdivided, its surface increases. When the particles become very small, the surface area is increased enormously and as a consequence, the surface free energy increases appreciably the total free energy. There is also a free energy change due to the process of subdivision. So the finely divided copper would have a free energy greater than that of the standard state by an amount equal to the sum of the two above mentioned free energy changes. This explains why the reduction potential of finely divided copper is greater than that for the standard state.

It was found that strain and fineness could be eliminated by growing the crystals in silica gels at the temperature at which they were to be used. Of the reducing agents tried, semicarbazide hydrochloride gave the best crystals which were free from oxide.

The potential of the single crystal electrode, as obtained by Getman,[4] checked well with the potential of the crystals used in this work, and the electrolytic copper, as determined by Lewis and Lacey,[5] gave a value of 0.3448 v., which is in good agreement with the finely divided copper made by rapid precipitation. This may indicate that it is a matter of subdivision of electrolytic copper rather than the presence of hydrogen in the copper that causes the reduction potential to be too great. The dark color of the electrolytic copper could be explained by the fineness of the metal as finely divided metals are dark in color.

Summary

1. The factors involved in the preparation of the standard state of copper were studied.

2. The crystals of copper that were grown slowly at 25° should be considered as the standard state and the value of the normal electrode potential is 0.3472 v.

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[3] Nielsen and Brown, THIS JOURNAL, **49**, 2423 (1927).

[4] Getman, *J. Phys. Chem.*, **34**, 1454 (1930).

[5] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923.