XLIX.—*The Influence of Salts and other Substances on the Vapour Pressure of Aqueous Ammonia Solution.*

By EDGAR PHILIP PERMAN.

THE author recently published a series of measurements of the vapour pressure of aqueous ammonia solution showing the effect of alteration of concentration for certain selected temperatures (Trans., 1901, 79, 718). These results may, of course, be looked at in another way,

namely, as expressing the solubility of ammonia under varying pressure, and it may be well to compare them with the results of other investigators in this line of research.

Roscoe and Dittmar (*Annalen*, 1859, 112, 349) determined the solubility at 0° at pressures varying from 18 mm. to 1963 mm. The pressures given are "partial pressures" obtained by subtracting the vapour pressure of water at the temperature of the experiment from the total pressure. It may be pointed out that this method of calculating partial pressure is quite inadmissible, for the ammonia solution may be regarded as a mixture of two liquids, and the total vapour pressure would be equal to the sum of the vapour pressures of the liquids taken separately only if they were completely immiscible. (The author is already engaged in determining the partial pressures of the ammonia and the water in an aqueous ammonia solution.) On adding the vapour pressure of water to the pressures recorded, the few results available for comparison agree well with those given by the author in his previous paper.

Sims (*Annalen*, 1861, 118, 345) found the solubility of ammonia in water at 0° , 20° , 40° , and 100° . The results are somewhat scanty, but free use was made of graphic interpolation. The pressures given are "partial," as in the previously named paper; when corrected to total pressure, the numbers are much lower than those obtained by me.

Watts (*Annalen Suppl.*, 1865, 3, 227) made experiments at 0° and 20° with a mixture of ammonia and air; when corrected to total pressures, as before, the results fall almost exactly on the curves representing the results of my experiments.

Raoult (*Ann. Chim. Phys.*, 1874, [v], 1, 262) made some single determinations at temperatures from 0° to 28° at a "partial pressure" of 760 mm. They cannot well be compared with those under consideration.

Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1894, 26, 48), as the result of experiments of which the numbers are not given, states that aqueous solutions of ammonia do not follow Dalton's law at the ordinary temperature, but with rise of temperature the disagreement becomes less, until at 100° the numbers are in accord with this law. This result was obtained approximately also by Sims. Konowaloff (*ibid.*, 1899, 31, 910) has also found the partial pressures of some solutions at 60° by the dynamical method, but the solutions used were so weak that the results are not comparable with mine.

The outcome of this comparison, so far as it can be carried out, is a confirmation of the accuracy of the numbers given in the previous paper, except in the case of the results obtained by Sims, which are probably erroneous.

Much work has also been done on the vapour pressure of ammonia

and salt solutions. Raoult (*loc. cit.*) investigated the solubility of ammonia in solutions of potassium hydroxide, sodium hydroxide, ammonium chloride, ammonium nitrate, sodium nitrate, and calcium nitrate respectively, and his results, briefly summarised, are:

(1) Potassium and sodium hydroxides greatly lessen the solubility; equivalent quantities have the same effect, and the effect of each is proportional to the amount present in a given volume.

(2) Ammonium chloride also decreases the solubility proportionally to the amount present.

(3) Ammonium and sodium nitrates have practically no effect on the solubility.

(4) Calcium nitrate increases the solubility in proportion to the amount present, but the effect of alteration of pressure on the solution is nearly the same as on an ammonia solution.

(5) Experiments on the heat of solution of ammonia in solutions of these substances appeared to show that they were approximately the same as the heat of solution in water.

Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 910) found by the dynamical method the effect of the presence of a number of salts on the partial pressure of the ammonia. The decrease in the pressure of the ammonia can be expressed by the formula

$$H = H_1 (n - km) \text{ where}$$

H_1 = pressure of the ammonia in pure aqueous solution of less than $1\frac{1}{2}$ normal strength.

H = pressure of the ammonia in solution containing the salt.

n = number of gram-molecules of ammonia per litre.

m = " " salt per litre.

