

Separation of the Nitrogen Isotopes by the Exchange Reaction between Ammonia and Solutions of Ammonium Nitrate

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Separation of the Nitrogen Isotopes by the Exchange Reaction between Ammonia and Solutions of Ammonium Nitrate*

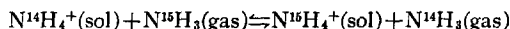
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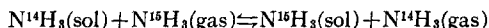
The fractionation factor for the exchange reaction between ammonia and ammonium nitrate was determined as a function of the dissolved ammonia content. It was found that for a stock solution containing 59.3–59.6 percent ammonium nitrate

$$\alpha = -0.029M + 1.034,$$

where α is the fractionation factor at 25°C and M the fraction (Moles NH_3)/(Moles NH_3 + Moles NH_4NO_3), in solution. From these data, the equilibrium constant for the exchange reaction



was calculated to be 1.034, while that for the reaction



was found to be 1.005. Vapor pressure and density data were determined for the ammonia-ammonium nitrate solutions as a function of the ammonia concentration.

INTRODUCTION

UREY and co-workers^{3–6} have studied the exchange reaction as a means of concentrating the nitrogen isotopes. They have shown that high concentrations of N^{15} can be obtained by the use of this exchange reaction in a cascade of packed columns operating as a counter-current system. The data obtained indicate that

the fractionation factor

$$\alpha = \left[\frac{\text{N}^{14}}{\text{N}^{15}} \right]_{\text{gas}} / \left[\frac{\text{N}^{14}}{\text{N}^{15}} \right]_{\text{sol}}$$

is larger the greater the concentration of NH_4^+ ion in solution. Thus the fractionation factor obtained by using a 60 percent ammonium nitrate solution in water with a total pressure over the solution of 180 mm of Hg was about 1.021 as compared to a value of only 1.012 for a 15 percent ammonium sulfate solution with a pressure of 200 mm of Hg. Additional data taken from the paper by Urey, Huffman, Thode, and Fox⁴ are summarized in Table I. It is for this reason, and also because the more concentrated the NH_4^+ solution the smaller the fractionating columns need be for a given throughput of NH_4^+ , that it was found advisable to use ammonium nitrate as the ammonium salt. Ammonium nitrate has a solubility of about 60 percent by weight at room temperature.

For proper design of a plant for the separation of the nitrogen isotopes by means of the exchange between ammonia and ammonium nitrate, it is necessary to know the fractionation factor as accurately as possible. This is so because the size of the plant, and therefore its cost, and perhaps feasibility, is inversely proportional to $(\alpha - 1)^2$. Three different values have been re-

TABLE I. Effect of NH_4^+ concentration upon the fractionation factor.

| Weight % $(\text{NH}_4)_2\text{SO}_4$ in stock solution | Fractionation factor (α) |
|--|--------------------------------------|
| 0 | 1.006 |
| 5 | 1.0067 |
| 14 | 1.012 |
| 31 | 1.021 |
| 34 | 1.022 |

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³ H. C. Urey and A. H. W. Aten, Jr., *Phys. Rev.* **50**, 575 (1936).

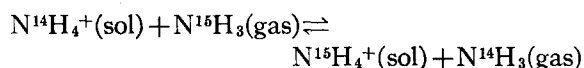
⁴ H. C. Urey, J. R. Huffman, H. G. Thode, and M. Fox, *J. Chem. Phys.* **5**, 856 (1937).

⁵ H. G. Thode, J. E. Gorham, and H. C. Urey, *J. Chem. Phys.* **6**, 296 (1938).

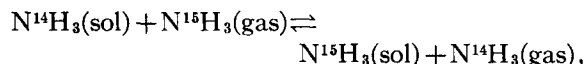
⁶ H. G. Thode and H. C. Urey, *J. Chem. Phys.* **7**, 34 (1939).

ported for the fractionation factor for the exchange between ammonia and ammonium ion. Urey and Aten³ reported a value of 1.027 using a Rayleigh distillation method with a solution of ammonium chloride. Urey, Huffman, Thode, and Fox⁴ obtained a value of 1.021 as calculated from the operational data obtained for a counter-current system in a glass column using a 60 weight percent ammonium nitrate solution and also using a 31–34 weight percent ammonium sulfate solution. Recently, Thode, Graham, and Ziegler⁷ published a value of 1.031 ± 0.003 for α at 25°C for the exchange reaction between ammonia and ammonium nitrate.

