

The method would be most useful in the analysis of mixtures of elements of nearly equal atomic weights, such as lanthanum and praseodymium, since the mean equivalent weight, unless determined with extreme accuracy, would give little information as to the composition of the mixture. The accuracy of this method depends on the standardization of working conditions.

Periodicity of Lines

One object of this investigation was to secure data on the absorption spectra of the rare earth elements, obtained under uniform conditions, for postulating a periodic relationship among the spectra, but no very definite relations were found. It is hoped to continue the study of this problem.

The author desires to express his appreciation of the suggestions given by Professor B. S. Hopkins during the progress of this work.

Summary

1. The absorption spectra of praseodymium, neodymium, samarium, dysprosium, holmium, erbium and thulium in the visible portion of the spectra have been measured at various concentrations and thicknesses of solution.

2. Absorption curves have been drawn and the last appearance of each band on dilution has been tabulated.

3. A method for the quantitative estimation of rare earths is outlined.

4. There seems to be no definite periodic arrangement of the absorption bands.

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INSTITUTE OF TECHNOLOGY, No. 14]

AN APPARENT DEVIATION FROM HENRY'S LAW FOR THE SYSTEM, AMMONIA-WATER

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According to Henry's law: "Any chemical substance present in a gaseous phase and in a condensed phase in equilibrium with it has, at any definite temperature, a mole fraction c in the condensed phase which is proportional to its mole fraction C in the gaseous phase: $C = ac$, where a is an equilibrium constant which is determined by the nature of the chemical substance, of the solvent, and by the temperature." The system ammonia-water, is reported by all experimenters as obeying Henry's law up to concentrations of 3.2 g. of ammonia per liter and over a temperature range from 0° to 100°.

We determined the value of this constant at 100° for aqueous ammonia solutions of concentrations from 0.005 to 1.5 g. of ammonia per liter. The

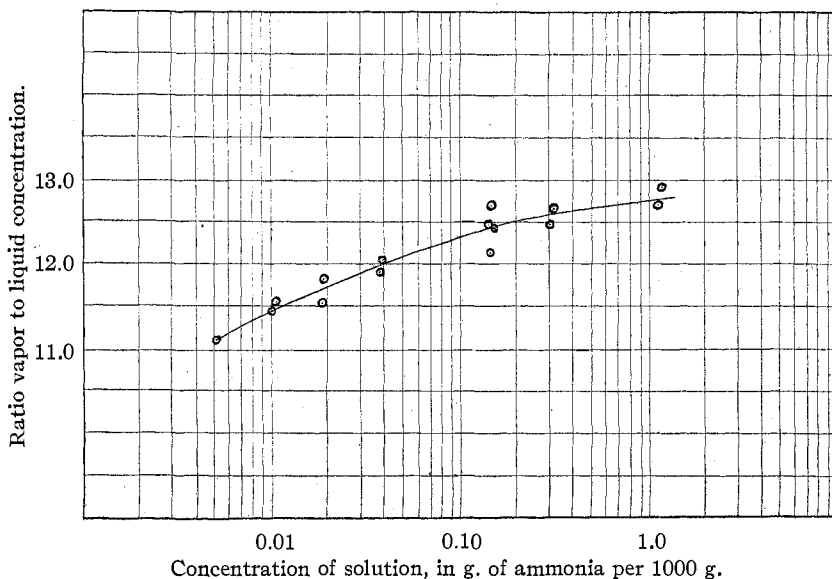


Fig. 1.—Henry's law constant for dil. aqueous ammonia solutions at 100°.

results of these determinations are given in Table I and Fig. 1, where the constant of Henry's law is plotted against the log of the concentration. According to Henry's law, this should be a straight, horizontal line, a being constant at constant temperature, whatever the concentration. It can be seen that this does not hold for ammonia-water mixtures and that a decreases steadily with the concentration, the greatest deviation observed amounting to 15%.