For silver nitrate $k=2$, and for cadmium nitrate, zinc nitrate, nickel chloride, copper nitrate, copper chloride, copper sulphate, and copper acetate, the value of k approaches H . This is taken to indicate the presence of complexes like $\text{AgNO}_3 \cdot 2\text{NH}_3$; $\text{CuSO}_4 \cdot 4\text{NH}_3$ in solution.

Gaus (*Zeit. anorg. Chem.*, 1900, **25**, 236), by a very interesting modification of the dynamical method, has determined the influence of a number of salts on the partial pressure of the ammonia, the results agreeing with those already mentioned. Ammonium nitrate and barium chloride produce hardly any effect. Copper sulphate causes a large depression which is proportional to the amount of salt present. Quite recently this work has been largely extended by Abegg and Riesenfeld (*Zeit. physikal. Chem.*, 1902, **40**, 84).

A consideration of the work of these investigators as well as that of Dawson and McCrae (*Trans.*, 1900, **77**, 1239), seems to indicate clearly the existence of metal ammonia complexes in solution, notwithstanding the opinion of Raoult concerning calcium nitrate, but the effect of salts

which would not be expected to have any chemical action has not yet been explained.

The experiments about to be described were directed towards the elucidation of (1) the effect of substances having no direct chemical action on the ammonia, (2) the effect of change of temperature on the copper sulphate ammonia solution, (3) the existence, or otherwise, of hydrates in solution.

The method was very nearly the same as that described in a previous paper (*loc. cit.*, p. 725) except that the vapour jacket was replaced by a water-bath with a toluene gas regulator; the temperature did not usually vary more than 0.01° during an experiment. The height of the mercury column, as well as that of the ammonia solution above it, was read by means of a mirror scale placed in front of the bath at an angle so that the reflection of the mercury could be easily read. With this arrangement, parallax can be easily avoided by making the scale line nearest the reading coincide with its reflection.

Influence of Substances having no direct Chemical Action on Ammonia.

Substances having no direct action on ammonia are hard to find; those employed as likely to have no action were urea, mannitol, potassium sulphate, and ammonium chloride. A preliminary experiment was made to discover whether urea undergoes any decomposition when heated with ammonia solution; 20 grams of urea were heated in a sealed tube with an aqueous ammonia solution of about four times normal strength at 40° for 6 hours. *Before* heating, 10 c.c. of the solution required (1) 41.98 c.c., (2) 42.07 c.c., and *after* heating (1) 41.90 c.c., (2) 41.90 c.c. of normal sulphuric acid solution for neutralisation.

To determine the vapour pressures, a solution was made containing a weighed quantity of urea (or other substance) and the ammonia then estimated by titration; after the vapour pressures had been measured, the ammonia was again estimated, and in every case the amount agreed well with the previous result. After the solution had been transferred to the vessel for measuring the pressures, the air was driven out of it by repeatedly lowering the pressure (by lowering the open tube containing mercury) and then driving out the liberated air by raising the mercury quickly and opening the stopcock at the top for a moment.

The pressures for a corresponding ammonia solution have been found by reading off the values for the particular strength on the curves given in the previous paper. These give values of pressure for 0° , 20° , 34.4° , 46.4° , and 61.3° . From these, a curve was constructed which may be called an *isosthen* or line of equal strength, and from it

the pressures for the temperatures employed were read off. The strength of the corresponding ammonia solution has been calculated in two ways (I) as a solution containing the same proportion of ammonia to water, (II) as a solution containing the same mass of ammonia in unit volume of the solution. Both are given where possible in the following tables.