It must be realized that in a solution containing both ammonia and ammonium ion in equilibrium with a gas phase containing ammonia, at least two equilibria are involved; namely,



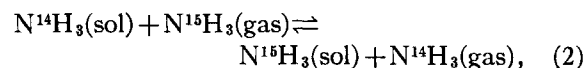
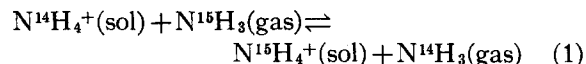
and



where $\text{NH}_3(\text{sol})$ refers to all compounds that the dissolved ammonia may form in solution. Thus the observed fractionation factor is probably a function of the equilibrium constants for both reactions. Its dependence upon these constants can be obtained mathematically if one makes several simple assumptions. This is done in the following section.

MATHEMATICAL CONSIDERATIONS

It is assumed that the following isotopic equilibria are involved in the liquid-vapor system H_2O , NH_3 , and NH_4NO_3 at 25°C:



where $\text{NH}_3(\text{sol})$ refers to all molecular species which the dissolved ammonia may form in solution. Designating the concentrations by the

following symbols:

$$\begin{aligned} A &= (\text{N}^{14}\text{H}_4^+)_{\text{sol}}, & B &= (\text{N}^{15}\text{H}_3)_{\text{gas}}, \\ C &= (\text{N}^{15}\text{H}_4^+)_{\text{sol}}, & D &= (\text{N}^{14}\text{H}_3)_{\text{gas}}, \\ E &= (\text{N}^{14}\text{H}_3)_{\text{sol}}, & \text{and } F &= (\text{N}^{15}\text{H}_3)_{\text{sol}}, \end{aligned}$$

then

$$K_1 = CD/AB \quad (3)$$

and

$$K_2 = FD/EB. \quad (4)$$

By definition,

$$\alpha = \frac{D}{B} \bigg/ \frac{A+E}{C+F}, \quad (5)$$

where α is the fractionation factor. It is easily shown from these equations that

$$\alpha = K_1 - (K_1 - K_2)E/A + E.$$

Defining M as the ratio of moles of ammonia in solution to moles of ammonia plus moles of ammonium ion in solution,

$$M = E + F/E + F + A + C.$$

In the experiments to be described $F \ll E$ and $C \ll A$, since both $E/E + F$ and $C/A + C$ are approximately 0.0038. Consequently, $M = E/E + A$, and

$$\alpha = M(K_2 - K_1) + K_1 \quad (6)$$

or

$$\alpha - 1 = M(K_2 - K_1) + (K_1 - 1). \quad (6')$$

If K_2 and K_1 are constant, then a plot of $\alpha - 1$ vs. M , or α vs. M , should give a straight line. This assumption presupposes that

(a) The presence of ammonium nitrate has no effect on the isotopic equilibrium between $\text{NH}_3(\text{sol})$ and $\text{NH}_3(\text{gas})$, i.e., K_2 is not a function of the ammonium nitrate concentration of the solution.

(b) The amount of water present as a solvent does not affect either equilibrium constant.

DETERMINATION OF THE FRACTIONATION FACTOR

Aliquots of stock solutions containing approximately 60 weight percent ammonium nitrate were equilibrated with gaseous ammonia at various pressures at 25°C. A sample of the vapor phase was taken under its own pressure by means of a mercury displacement device. A sample of the liquid phase was then taken by means of a syphon. Alkali was added to the

⁷ H. G. Thode, R. L. Graham, and J. A. Ziegler, Can. J. Research **23B**, 40 (1945).

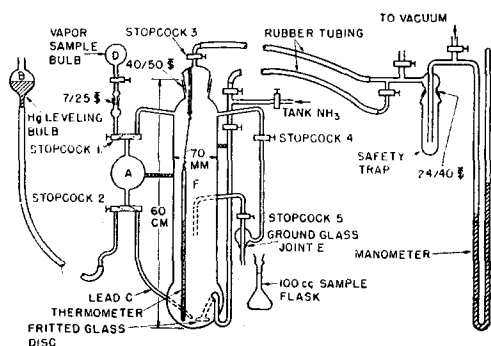


FIG. 1. Apparatus for the determination of the fractionation factor.

liquid sample and the liberated ammonia was completely removed. This ammonia, as well as that obtained as a vapor sample, was oxidized over copper oxide to nitrogen. Since in all cases conversions were complete, the isotopic content of a nitrogen sample was considered to represent that of the ammonia sample from which it was formed. The nitrogen samples were then analyzed on a Nier 60° sector field mass spectrometer for isotopic content. The $N^{14}N^{15}/N^{14}N^{14}$ ratio for the nitrogen from the ammonia of the liquid sample was compared directly to the same ratio for the nitrogen of the ammonia from the vapor sample. Thus the mass spectrometer readings gave α (the fractionation factor) directly.

