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The $Cu–Cu^+–Cu^{++}$ Equilibrium in Liquid Ammonia

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The equilibrium quotient for the reduction of cupric ion by copper has been measured for liquid ammonia solutions at room temperature. A tentative value for the equilibrium constant, $K = 10^4$, is obtained by extrapolating the data to zero ionic strength.

Introduction

Pleskov and Monossohn[1,2] determined the oxidation potentials of the Cu,Cu^+ and Cu,Cu^{++} couples at $-50°$. Their values are, respectively, -0.41 and -0.43 v. (*vs.* the hydrogen electrode). These values are probably of little thermodynamic significance for several reasons. (1) The cells which were studied involved liquid junctions whose potentials are unknown. (2) The activity coefficients employed by Pleskov and Monossohn were little more than guesses. (3) The copper electrode was found to behave erratically in a cupric salt solution.[3] (4) When the potentials are corrected to 25° (using estimated[4] entropies) and are used to calculate the equilibrium constant for the reaction

$$Cu + Cu^{++} = 2Cu^+ \qquad (1)$$

a value $K = 22$ is obtained. Such a low equilibrium constant is in disagreement with reports[5,6] which indicate that the reaction proceeds nearly to completion.

In the present investigation, the concentration equilibrium quotient for reaction 1 was determined at room temperature at ionic strengths of 0.5 to 1.9 molar. In the main series of experiments, solutions of cupric nitrate were equilibrated with excess copper metal. In two other experiments, cuprous iodide was allowed to disproportionate into copper and cupric iodide.

Experimental

Materials and General Procedure.—Cupric nitrate tetrammoniate was prepared by a method described by Mellor.[7]

Anal. Calcd. for $Cu(NO_3)_2 \cdot 4NH_3$: Cu, 24.85. Found: Cu, 24.73.

Cuprous iodide was prepared by the reaction of aqueous solutions of cupric nitrate and potassium iodide, followed by the addition of sufficient sodium bisulfite to reduce the iodine formed. The product was washed and then dried *in vacuo*.

The reaction tubes were made of 12 mm. o.d. Pyrex tubing which had been carefully selected for uniformity of bore. In each experiment, the reactants were weighed directly into a tube. After distilling about 5 ml. of carefully dried liquid ammonia into the tube, the tube was sealed off and stored at a temperature of 22–26°.

The total volume of solution and copper metal in a tube was determined by measuring the length of the liquid column with a cathetometer, the tube having been calibrated with water previously. This method permitted estimation of the solution volumes (corrected for copper metal) to ±0.05 ml.

The concentration of cupric ion was determined by visual comparison with a set of tubes containing known amounts of $Cu(NO_3)_2 \cdot 4NH_3$ and ammonia. The range of these standard tubes was conveniently extended by the use of tubes containing aqueous ammonia–cupric nitrate solutions. These latter solutions were calibrated by assuming that Beer's law is obeyed by $Cu(NH_3)_4^{++}$ in both liquid ammonia and aqueous ammonia solutions. The *colors* of the solutions are practically identical. The visually estimated concentrations are probably accurate to ±5% in the concentration region around 50×10^{-4} *M;* the percentage error is higher for higher and lower concentrations.

Experiments with $Cu(NO_3)_2 \cdot 4NH_3$.—Weighed amounts of $Cu(NO_3)_2 \cdot 4NH_3$ were allowed to equilibrate in solution with pieces of bare copper wire. Equilibrium was apparently established in about two days at room temperature, but the cupric ion concentrations were measured only after two weeks of equilibration. The results are summarized in Table I.

TABLE I

THE EQUILIBRATION OF $Cu(NO_3)_2 \cdot 4NH_3$ SOLUTION WITH Cu METAL

(Concentrations in moles/liter)

(Cu^+)	$(Cu^{++}) \times 10^4$	$(Cu^+)^2/(Cu^{++})$
0.029	<1	>8
.107	<1	>100
.217	<1.5	>300
.490	2.5	960
.83	9	760
1.40	39	500
1.89	74	480

Experiments with CuI.—Saturated cuprous iodide solutions (probably in equilibrium with $CuI \cdot 3NH_3$[8]) were allowed to reach equilibrium in the presence of a small piece of copper metal. (The copper metal was added as a precaution against possible iodine impurity in the CuI.) Two experiments were performed. In one case, only a very small amount of $CuI \cdot 3NH_3$ remained undissolved, permitting an estimate of the solubility, *i.e.*, 1.10 *M*. The estimated concentrations of cupric ion were 4×10^{-4} *M* and 5×10^{-4} *M*. From these data we calculate an equilibrium quotient of about 2700.

Discussion

The concentration equilibrium quotients of Table I show a somewhat regular trend with ionic strength, but the extrapolation to zero ionic strength is extremely uncertain. As a tentative value we give $K = 10^4$.

The quotient obtained from the experiments with cuprous iodide (2700) is much higher than that obtained at comparable ionic strengths from the nitrate experiments. It is suggested that, in the iodide experiments, the concentration of cuprous ion was reduced from 1.10 *M* to *ca.* 0.5 *M* by the formation of iodide complexes.

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[1] V. A. Pleskov, *Acta Physicochim.* (*U.S.S.R.*), **13**, 659 (1940).

[2] V. A. Pleskov and A. M. Monossohn, *ibid.*, **1**, 871 (1935).

[3] In view of the thermodynamic instability of the $Cu–Cu^{++}$ system, it is difficult to understand how Pleskov and Monossohn obtained any reasonable results with the Cu,Cu^{++} couple.

[4] W. L. Jolly, *J. Phys. Chem.*, **58**, 250 (1954).

[5] W. H. Sloan, THIS JOURNAL, **32**, 972 (1910).

[6] E. C. Franklin, "The Nitrogen System of Compounds," Reinhold Publ. Corp., New York, N. Y., 1935, pp. 56–57.

[7] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, Longmans, Green and Co., London, 1923, p. 284.

[8] W. Biltz and W. Stollenwerk, *Z. anorg. Chem.* **119**, 97 (1921).