CXCIV.—*The Distribution of Ammonia between Chloroform and Water at 25°.*

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FOR another purpose it was necessary to know the value of the distribution coefficient of ammonia between chloroform and water at 25° for concentrations of ammonia in the aqueous layer varying up to molar. No such investigation appears to have been carried out at this temperature and over this concentration range. Hantzsch and Sebaldt (*Z. physikal. Chem.*, 1899, **30**, 268) give the coefficient at 25° as 25·1, the mean of five determinations in which the ammonia concentration in the aqueous layer varied from 0·00275*M* to 0·04425*M*; Dawson and McCrae (J., 1900, **77**, 1239) give 24·9 as the mean of three determinations in which the same concentration varied from 0·275*M* to 0·4492*M*; also Moore and Winmill (J., 1912, **101**, 1662) obtained values of 24·23, 24·25, and 24·26 for aqueous ammonia concentrations of 0·1498*M*, 0·1691*M* and 0·1987*M* respectively. All the above results are higher than those now obtained. Bell and Feild (*J. Amer. Chem. Soc.*, 1911, **33**, 940), using aqueous ammonia concentrations of 1—12·23*M*, obtained a result for their weakest solution which agrees well with the values now determined.

In the present investigation it was found that the value of the distribution coefficient decreases with increasing concentration of ammonia, as was found to be the case at 19·5° by Dawson (J., 1906, **89**, 1666). When the value of the distribution coefficient, k, is plotted as a function of the concentration of ammonia in the chloroform layer, c', the linear relationship $k = 24{\cdot}10 - 28{\cdot}45c'$ is found to hold over the concentration range investigated. When this relationship is used to calculate the coefficients for solutions of higher ammonia concentrations, the values obtained are smaller than those determined experimentally by Bell and Feild (*loc. cit.*), and, as would be expected, the deviation is greater the higher the ammonia concentration.

Since this work was completed, Dietrich (*J. Physical Chem.*, 1929, **33**, 95) has given data for the distribution of ammonia between chloroform and water at 25°, using ammonia solutions varying from 0·02*M* to 0·1*M*. He finds a mean value of 35·83 for the coefficient, using weight concentrations and correcting for the ammonia not present as NH_3 as a consequence of the equilibrium $NH_3 + H_2O \rightleftharpoons NH_4^{\cdot} + OH'$ for which K at 25° has the value $18{\cdot}1 \times 10^{-6}$ (Burke, *J. Amer. Chem. Soc.*, 1920, **42**, 2500). When this value is converted to a volume concentration ratio it becomes 24·1, if it be assumed that the specific gravities of the chloroform and aqueous solutions of ammonia are the same as those of the pure solvents. If this correction is applied to the result obtained with the solution of lowest concentration dealt with in this work, *viz.*, 0·1388M, the value for k becomes 23·7. To a great extent this divergence is due to the fact that in this work no special precautions were taken to free the chloroform layer from water, whereas Dietrich filtered it through cotton-wool and, after neglecting the first 50 c.c. of filtrate, determined ammonia in the remainder, using sodium alizarinsulphonate as indicator, whereas methyl-orange was used in the present work. If, however, additional correction is made for the error existing in the determinations of ammonia (see p. 1438) the value for this distribution coefficient becomes 24·12. When the distribution coefficients now given are corrected for the equilibrium $NH_3 + H_2O \rightleftharpoons NH_4^{\cdot} + OH'$ a constant value is not obtained, the variation being from 23·7 to 22·8. As ammonia obeys the mass-action law in dilute solution only, the use of this correction with solutions of much higher concentration than 0·1M seems open to question.

EXPERIMENTAL.

The solutions of ammonia were made from a stock solution prepared by distilling concentrated aqueous ammonia over barium hydroxide and collecting the gas in air-free water, the resulting solution being protected from the atmosphere. The chloroform used was a 'B.P.' product, which was shaken with concentrated sulphuric acid, then with water, and distilled; immediately before use, it was shaken with a dilute solution of ammonia, then with very dilute sulphuric acid, and redistilled. About 150 c.c. of chloroform were put in a cylindrical separating funnel, and the air remaining in the latter was replaced by hydrogen. Then about 80 c.c. of the ammonia solution were transferred, out of contact with air, into the separating funnel, which was at once closed and placed in a thermostat at 25° ± 0·05°. (This procedure was adopted because the investigation in which it was hoped to apply these results necessitated a similar treatment of the solutions to be used.) When the contents of the funnel had reached the desired temperature, it was shaken at intervals during an hour, previous experiment having shown that equilibrium was attained in this time. The funnel was then kept in the thermostat for another hour to allow complete separation of the two layers.

To determine the ammonia in the chloroform layer, 50 c.c. of this were quickly added to 75 c.c. of distilled water in a stoppered flask and titrated with N/20- or N/10-sulphuric acid, methyl-orange being used as indicator (chloroform extracts methyl-red from aqueous solution). The first appearance of a permanent pink colour in the aqueous layer after shaking was taken as the end-point. The ammonia in the original aqueous layer was similarly determined by direct titration of a measured volume.

Results.—The following results were obtained, c and c' being the concentrations (in g.-mols./l.) of ammonia in the aqueous and the chloroform layer respectively; k is the distribution coefficient c/c', and k' is the coefficient corrected for the equilibrium $NH_3 + H_2O \rightleftharpoons NH_4^{\bullet} + OH'$.

c.	c'.	k.	k'.	c.	c'.	k.	k'.
0·1388	0·005794	23·94	23·68	0·5805	0·02490	23·32	23·18
0·1404	0·005868	23·93	23·66	0·6586	0·02823	23·32	23·20
0·2330	0·009777	23·83	23·61	0·6882	0·02960	23·24	23·13
0·3232	0·01360	23·75	23·59	0·7089	0·03060	23·17	23·05
0·3835	0·01624	23·61	23·45	0·8019	0·03468	23·12	23·01
0·4677	0·01993	23·47	23·31	0·9661	0·04223	22·87	22·78
0·4785	0·02032	23·54	23·41	1·022	0·04466	22·88	22·78
0·4868	0·02074	23·47	23·32				

These results are selected from a much larger number obtained over this concentration range, and in many cases represent the average of three closely agreeing determinations.

An aqueous solution of ammonia was prepared and its concentration, as determined by titration with standard sulphuric acid and methyl-red as indicator, was taken as absolute. From this, other solutions were prepared by dilution, and their concentrations determined by titration with $N/20$- or $N/10$-sulphuric acid and methyl-orange, the conditions being similar to those used in the determination of the distribution ratios. In this way, it has been found that the chloroform solutions of ammonia are in error by not more than + 2% and + 0·9% respectively for the lowest and highest concentrations, whereas the errors for the corresponding aqueous solutions do not exceed + 0·25% and + 0·2% respectively.

Summary.

The distribution coefficient of ammonia between chloroform and water has been determined at 25° over the concentration range of 0·1388—1·022M in the aqueous layer.

Within this range the coefficient can be represented by the linear equation $k = 24·10—28·45c'$, where c' is the ammonia concentration in the chloroform layer.

When the distribution coefficient is corrected for the equilibrium $NH_3 + H_2O \rightleftharpoons NH_4^{\bullet} + OH'$ ($K = 18·1 \times 10^{-6}$ at 25°), a constant is not obtained, but the value of the coefficient still decreases with increasing concentration of ammonia.

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