The apparatus used for the equilibration is shown schematically in Fig. 1. Actually two equilibration flasks (F in Fig. 1) were used, one for equilibration with ammonia at relatively low pressures (~ 150 mm) and the other for the equilibration experiments with ammonia gas at higher pressures. The two apparatus were similar, differing only in length and in the relative position of the liquid syphon, with a larger vapor phase in the apparatus used for the lower pressures.

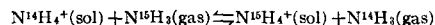
An aliquot of stock solution containing approximately 60 weight percent ammonium nitrate was poured into the well-dried equilibration flask. The amount of solution used for an experiment was governed primarily by the pressure of ammonia at which the equilibration was to be done. The volume of the solution was not at all critical except that, since the volume increased as ammonia dissolved in the solution during the equilibration, care had to be taken to assure that

an adequate size vapor sample could be obtained. The greater the initial liquid volume and the greater the final pressure of ammonia, the smaller the available vapor phase.

After addition of the solution, the system was connected as shown and evacuated. Care was taken not to boil off too much water from the solution during evacuation. It might be stated at this point that all of the stopcocks and ground glass joints were lubricated with Lubriscal grease. After evacuation, ammonia was passed into the solution *via* the fritted glass disk. In some experiments the ammonia gas was passed into the solution rapidly, whereas in others the rate of addition of ammonia was very slow. When the predetermined total pressure (sum of the partial pressures of both the ammonia and water) was reached, as indicated on the mercury manometer, the system was isolated from the tank of ammonia and then pumped upon for a few moments. This was done in order to assure the absence of all air. Then a little ammonia was added to readjust the pressure to the proper value at 25°C. During the addition of the ammonia, an attempt was made to maintain the temperature of the solution at 25°C. This was not too difficult except during those experiments in which ammonia was added rapidly. But in all experiments, after the proper pressure was attained at 25°C, the equilibration flask was submerged in a thermostat maintained at $25.00 \pm 0.01^\circ\text{C}$. Periodically the flask was removed from the thermostat and well shaken, care being taken to mix the liquid and vapor phases efficiently. This mixing assured isotopic exchange equilibrium at 25.0°C.

To understand best how a gas sample was taken, reference should be made to Fig. 1. Bulb A was well dried and filled completely with mercury by means of the leveling bulb B . Stopcock 1 was then turned to connect the mercury-filled bulb A to the vapor in the equilibration flask, F , proper. Following this, stopcock 2 was turned connecting bulb A with lead C . As the mercury flowed into the bottom of the equilibration flask it displaced solution which in turn forced an equal volume of vapor into the bulb A without any pressure changes occurring. Stopcocks 1 and 2 were then turned so that mercury could flow into A from the leveling bulb, and in

TABLE II. Fractionation factors for the exchange.