Urea Solution I.— NH_3 , 16.36; $\text{CO}(\text{NH}_2)_2$, 10.43; H_2O , 73.21 per cent. Density, 0.9591 at 22° . Strength of corresponding NH_3 solution, (I) 18.26, (II) 16.73 per cent. :

Temperature.	Pressure in mm.	Aqueous NH_3 solution.	
		Pressure I in mm.	Pressure II in mm.
24.58°	255.4	258	221
29.39	312.0	318	276
35.20	403.0	405	354
40.38	496.8	500	438
45.59	611.4	611	532
54.43	856.1	854	738
59.07	1014.4	1008	880

Urea Solution II.— NH_3 , 17.22; $\text{CO}(\text{NH}_2)_2$, 5.29; H_2O , 77.49 per cent. Density, 0.9425 at 21° . Strength of corresponding NH_3 solution (I) 18.18, (II) 17.38 per cent. :

Temperature.	Pressure in mm.	Aqueous NH_3 solution.	
		Pressure I in mm.	Pressure II in mm.
25.05°	260.4	263	240
29.58	316.6	322	294
34.96	400.3	402	373
39.68	485.1	485	452
45.90	621.8	618	569
50.07	726.2	722	659
54.45	856.9	854	775
58.00	973.7	970	886

When the vapour pressure of the urea-ammonia solution is compared with that of an aqueous ammonia solution having the same ratio of ammonia to water, the agreement is remarkable, but when it is compared with that of a solution containing the same amount of ammonia in a given volume, the apparent effect of the urea is to decrease the solubility of the ammonia. This may be due simply to the increase in volume of the solution on addition of the urea.

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Mannitol Solution.— NH_3 , 12.27; mannitol, 4.56; H_2O , 83.17 per cent. Density, 0.9636 at 15° . Corresponding NH_3 solution, (I) 12.86, (II) 12.43 per cent. :

Temperature.	Pressure in mm.	NH_3 solution.	
		Pressure I in mm.	Pressure II in mm.
22.92°	143.8	150	141
29.77	197.7	205	196
36.78	271.2	275	262
42.74	348.8	355	332
50.61	479.1	484	453
57.79	629.6	636	595

When the vapour pressure of the mannitol-ammonia solution is compared with that of an aqueous ammonia solution, a small but regular decrease is shown, due, possibly, to the formation of a compound of mannitol and ammonia. Mannitol is known to form stable compounds with the alkaline earths.

Potassium Sulphate Solution.— NH_3 , 7.49; K_2SO_4 , 3.05; H_2O , 89.46 per cent. Density, 0.9826 at 35° . NH_3 , 7.73 per cent. of NH_3 and H_2O :

Temperature.	Pressure in mm.	Pressure of 7.73 per cent. NH_3 solution in mm.
40.42°	203.5	192
46.70	265.2	250
51.14	320.0	302
58.51	427.5	407

It was difficult to make a suitable solution owing to the slight solubility of the potassium sulphate, and with the solution employed the measurements could not be begun below 40° . The large increase in pressure may be due to a displacement of ammonia molecules by salt molecules, or possibly to the formation of hydrates producing a concentration of the solution. Potassium and sodium chlorides were found by Gaus to increase the pressure largely, and the hydroxides still more. The increase in pressure must be ascribed to the change in the nature of the solvent, and the relation between the two changes reserved for further investigation.

Ammonium Chloride Solution I.— NH_3 , 16.85; NH_4Cl , 5.27; H_2O , 77.88 per cent. Density, 0.9472 at 14° . Corresponding NH_3 solution, (I) 17.79, (II) 17.07 per cent. :

Temperature.	Pressure in mm.	NH ₃ solution.	
		Pressure I in mm.	Pressure II in mm.
19·01°	(182·1)	183	169
26·04	251·1	263	245
32·93	343·0	355	333
39·24	449·3	457	430
49·26	667·2	675	622
57·83	913·2	933	860

Ammonium Chloride Solution II.—NH₃, 12·90 ; NH₄Cl, 10·26 ; H₂O, 76·84 per cent. Density, 0·9724 at 16°. Corresponding NH₃ solution, (I) 14·37, (II) 13·24 per cent. :

Temperature.	Pressure in mm.	NH ₃ solution.	
		Pressure I in mm.	Pressure II in mm.
23·12°	158·5	171	154
30·89	230·5	243	223
38·26	318·5	334	301
45·37	428·8	447	402
51·18	543·2	560	502
58·14	707·6	723	651

If the results are compared with those obtained with ammonia solution I, the ammonium chloride is seen to produce a decrease in pressure, and the decrease is approximately twice as much in solution II as in I (except at the low temperatures, where there seems to be some experimental error in solution I). This suggests the formation of some compound of the ammonia with the ammonium chloride. Since the completion of these experiments, the author has found that compounds such as NH₄Cl,3NH₃ and NH₄Cl,6NH₃ have been isolated (*Compt. rend.*, 1879, **88**, 578), and it is probably due to the formation of compounds like these that the vapour pressure of the solution is diminished.