TABLE I

EXPERIMENTAL DATA ON THE DETERMINATION OF THE RATIO, VAPOR TO LIQUID COMPOSITION, OF AMMONIA SOLUTIONS

W_0	W_1	x_0	x_1	x	$1-n$	a	A
1006.4	972.2	1.510	1.001	1.256	0.987	12.92	13.1
1003.7	968.4	1.510	0.992	1.251	0.987	12.72	12.9
1006.0	965.1	0.7835	0.4862	0.633	0.981	12.67	12.9
1005.3	963.9	0.735	0.4767	0.630	0.981	12.81	13.05
1009.5	963.5	0.7835	0.4582	0.621	0.981	12.50	12.9
1010.1	961.6	0.3884	0.2212	0.305	0.973	12.44	12.8
1001.6	958.5	0.1895	0.1146	0.152	0.963	12.44	12.95
999.8	948.6	0.1895	0.1056	0.148	0.963	12.13	12.65
1004.8	949.6	0.1895	0.0978	0.144	0.963	12.70	13.2
1005.1	945.0	0.1895	0.0934	0.142	0.961	12.47	13.0
1004.2	960.5	0.0479	0.0293	0.336	0.926	12.06	13.0
1002.1	951.0	0.0479	0.0271	0.0375	0.925	11.91	12.9

1005.6	958.9	0.0238	0.0142	0.0190	0.896	11.83	13.2
1005.8	957.7	0.0238	0.0142	0.0190	0.896	11.54	12.9
1020.9	979.2	0.0130	0.00836	0.0107	0.864	11.53	13.35
1004.8	949.9	0.0130	0.00723	0.0101	0.861	11.43	13.3
1004.4	947.5	0.00578	0.00335	0.0046	0.800	11.05	13.6

W_0 is the initial weight of solutions, in g.; W_1 , the final weight of same; x_0 , the initial concentration, in g. of ammonia per kg.; x_1 , the final concentration of same; x_{av} , the average concentration; $1-n$, the fraction of undissociated ammonia = $(NH_3)/x_{av}$; a , the observed value of the ratio vapor to liquid composition, and A , the calculated value of the ratio, vapor composition to true (NH_3) concentration in liquid.

Discussion

Henry's law, being a perfect-solution law, must be followed more closely as the pressure of the gas and the concentration of the solute approach zero; but, from a molecular standpoint, it relates to the distribution of some definite kind of molecule between the gas and the liquid phase. Hence, in application of it, the same chemical substance in the 2 phases

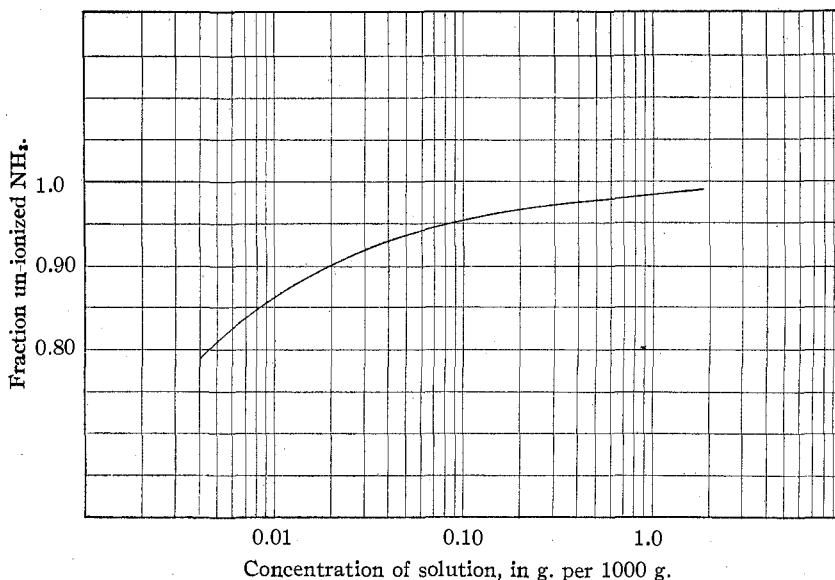
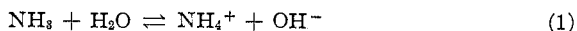


Fig. 2.—Fraction un-ionized ammonia in aqueous ammonia solutions at 100°.

must be considered. The chemical properties and conductivity of aqueous ammonia solutions show that ammonia when dissolved in water undergoes dissociation.