| Solution | Exp. No. | Composition of solution in wt. % | | | Moles NH_3 Moles NH_3 + Moles NH_4NO_3 | Obs.** | Fractionation factor | |
|---------------|----------|----------------------------------|----------------------|--------------------------|---|-------------------|----------------------|--------|
| | | NH_3 | H_2O | NH_4NO_3 | | | Calc. | Diff. |
| C-1 | 20 | 7.3 | 37.8 | 54.9 | 0.385 | 1.023 \pm 0.004 | 1.023 | 0.000 |
| C-2 | 22 | 8.2 | 37.4 | 54.4 | 0.414 | 1.020 \pm 0.004 | 1.022 | +0.002 |
| D-1 | 15 | 9.0 | 38.4 | 52.6 | 0.446 | 1.017 \pm 0.004 | 1.021 | +0.004 |
| B-2 | 5 | 11.5 | 35.8 | 52.7 | 0.507 | 1.026 \pm 0.003 | 1.019 | -0.007 |
| D-3 | 12 | 13.0 | 36.7 | 50.3 | 0.550 | 1.026 \pm 0.005 | 1.018 | -0.008 |
| D-4 | 16 | 15.3 | 35.7 | 48.9 | 0.596 | 1.015 \pm 0.002 | 1.017 | +0.002 |
| B-4 | 10 | 16.0 | 34.0 | 50.1 | 0.599 | 1.018 \pm 0.005 | 1.017 | -0.001 |
| B-5 | 6 | 16.8 | 33.7 | 49.6 | 0.615 | 1.011 \pm 0.005 | 1.016 | +0.005 |
| C-3 | 19 | 17.8 | 33.5 | 48.6 | 0.633 | 1.013 \pm 0.004 | 1.016 | +0.003 |
| D-5 | 13 | 17.8 | 34.7 | 47.5 | 0.639 | 1.020 \pm 0.002 | 1.015 | -0.005 |
| E-1 | 3 | 21.9 | 32.4 | 45.7 | 0.693 | 1.010 \pm 0.003 | 1.014 | +0.004 |
| B-6 | 9 | 25.0 | 30.4 | 44.7 | 0.725 | 1.008 \pm 0.005 | 1.013 | +0.005 |
| D-7 | 14 | 25.6 | 31.4 | 43.0 | 0.737 | 1.011 \pm 0.003 | 1.013 | +0.002 |
| Thode | | * | * | * | 0.058 | 1.031 \pm 0.003 | 1.032 | +0.001 |
| Urey and Aten | | — | — | — | 1.000 | 1.006 | 1.005 | -0.001 |

* This equilibrium mixture contained 0.195 moles of NH_4NO_3 , 0.578 moles of H_2O , and 0.012 moles of NH_3 . The NH_3 was introduced by the addition of 0.012 moles of NaOH to the NH_4NO_3 solution in an evacuated 100 cc flask.

** The ± 0.004 , etc., give the spectrometer precision (or, in some cases, an estimate of the accuracy of the spectrometer analyses).

this manner the vapor was forced into sample bulb *D*. The stopcocks were then turned so that another vapor sample was taken. This sample was also forced into the sample bulb. This procedure was continued until a vapor sample of about 200 cc at one atmosphere pressure was obtained. Air was then admitted into the vapor space *via* stopcock 3, and a liquid sample taken through the syphon by opening stopcocks 4 and 5. The liquid sample was taken directly into a 100 cc volumetric flask, joint *E* being a male ground glass joint fitting all standard 100 cc volumetric flasks. Since the volumetric flasks used had been calibrated, the density of the solution was obtained quite easily. After the density was determined, several aliquots of solution were removed from the volumetric flask and analyzed by titration for free ammonia. Knowing the composition of the stock solution, only this analysis was necessary to permit calculation of the composition of all components in the final solution. In some cases these calculated values were checked by a Kjeldahl analysis for total ammonia and a Karl Fischer analysis for water. Incidentally, the stock solutions were analyzed by means of the Kjeldahl method for the ammonium nitrate content and usually also for the water content by means of the Karl Fischer reagent. The analytical methods are discussed later in this paper.

Another aliquot of the final solution was then taken from the volumetric flask and *all* of the ammonia liberated. This ammonia was converted

to nitrogen by circulating over hot copper oxide. The vapor sample was then frozen down with liquid nitrogen and any air present was removed by pumping. Actually very little air was found in these samples. In one case in which a large amount of air was present, the sample was rejected. After pumping, if any was necessary, the vapor sample was admitted into the conversion apparatus and oxidized to nitrogen. Thus, for any one equilibration experiment there were two nitrogen gas samples, one corresponding to the vapor phase and one to the liquid phase. During the conversions, precautions were taken to minimize errors that might arise from either dilution or fractionation.