Gaus found barium chloride and ammonium nitrate to have only a very slight effect on the ammonia pressure, and Raoult found ammonium nitrate and potassium nitrate to have none; Raoult's experiments, however, were carried out with such strong solutions that they are hardly comparable with those now described.

From the results hitherto obtained, it seems impossible to predict what effect will be produced by introducing into the solution a sub-

stance which would be expected to have no direct chemical action on the ammonia; the influence, however, would appear to be small except in the case of salts of the alkalis. If, however, a substance, as, for example, silver chloride or zinc sulphate, is known to form a definite compound with ammonia, the pressure of the ammonia is invariably diminished, but the effect of the ammonia going into combination may be complicated by other effects not yet understood.

Effect of Change of Temperature on a Solution of Cupri-ammonium Sulphate.

It was found necessary to use weak ammonia solutions, otherwise a sufficient amount of copper sulphate could not be kept in solution at the lower temperatures. An attempt was made to measure the vapour pressure at 0°, but without success; the height of the mercury column could not be read, for the solution stuck to the glass and the mercury rose inside it. This phenomenon, which is presumably a surface-tension effect, did not occur at about 20°.

Copper Sulphate Ammonia Solution I.— NH_3 , 14.65; CuSO_4 , 2.68; H_2O , 82.67 per cent. Density, 0.9652 at 15°. Corresponding NH_3 solution (I) 15.05, (II) 15.01 per cent. :

Temperature.	Pressure in mm.	Pressure NH_3 solution in mm.	Pressure of NH_3 solution in mm.
18.88°	138.5	145	138 } subtracting 3 NH_3
26.37	197.6	212	197 } mols. for each mol.
36.08	306.9	324	303 } CuSO_4 .
43.64	421.6	446	419 }
47.49	492.6	518	491 } „ 2 NH_3 „
50.81	559.9	588	555 }
			{ 686 }
56.54	692.6	725	{ 700 } „ 1 NH_3 „

The copper sulphate produces a large decrease in the pressure, in all probability due to the formation of a cupri-ammonium compound. If the copper sulphate in the solution combines with ammonia, forming the compound $\text{CuSO}_4 \cdot 4\text{NH}_3$, the amount of free ammonia remaining in the solution can be calculated by subtracting 4 mols. NH_3 for every CuSO_4 mol.; an aqueous ammonia solution calculated of this strength has lower pressures than any found for the copper-ammonium sulphate solution at the same temperatures. Subtracting 3 mols. NH_3 , the pressures coincide at 19° and 26°; subtracting 2 mols. NH_3 , the pressures are nearly coincident at 44° and 47°. There is evidently progressive dissociation, until at 56.5° only about $1\frac{1}{2}$ mols. NH_3 for

every CuSO_4 mol. remain in combination. Unfortunately, a great assumption has to be made in calculating out these numbers, namely, that the copper sulphate has no influence on the pressure other than that caused by the ammonia going into combination with it. The uncertainty in this matter makes it useless to develop the theory of the decomposition from the numbers obtained. The compound at first in solution is probably $\text{SO}_2 \left\langle \begin{smallmatrix} \text{O} \cdot \text{NH}_3 \cdot \text{NH}_3 \\ \text{O} \cdot \text{NH}_3 \cdot \text{NH}_3 \end{smallmatrix} \right\rangle \text{Cu}$, which dissociates into $\text{SO}_2 \left\langle \begin{smallmatrix} \text{O} \cdot \text{NH}_3 \\ \text{O} \cdot \text{NH}_3 \end{smallmatrix} \right\rangle \text{Cu}$, and very possibly $\text{SO}_2 \left\langle \begin{smallmatrix} \text{O} \cdot \text{NH}_3 \cdot \text{NH}_3 \\ \text{O} \text{---} \text{NH}_3 \end{smallmatrix} \right\rangle \text{Cu}$, is also formed.