Thus, only the concentration of that part of the dissolved ammonia which is not dissociated must be proportional to the ammonia concentration in the vapor phase.

In order to determine whether the electrolytic dissociation of aqueous ammonia solution, though very small, was large enough to account for the observed deviation from Henry's law, we calculated the percentage of unionized ammonia in terms of the total ammonia concentration, over the range of concentration investigated. Calling m the total ammonia concentration in mole/liter, (NH_3) the concentration of undissociated ammonia, (NH_4) the concentration of dissociated ammonia, and $n = (\text{NH}_4)/m$ the fraction dissociated, and taking account of the hydroxyl and hydrogen ions in the solution due to the dissociation of water, we find $(\text{NH}_4)(\text{OH}) = k_1(\text{NH}_3)$; $(\text{H})(\text{OH}) = k_2$; $(\text{NH}_3) + (\text{NH}_4) = m$; and $(\text{NH}_4) = mn$.

Solving for m in terms of n ;

$$m = k_1 \frac{1-n}{n^2} - \frac{k_2}{k_1} \frac{1}{1-n} \quad (2)$$

k_1 , the ionization constant of ammonia at 100° , is given¹ as, $k_1 = 1.35 (10^{-5})$; k_2 , the concentration product of water,² = $48 (10^{-14})$.

From Equation 2 we were able to determine the fraction of undissociated ammonia, over the concentration range employed. The results are given in Table I and Fig. 2, where the fraction of undissociated ammonia, $(1-n)$, is plotted against the total ammonia concentration.

Verification

Calling "A" the true constant of Henry's law, which must apply to the undissociated fraction, we have: $A = \frac{C}{(\text{NH}_3)} = \frac{C}{c(1-n)}$. On the other hand, on applying our experimentally determined value of a to the total ammonia concentration, $a = C/c$, we find

$$A = a/(1-n) \quad (3)$$

The values of A thus calculated are given in Table I. It can be seen that this gives for A an average value of 13.04, with deviation not exceeding 3%, except at the lowest concentration investigated (0.005 g. of ammonia per liter), where the accuracy of the experimental results may be doubtful.

Conclusions

1. These results confirm our first assumption that the apparent deviation from Henry's law is due to the electrolytic dissociation of aqueous ammonia solutions.

2. A further consequence of this deviation is that for an aqueous ammonia solution sufficiently diluted, the apparent constant of Henry's law will be $a = 1$. Such a solution, having the same ammonia concentration in the liquid and in the vapor phase, must distil without variation of concentration and correspond to a maximum boiling-point mixture. Its concentration, calculated from Equations 2 and 3, taking $A = 13.04$ and

¹ Goldschmidt, *Z. anorg. Chem.*, **28**, 97 (1901).

² *Z. physik. Chem.*, **73**, 1 (1910).

$a = 1$ gives, $1 - n = 0.0767$; $m = 5.9(10^{-7})$; $x = 0.000010$ g. of ammonia per liter.

The verification of this latter conclusion would be somewhat difficult, the slightest increase in hydroxyl-ion concentration due to any impurity resulting in a large decrease in the dissociation of ammonia, and in an increase of the observed value of a ; but this would show that the distillation curve of ammonia solutions must be similar to those of the other gases which are ionized in aqueous solutions, such as hydrochloric and hydrobromic acids; the only difference being that in the case of ammonia, which is a weaker electrolyte, the constant-boiling-point mixture corresponds to a much lower concentration than in the case of a strong electrolyte.

Experimental Part

The method generally used for the determination of the partial pressure of a gas is to measure the total pressure and the vapor concentration. The vapor concentration being too low in this case, we used the distillation method, derived from Rayleigh's equation³ of distillation.