The nitrogen gas samples were analyzed on a Nier mass spectrometer. The vapor phase sample was compared with the corresponding liquid phase sample. First, the isotopic ratio of one sample was obtained by measuring galvanometer deflections caused by the $(\text{N}^{14}\text{N}^{14})^+$ and $(\text{N}^{14}\text{N}^{15})^+$ ion beams. This was then done for the second sample and then again for the first. This procedure was followed two or more times, giving a number of isotopic ratios obtained alternately

TABLE III. Composition of stock solution.

| Solution | Weight percent | |
|----------|--------------------------|----------------------|
| | NH_4NO_3 | H_2O |
| <i>B</i> | 59.6 | 40.4 |
| <i>C</i> | 59.2 | 40.8 |
| <i>D</i> | 57.8 | 42.2 |
| <i>E</i> | 58.5 | 41.5 |

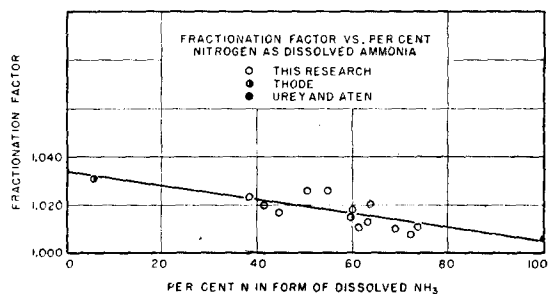


FIG. 2.

for the corresponding vapor and liquid samples. The fractionation factor, α , was obtained directly from these ratios. Thus for experiment No. 20, the following analyses were obtained:

| Sample | No. of readings | $R \propto \frac{\text{Mass 28 intensity}}{\text{Mass 29 intensity}}$ | $\frac{R_{\text{vapor}}}{R_{\text{solution}}} = \alpha$ |
|----------|-----------------|---|---|
| Vapor | 12 | 1.136 | |
| Solution | 9 | 1.111 | 1.023 |
| Vapor | 10 | 1.141 | 1.027 |
| Solution | 9 | 1.108 | 1.030 |
| Vapor | 11 | 1.135 | 1.024 |
| Solution | 9 | 1.119 | 1.014 |
| Vapor | 9 | 1.142 | 1.021 |
| average | | | 1.023 ± 0.004 |

It is obvious that the use of different shunts for the 28 and 29 mass peaks did not introduce any error into α . In analyzing samples from experiments 12 to 22 (Table II), the background contributed about 2 percent to the intensities of the 28 and 29 peaks. This introduced a negligible error in α because of the cancellation of errors in taking a ratio of ratios. The back-

ground was slightly worse for the analyses of the samples from experiments 3, 5, 6, 9, and 10 (Table II). Samples 3 and 5 were analyzed by comparing the intensity of the mass 14 and 15 peaks as well as the 28 and 29 peaks. The agreement was just within experimental error. In every case the gas samples were analyzed qualitatively for significant quantities of oxygen. None was found.

The experimental results are summarized in Table II.

The first column indicates the stock solution used. The compositions of the stock solutions are given in Table III.

The second column gives the experiment number and the third, fourth, and fifth show the composition of the final solution. The sixth column gives the fraction of the total nitrogen ($\text{NH}_3 + \text{NH}_4^+$) in solution that is present in the form of ammonia. This corresponds to M in Eq. (6). The next column lists the observed fractionation factors. These are plotted as a function of M in Fig. 2. Applying Eq. (6),

$$\alpha = M(K_2 - K_1) + K_1,$$

to the data and solving for K_1 and $K_2 - K_1$ by means of the method of least squares, the equation

$$\alpha = -0.029M + 1.034 \quad (7)$$

is obtained as representing the experimental data. Column 8 gives the values for α as calculated from this equation. The differences between the observed and calculated values for α are given in the last column. These differences indicate a random scattering.

The data in Table II and Fig. 2 include the value for α as observed by Thode *et al.*^{7,8} for a solution with $M = 0.058$. The equilibrium mixture contained 0.195 moles of ammonium nitrate, 0.578 moles of water, and 0.012 moles of ammonia. The latter was introduced by the addition of 0.012 moles of sodium hydroxide to the ammonium nitrate solution in an evacuated 100 cc flask. After 24 hours at 25°C, a sample was obtained by the rapid turning of a stopcock. The table and figure also include the value for the frac-

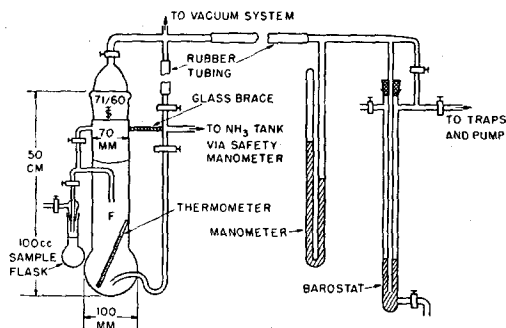


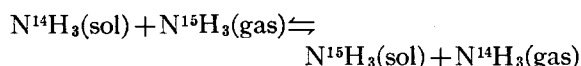
FIG. 3. Apparatus for the determination of the densities and vapor pressures of solutions of ammonia in water.