On evaporation of the ammonia, or on dilution of the solution, decomposition takes place, probably thus :

These compounds will also be more or less ionised.

Copper Sulphate Ammonia Solution II.— NH_3 , 6.54; CuSO_4 , 3.94; H_2O , 89.52 per cent. Density, 1.010 at 15° . Corresponding NH_3 solution, (I) 6.81, (II) 6.80 per cent. :

Temperature.	Pressure in mm.	Pressure NH_3 solution in mm.	Pressure NH_3 solution in mm.
30.57	91.8	112	93
36.97	126.2	148	124
41.51	155.1	180	154
46.85	194.7	227	197
52.61	250.1	294	251
57.68	308.8	367	313

} Subtracting 3NH_3

In this case, the amount of ammonia held in combination by the copper is apparently the same as before, but no dissociation takes place, no doubt owing to the much smaller proportion of water with regard to the copper sulphate. After each experiment was completed, the copper solution was tested for mercury, but only a trace was found in each case.

The Existence of Hydrates in Solution.

The experiments on potassium sulphate before described have an interesting bearing on this question. The author has shown in a recent paper (Trans., 1901, 79, 725) that anhydrous sodium sulphate has a great effect in raising the ammonia pressure, but it is now found that potassium sulphate has a similar effect. The experimental data available for the comparison are given in the table on page 489.

From these numbers we find that the ratio $\frac{\text{number mols. Na}_2\text{SO}_4}{\text{number mols. K}_2\text{SO}_4} = 1.71$,

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Composition of solution.	Temperature.	Pressure in mm.	Pressure of corresponding NH_3 solution in mm.	Per cent. increase of pressure.
$\left\{ \begin{array}{l} \text{K}_2\text{SO}_4 \quad 3\cdot05 \\ \text{NH}_3 \quad 7\cdot49 \\ \text{H}_2\text{O} \quad 89\cdot46 \end{array} \right\}$	40·42°	203·5	192	5·99
	46·70	265·2	250	6·08
$\left\{ \begin{array}{l} \text{Na}_2\text{SO}_4 \quad 4\cdot25 \\ \text{NH}_3 \quad 9\cdot90 \\ \text{H}_2\text{O} \quad 85\cdot85 \end{array} \right\}$	40·42	276	246	12·2
	46·70	360	320	12·5

whilst the ratio $\frac{\text{per cent. increase of press. caused by the Na}_2\text{SO}_4}{\text{per cent. increase of press. caused by the K}_2\text{SO}_4} = 2\cdot05$ (2·04 at 40·42° and 2·06 at 46·70°).

These ratios are sufficiently near to each other to show that molecular proportions of potassium sulphate, which crystallises without water, and of anhydrous sodium sulphate have approximately the same effect. There is no difference, such as would be caused by one forming a hydrate in solution and the other not. Supposing the sodium sulphate to take up 10 mols. of water, the concentration of the solution thereby produced would cause an increase in pressure of about 10 per cent.

The increase of pressure caused by the potassium sulphate is 6 per cent., and the number of molecules of sodium sulphate is 1·7 times as great as the number of potassium sulphate molecules; the effect of the sodium sulphate should therefore be (supposing molecular proportions to have the same effect) an increase of pressure of $6 \times 1\cdot7 = 10\cdot2$ per cent.: adding this to the 10 per cent. for the increase in concentration of the solution, we obtain a total increase of 20·2 per cent. This, divided by the increase for the potassium sulphate (6 per cent.), gives 3·37 for the ratio $\frac{\text{increase by Na}_2\text{SO}_4}{\text{increase by K}_2\text{SO}_4}$ instead of 2·05, the number found, a difference far beyond the limits of experimental error.

There is little reason for supposing potassium sulphate to form a hydrate in solution, so that these experiments seem to indicate the non-existence of a hydrate of either sodium sulphate or potassium sulphate in solution.

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