Let us consider a number, M , of moles of the ammonia-water mixture in which the fraction of ammonia is c . After a differential amount, dM , according to Henry's law, has been distilled the concentration of the distillate will be ac . Calling dc the variation of concentration of the liquid due to distillation, we find $Mc = (M - dM)(c - dc) + ac(dM)$. Neglecting the second order differentials, $\frac{dM}{m} = \frac{1}{a-1} \times \frac{dc}{c}$. Assuming that Henry's law holds between narrow limits of concentration, and integrating between such limits

$$\ln \frac{M_0}{M_1} = \frac{1}{a-1} \ln \frac{c_0}{c_1} \quad (4)$$

A simple calculation shows that even in the most concentrated solutions the values of the Henry's law ratio, expressed in mole fractions, differ by less than 0.1% from those expressed in grams of ammonia per 1000 g. of solution, and in the weaker solutions the difference is, of course, still smaller. In view of this close agreement, the concentration of ammonia in g. per kg. and the total weight of the solution are substituted here for the mole fraction of ammonia and the total number of moles, and our formula becomes

$$\ln \frac{W_0}{W_1} = \frac{1}{a-1} \ln \frac{x_0}{x_1} \quad (5)$$

This gives

$$a = 1 + \frac{\log W_0 - \log W_1}{\log x_0 - \log x_1} \quad (6)$$

in which x_0 and x_1 are the concentration of ammonia in g. per kg. of solution and W_0 and W_1 the total weight of the solution, before and after distillation.

³ Rayleigh, *Phil. Mag.*, [6] 4, 531 (1902).

Material.—The solutions were made up with conductivity water and an ammonia solution redistilled over sodium hydroxide.

Method.—The distillation equation applies to a simple distillation where the vapor leaving the liquid is condensed as distillate without allowing any further redistillation. Therefore, it was necessary to superheat the vapor leaving the surface of the boiling liquid by enclosing the distilling flask in a sheet iron chimney, with a sheet of asbestos across the top. The flames of the burner surrounded the flask, and the temperature of the gas around it was from 180° to 190°, showing that the vapors leaving the liquid were superheated. The flask, carefully dried, was filled through a tube leading to the bottom so that no liquid was on the neck. Where the initial concentration was greater than 0.1 g. per liter, the final concentration was obtained by titrating the residual solution. Where the initial concentration was too low to be determined by titration, the initial solution was made by diluting a solution of known strength. The final concentration was calculated from the amount of ammonia caught in the distillate.

Summary

1. The ratio of vapor to liquid composition has been determined for ammonia-water solutions at the boiling point for concentrations of 0.005 to 1.25 g. of ammonia per liter.

2. A deviation from Henry's law has been observed which might be attributed to the electrolytic dissociation of ammonia.

3. It has been shown that there must exist a maximum boiling point for the system, ammonia-water, the concentration of which is 0.000010 g. of ammonia per liter, and that the distillation curve of this system must be similar to that of hydrochloric and hydrobromic acid solutions, the only difference being that, on account of the high dissociation of the acids, the maximum boiling point of their solutions corresponds to a much higher concentration than in the case of ammonia where the ionization is very small.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE INFLUENCE OF TEMPERATURE, PRESSURE AND SUPPORTING MATERIAL FOR THE CATALYST ON THE ADSORPTION OF GASES BY NICKEL

BY ALFRED WILLIAM GAUGER AND HUGH S. TAYLOR

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The importance of the determination of the adsorptive power of catalytic materials for various reaction processes has previously been emphasized and the results accruing from a preliminary experimental investigation of a number of metallic hydrogenation catalysts have already been published by Taylor and Burns.¹ The results suggested that the adsorption obtained with a given catalyst might be largely dependent on the method of prepara-

¹ (a) Taylor, *J. Ind. Eng. Chem.*, **13**, 75 (1921). (b) Taylor and Burns, *This Journal*, **43**, 1277 (1921).