⁸ H. G. Thode (private communication, May 16, 1945).

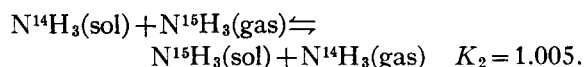
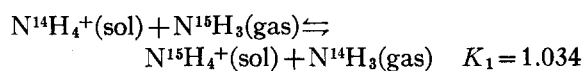
TABLE IV. Vapor pressures and densities of ammoniacal solutions of ammonium nitrate.

| Solution | Exp. No. | Density g/cc | Total pressure of sol'n mm Hg | NH ₃ | Composition of solution in Wt. % | | | | |
|----------|----------|-----------------|---|-----------------|----------------------------------|--|-----------------|------------------|---------------------------------|
| | | | | | by analysis | from dilution data using NH ₃ analysis | | | |
| | | | | | H ₂ O | NH ₄ NO ₃ | NH ₃ | H ₂ O | NH ₄ NO ₃ |
| Stock A | | 1.2748 | — | | 40.6 | 59.1 | | 40.7 | 59.3 |
| A-1 | A | 1.2107 | 110 | 5.5 | 38.2 | 56.0 | (5.5) | 38.4 | 56.1 |
| A-2 | B | 1.2044 | 113 | 6.1 | 38.4 | 55.7 | (6.1) | 38.2 | 55.6 |
| A-3 | C | 1.1367 | 260 | 12.8 | 35.2 | 51.2 | (12.8) | 35.4 | 51.6 |
| A-4 | D | 1.1151 | 347 | 15.2 | — | 50.5 | (15.2) | 34.5 | 50.6 |
| A-5 | E | 1.0692 | 538 | 20.3 | — | 47.4 | (20.3) | 32.5 | 47.2 |
| A-6 | F | 1.0434 | 730 | 23.6 | — | 45.5 | (23.6) | 31.1 | 45.3 |
| A-7 | G | 1.0335 | 762 | 24.1 | 30.9 | 45.3 | (24.1) | 30.9 | 45.0 |
| Stock B | | 1.2748 | — | | — | 59.6 | | 40.4 | (59.6) |
| B-1 | 8 | 1.1794 | — | 8.6 | — | — | (8.6) | 36.9 | 54.5 |
| B-2 | 5 | 1.1493 | — | 11.5 | — | — | (11.5) | 35.8 | 52.7 |
| B-3 | 7 | 1.1202 | — | 14.5 | — | — | (14.5) | 34.5 | 51.0 |
| B-4 | 10 | 1.1070 | — | 16.0 | — | — | (16.0) | 33.9 | 50.1 |
| B-5 | 6 | 1.1002 | — | 16.8 | — | — | (16.8) | 33.6 | 49.6 |
| B-6 | 9 | 1.0311 | — | 25.0 | — | — | (25.0) | 30.3 | 44.7 |
| Stock C | | 1.2740 | 15.5 | | — | 59.2 | | 40.8 | (59.2) |
| C-1 | 20 | 1.1927 | 133 | 7.3 | — | — | (7.3) | 37.8 | 54.9 |
| C-2 | 22 | 1.1838 | 147 | 8.2 | — | — | (8.2) | 37.5 | 54.4 |
| C-3 | 19 | 1.0897 | 415 | 17.8 | — | — | (17.8) | 33.5 | 48.6 |

tiation factor for the exchange reaction



as observed by Urey and Aten.^{3,4} By comparing Eqs. (6) and (7), one obtains the equilibrium constants for the two ammonia exchange reactions



DENSITIES AND VAPOR PRESSURES OF THE AMMONIACAL SOLUTIONS

In addition to fractionation factors, the densities and vapor pressures at 25°C of various solutions containing both ammonium nitrate and ammonia were obtained. The apparatus used for these experiments is shown in Fig. 3. As in the determination of the fractionation factor, an appropriate amount of stock solution was placed into vessel *F* and saturated with ammonia gas. The saturation pressure was fixed by adjustment of the mercury barostat and measured on the mercury manometer. After saturation with ammonia, the liquid level was well above the top of the syphon. As in the case of the fractionation experiments, after saturation was attained, the

entire system was evacuated for a few moments and then a little ammonia was added to adjust the pressure to the desired value. This evacuation was necessary because tank ammonia was found to contain some inert gases.

