

Cryoscopic Measurement of the Coordination Number of Copper

The lowering of the freezing point of a dilute aqueous solution of tetraamine copper(II) sulphate is a colligative property and therefore proportional to the sum of the molalities of the solutes.¹

Assuming that all the copper(II) is present as the complex ion $\text{Cu(II)}(\text{NH}_3)_X$ and that ion pair association between the copper(II) complex and sulphate ion is negligible the observed freezing point depression will be

$$\Delta = K(m_{\text{SO}_4} + m_{\text{Cu(II)}(\text{NH}_3)_X} + m_{\text{NH}_3})$$

where K represents the molal freezing point depression of water and m stands for molalities.

The molality of free ammonia, m_{NH_3} is the difference between the molality of total ammonia $m_{t\text{NH}_3}$ and that of the complex ammonia $m_{\text{C}_{\text{NH}_3}}$. The molality of complexed ammonia must be, according to the formula of the complex, X times the molality of Cu(II) ion, i.e.,

$$m_{\text{C}_{\text{NH}_3}} = X m_{\text{Cu(II)}}$$

so we have

$$m_{\text{NH}_3} = m_{t\text{NH}_3} - X m_{\text{Cu(II)}}$$

As each copper ion gives a complex ion, it follows that the molalities of Cu(II) , $\text{Cu(II)}(\text{NH}_3)_X$ and SO_4 must be equal. Therefore

$$\Delta = K(2m_{\text{Cu(II)}} + m_{t\text{NH}_3} - X m_{\text{Cu(II)}})$$

from which

$$X = 2 + \frac{m_{t\text{NH}_3} - \Delta/K}{m_{\text{Cu(II)}}} \quad (1)$$

This equation permits one to calculate X , when Δ , $m_{t\text{NH}_3}$ and $m_{\text{Cu(II)}}$ are known. Δ was measured by the equilibrium method,³ using a Beckman thermometer graduated in 0.01°C . To do this once the freezing point of water was determined (half a liter of an ice-water mixture was used), small amounts of a concentrated solution of the complex ($0.6 M \text{CuSO}_4$ in $5 M \text{NH}_3$) were added to produce a small depression of temperature (near 0.5°C) as corresponding to a dilute solution.

The mixture was stirred continuously until equilibrium was attained; the constant temperature was re-

corded and a sample of 10 ml of the solution was pipetted off for measuring both total ammonia and Cu(II) concentration.

The sample was poured in a weighed flask containing 25.0 ml of $0.1 N \text{HCl}$ in excess with respect to ammonia. The increment of weight gave the weight of the sample. The excess of acid was measured by titration against $0.1 N \text{NaOH}$ with methyl red as the indicator. The difference between the added amount of acid and the excess of it corresponded to total ammonia in the sample.

Cu(II) concentration was measured in the resulting weakly acid solution (pH about 5) by adding 10 ml of 20% KI and titration with $0.1 N \text{Na}_2\text{S}_2\text{O}_3$,⁴ using starch solution as the end point indicator. The amount of $\text{Na}_2\text{S}_2\text{O}_3$ consumed enabled us to calculate the weight of Cu(II) . The weight of solvent in the sample, necessary for calculating the molalities required by eqn. (1) was found as the difference: weight of sample minus weight of Cu(II) sulphate plus weight of ammonia.

Table I shows typical results obtained by students with this method.

It is interesting to investigate if the experimental values of X fall in the interval calculated from the standpoint of error calculations.

According to the eqn. (1), the maximum error in X (Δ^*X), will be given by

$$\Delta^*X = \frac{m_{\text{Cu(II)}}\Delta^*(m_{t\text{NH}_3} - \Delta/K) + (m_{t\text{NH}_3} - \Delta/K)\Delta^*m_{\text{Cu(II)}}}{(m_{\text{Cu(II)}})^2}$$

which can be put in the form

$$\begin{aligned} \Delta^*X &= \frac{\Delta^*(m_{t\text{NH}_3} - \Delta/K)}{m_{\text{Cu(II)}}} + \frac{m_{t\text{NH}_3} - \Delta/K}{m_{\text{Cu(II)}}} \times \frac{\Delta^*m_{\text{Cu(II)}}}{m_{\text{Cu(II)}}} \\ &\cong \frac{\Delta^*m_{t\text{NH}_3}}{m_{\text{Cu(II)}}} + \frac{2\Delta^*m_{\text{Cu(II)}}}{m_{\text{Cu(II)}}} \end{aligned}$$

In the foregoing experiments

$$\Delta^*m_{t\text{NH}_3} \cong 0.27 \times 10^{-2}$$

$$\frac{\Delta^*\Delta}{K} \cong 0.005$$

$$\frac{2\Delta^*m_{\text{Cu(II)}}}{m_{\text{Cu(II)}}} \cong 0.04$$

hence, Δ^*X can be estimated as 0.2 in good agreement with experimental values.

Experimental Data

$\Delta^\circ\text{C}$	Weight of sample (g)	NH_3 (mg)	Cu(II) (mg)	H_2O in the sample (g)	$m_{\text{Cu(II)}}$	$m_{t\text{NH}_3}$	X
0.362	9.889	41.0	14.9s	9.811	0.024 ₀	0.24 ₁	4.0
0.360	9.885	39.0	16.8s	9.803	0.027 ₀	0.23 ₉	3.7
0.360	9.911	41.0	16.2s	9.829	0.026 ₀	0.24 ₆	4.0
0.474	9.925	53.8	21.6s	9.817	0.034 ₆	0.32 ₃	4.0
0.474	9.878	55.2	21.6s	9.768	0.034 ₈	0.33 ₃	4.2
0.472	9.901	53.4	21.3s	9.794	0.034 ₂	0.32 ₆	3.9
0.472	9.897	55.1	20.4	9.790	0.032 ₇	0.33 ₂	4.3
0.598	9.912	68.3	28.0	9.773	0.045	0.41 ₀	3.9

¹ MARON, H. S., AND PRUTTON, C., "Principles of Physical Chemistry," Macmillan Company, New York, 1962.

² According to the dissociation constant of the complex ($K = 4.6 \times 10^{-14}$), in solutions in equilibrium with ice the ratio of Cu(II) to $\text{Cu(II)}(\text{NH}_3)_4$ will be around 10^{-10} . KOLTOFF, I., AND LINGANE, J., "Polarography," (2nd ed.), Interscience (division of John Wiley & Sons, Inc.), New York, 1955.

³ DANIELS, F., MATTHEWS, J. H., WILLIAMS, W. J., BENDER, P., AND ALBERTY, R., "Experimental Physical Chemistry" (5th ed.), McGraw-Hill Book Co., New York, 1956.

⁴ KOLTOFF, I., AND SANDELL, E., "Textbook of Qualitative Inorganic Analysis, The Macmillan Co., New York, 1947.