(*a*) The salt is freed in large part from compression due to chemical affinity and to molecular cohesion.

(*b*) When the ions and probably the molecules are combined with the water both the hydrated substance and the water undergo compression. This latter effect varies regularly with the compressibilities of the substances involved as well as with their affinities for each other.

(4) It is shown that the change in volume in the formation of the ions from the elements, as measured by the sum of the change in volume in the formation of the solid salt and the change in volume during solution, is an additive property.

(5) The part which the polymerization of water plays in the change is uncertain. Probably this effect varies in importance with varying temperature. It is also probable that at the temperature of the experiments cited, the effect is small, since the observed effects are not in accord with those to be expected if the contraction is due wholly to changing polymerization.

It is obvious that the data furnished at the beginning of this paper allow the calculation of the densities of aqueous solutions of many of the salts considered up to moderately high concentrations.

The study of change in volume during solution will be continued in this laboratory by the examination of other salts and other solvents, and by the determination of the effect of varying temperature on the magnitude of the observed effect.

CAMBRIDGE, MASS.

THE DISTRIBUTION OF AMMONIA BETWEEN WATER AND CHLOROFORM.

BY JAMES M. BELL AND ALEXANDER L. FEILD.

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The distribution of ammonia between water and chloroform has been studied by several investigators. The results have been employed to determin the concentration of free ammonia in an aqueous solution, which contains also some compound of ammonia, such as the blue cuprammonia compounds and the phosphates of ammonium. Until recently the distribution was determined only for dilute solutions, where the concentration of ammonia in the water layer was not greater than normal.

Hantzsch and Sebaldt[1] found that the ratio of the concentrations of ammonia in water and chloroform is 25.1 at 25°, the mean of five determinations in which the concentration in the water layer varies from 0.00275 to 0.04425 normal. At 2° this ratio is 38.53. Dawson and McCrae[2] give the following values for the distribution ratio: 26.3 at 20°, 24.9 at

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[1] *Z. physik. Chem.*, 30, 258 (1899).

[2] *J. Chem., Soc.*, 77, 1239 (1900).

25°, and 23.2 at 30°, the highest concentration in the water layer being 14.14 grams NH_3 per liter. In a later paper Dawson and McCrae[1] repeated their determinations at 20°, the extreme concentrations of ammonia in the water layer being 5.160 and 17.168 grams NH_3 per liter. Between these limits the distribution ratio is not quite independent of the ammonia concentration. The ratio varies from 26.36 for the most dilute solution to 25.32 for the most concentrated.

The following quotation is from a later paper by Dawson:[2] "In reference to the distribution of ammonia between pure water and chloroform, it has already been shown that the concentration ratio H_{H_2O}/C_{CHCl_3} decreases with increasing ammonia concentration, but the relationship between these two factors could not be determined with a desirable degree of accuracy in the case of dilute solutions containing less than 0.5 mol. of ammonia per liter of aqueous solution." Consequently new determinations were made at 19.5° by an improved method. Representing k (the distribution ratio) as a function of c' (the concentration in the chloroform layer) the points so obtained lie approximately on the straight line corresponding to the equation

$$k = 26.16 - 34.14c'.$$

Abbott and Bray[3] have also found the distribution ratio with the object of determining the degree of hydrolysis of several phosphates of ammonium in aqueous solution. At 18° the ratio is 27.45, where the aqueous layer has a concentration between 0.02 and 0.05 normal.

In more concentrated ammonia solutions, Dawson[4] has found that at 18° the distribution ratio decreases from 26.46 at 0.928 normal to 21.70 at 4.333 normal.

The present paper contains the results of an investigation of this distribution at 25° and over a much wider range of concentration. Chloroform was added to aqueous solutions of ammonia of varying strength. The bottles were placed in an electrically heated and controlled thermostat at 25° and were frequently shaken. When equilibrium had been reached, a known volume of each layer was titrated against standard acid. The following table contains the concentration of ammonia in each layer expressed in gram molecules per liter and also the distribution ratio between the two layers.

It will be seen from the table that the distribution varies from 22 in dilute solution to about 10 in concentrated solution. The limit to which the distribution tends at very great dilution appears to be about 24.

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[1] *J. Chem. Soc.*, **79**, 493 (1901).

[2] *Ibid.*, **99**, 1668 (1906).

[3] THIS JOURNAL, **31**, 729 (1909).

[4] *Z. physik. Chem.*, **69**, 110 (1909).

TABLE I.