The density of the solution was determined using a calibrated 100 cc volumetric flask. The saturated solutions were also analyzed for their composition. In all cases the free ammonia was determined directly by adding excess standardized hydrochloric acid from a weight-burette to

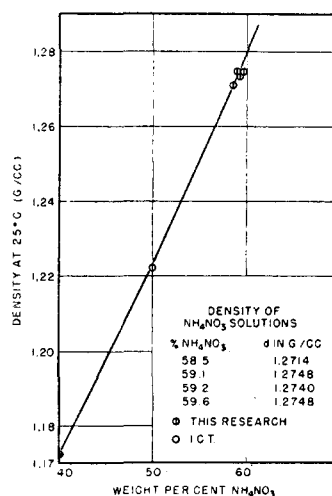


FIG. 4.

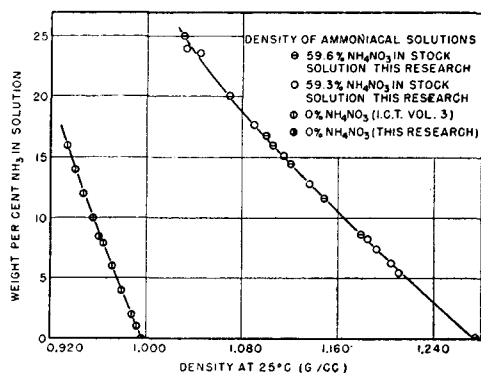


FIG. 5.

a weighed aliquot of the solution and then back-titrating with standard sodium hydroxide solution using methyl red as indicator. Since the composition of the stock solution was known, this one analysis permitted calculation of the composition of the final solution. In a number of experiments, the calculation was checked by a direct determination of the amounts of ammonium nitrate and water in the solution. The agreement was very good.

The ammonium nitrate content was found by determining the total amount of ammonia in solution by means of a modified Kjeldahl analysis similar to that described by Rieman, Neuss, and Naiman.⁹ The difference between the total ammonia and free ammonia content of the solution permitted calculation of the weight percent of ammonium nitrate. The water content of the solutions was determined by a Karl Fischer titration. A 2 gram sample of the solution to be analyzed was diluted to 100 cc with dry dioxane. After mixing well, a 2–10 cc aliquot was titrated with the Karl Fischer reagent.

The experimental data are summarized in

⁹ W. Rieman, J. D. Neuss, and B. Naiman, *Quantitative Analysis* (McGraw-Hill Book Company, Inc., New York, 1942).

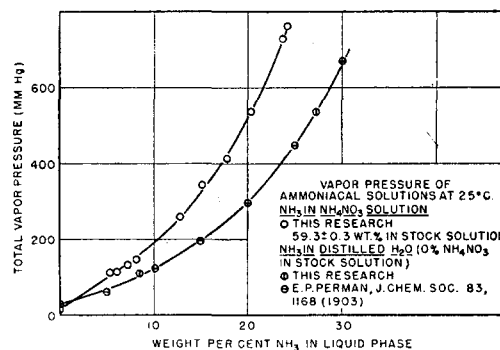


FIG. 6.

Table IV and Figs. 4–6. The headings on the various columns of the table are self-explanatory. The accuracy of the method used in this work was checked by two experiments using only ammonia and water. The agreement with the values in the literature may be seen from the data in Figs. 5 and 6 and Table V. This agree-

TABLE V. Vapor pressures and densities of ammonia and water solutions.

| Weight % NH ₃ | Density g/cc | | Total vapor pressure mm Hg at 25°C | |
|-----------------------------|--------------|---------------|---------------------------------------|--|
| | Observed | I.C.T. Vol. 3 | Observed | Perman. J. Chem. Soc. 83, 1168 (1903) |
| 8.46 | 0.9611 | 0.962 | 112 | 103 |
| 27.31 | 0.8969 | — | 540 | 538 |

ment is within the experimental errors involved in this research and in the work in the literature.

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