Normality NH_3 in water layer. C.	Normality NH_3 in $CHCl_3$ layer. C'.	Distribution ratio. K.
1.02	0.045	22.7
2.08	0.095	21.9
3.13	0.146	21.4
3.98	0.205	19.4
5.24	0.283	18.5
6.25	0.365	17.1
7.29	0.457	15.9
8.34	0.549	15.2
9.35	0.710	13.2
10.23	0.864	11.8
11.24	1.045	11.0
12.23	1.227	10.0

The following table contains the limiting values of the distribution ratio for very dilute solutions as found at different temperatures by the various workers in this field.

TABLE II.

Temp.	Dist. Ratio.	Observer.
2°	38.5	Hantzsch and Sebaldt.
18	27.45	Abbott and Bray.
18	27.5 approx.	Dawson.
20	26.5	Dawson and McCrea, I.
20	25.3	Dawson and McCrae, II.
25	25.1	Hantzsch and Sebaldt.
25	24.9	Dawson and McCrea, I.
25	24. approx.	Bell and Feild.
30	23.2	Dawson and McCrae, I.

The accompanying table (II) shows clearly that the distribution ratio falls as the temperature rises.

The points obtained by plotting the values of c and k in Table I lie on a curve which deviates rather far from a straight line, so that the formula given by Dawson holds only for the more dilute solutions, and is of value in giving the limiting direction of the curve. This result is confirmed by the later results of Dawson where more concentrated solutions have been used.

The effect of other compounds on the distribution ratio has been investigated by Hantzsch and Sebaldt[1] and by Dawson and McCrae.[2] As ammonia is a weak base it is but slightly ionized even at great dilutions, and consequently the addition of an ammonium salt would increase the number of undissociated molecules very slightly, while the percentage decrease of ionization would be greatly diminished. If unionized ammonia is the substance distributed, then the presence of ammonium chloride

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[1] *Z. physik. Chem.*, 30, 258 (1899).

[2] *J. Chem. Soc.*, 79, 493 (1901).

should affect the distribution very slightly and then only on account of the "salting out" effect. If, on the other hand, the ionized portion were distributed, the presence of the highly ionized salt would affect the distribution very greatly. In very dilute solutions Hantzsch and Sebaldt have found that ammonium chloride has almost no effect. Dawson and McCrae have, however, shown that the effect is measurable, the distribution ratio at 20° decreasing by 0.88 for each mol. of salt per liter of solution. The nitrate and sulfate also lower the distribution ratio, while the bromide increases it. The following table (III) gives the results of experiments on the distribution of ammonia between chloroform and a solution of ammonium chloride containing about 3 mols. per liter. At each concentration of ammonia the distribution ratio is very close to that found in the absence of ammonium chloride.

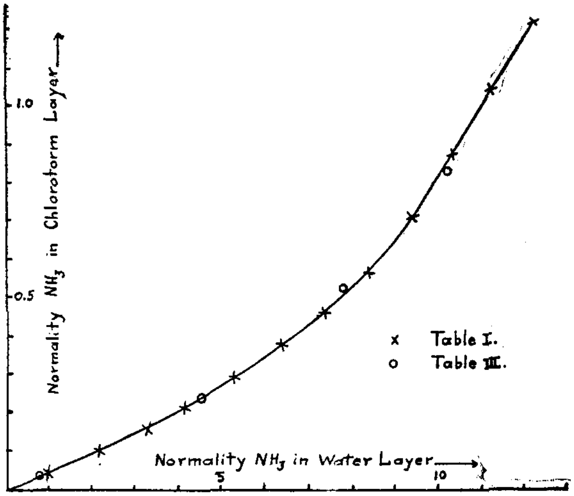

TABLE III.

Normality NH_3 in water layer (NH_4Cl—3N).	Normality NH_3 in $CHCl_3$ layer calc.	Normality NH_3 in $CHCl_3$ layer obs.
0.84	0.037	0.037
4.32	0.226	0.228
7.72	0.494	0.512
10.16	0.837	0.820

In this paper it has been shown that at 25° the distribution ratio for ammonia between water and chloroform varies with the concentration, from about 24 in dilute solution to about 10 in concentrated solution. The presence of ammonium chloride affects the distribution very slightly.

UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, N. C

ACTION OF THE OXIDES OF LEAD ON POTASSIUM TARTRATE.

BY FRANCIS C. KRAUSKOPF.

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The solvent action of solutions of normal alkali tartrates on litharge