*The Nitrogen Isotopic Equilibrium between Ammonia and Ammonium Ion**

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(Received September 21, 1959)

A number of studies have been reported on the enrichment of ^{15}N with the isotopic exchange reaction between ammonia gas and aqueous ammonium ion. The fractionation factor for this exchange reaction has been reported[1-3]. A separation of nitrogen isotopes has been made by the use of cation exchange resins[4]. One of the equilibria involved in the separation process is the equilibrium of nitrogen isotopes between ammonia and ammonium ion in aqueous solution. This paper is a report on the investigation of the equilibrium by the use of cation exchanger. The equilibrium constants and enthalpy of the reaction have been measured. It is found that the use of ion exchanger will be useful to study such an equilibrium existing in aqueous solution. Further, the measurement of the equilibrium of nitrogen isotopes between ammonia gas and ammonium ion of its solid chloride has been carried out and is described in this paper.

In an aqueous solution of ammonia and ammonium ion at isotopic equilibrium with the ammonium ion adsorbed on a cation exchange resin, the equilibria involved are described by the equations:

$$^{15}NH_{3(aq)} + {}^{14}NH^{+}_{4(aq)} = {}^{14}NH_{3(aq)} + {}^{15}NH^{+}_{4(aq)} \qquad K_1 \quad (1)$$

$$^{14}NH_4R + {}^{15}NH^{+}_{4(aq)} = {}^{15}NH_4R + {}^{14}NH^{+}_{4(aq)} \qquad K_2 \quad (2)$$

$$^{14}NH_4R + {}^{15}NH_{3(R)} = {}^{15}NH_4R + {}^{14}NH_{3(R)} \qquad (3)$$

$$^{15}NH_{3(aq)} + {}^{14}NH_{3(R)} = {}^{14}NH_{3(aq)} + {}^{15}NH_{3(R)} \qquad (4)$$

where NH_4R represents ammonium ion taken up into the cation exchanger phase by ion-exchange mechanism and $NH_{3(R)}$ ammonia adsorbed on an ion exchange resin. Equilibria 3 and 4 can be neglected in a solution of low pH, while they exist with the solution of high pH. However, the concentration of $NH_{3(R)}$ is small compared to that of NH_4R when the concentration of $NH_{3(aq)}$ is low. The amount of $NH_{3(R)}$ is also smaller than that of $NH_{3(aq)}$ if the volume of the exchanger is smaller than that of the solution. Thus, the fractionation factor between the exchanger and solution phase may not greatly involve the contribution by $NH_{3(R)}$. Further, the equation

$$^{14}NH_4R + {}^{15}NH_{3(aq)} = {}^{15}NH_4R + {}^{14}NH_{3(aq)} \qquad (5)$$

which is the sum of Eqs. 3 and 4, results also from Eqs. 1 and 2. Hence, Eqs. 1 and 2 are enough to represent the equilibria involved in the system of an aqueous solution of ammonia and ammonium ion, and an exchanger of ammonium ion form.

The following quantity can be measured conveniently:

$$\frac{(^{15}N/^{14}N)_{\text{solution}} - (^{15}N/^{14}N)_{\text{exchanger}}}{(^{15}N/^{14}N)_{\text{exchanger}}} = \delta \qquad (6)$$

where $(^{15}N/^{14}N)_{\text{exchanger}}$ and $(^{15}N/^{14}N)_{\text{solution}}$ are the nitrogen isotope ratios in the exchanger and solution phase, respectively. The fractionation factor between the exchanger and solution phase is defined as follows:

$$K = \frac{(^{15}N/^{14}N)_{\text{exchanger}}}{(^{15}N/^{14}N)_{\text{solution}}} = \frac{1}{1+\delta} \qquad (7)$$

This value can be obtained experimentally. Let the following concentrations be represented by the associated symbols:

$$(^{15}NH_{3(aq)}) = a', \quad (^{15}NH^{+}_{4(aq)}) = b', \quad (^{15}NH_4R) = c'$$

$$(^{14}NH_{3(aq)}) = a, \quad (^{14}NH^{+}_{4(aq)}) = b, \quad (^{14}NH_4R) = c$$

Then, the following relationship between K_1, K_2 and K can be readily derived:

$$\frac{1}{K} = \frac{a}{a+b}\left[\frac{1}{K_1K_2} + \frac{b}{aK_2}\right] \qquad (8)$$

The value of $a/(a+b)$ and b/a can be calculated from the dissociation constants of ammonia and water: K_{dis} and K_{w}; if the pH value of the solution is known:

$$\frac{b}{a} \simeq \frac{b+b'}{a+a'} = \frac{K_{\text{dis}}}{K_{\text{w}}}(H^+) \qquad (9)$$

$$\frac{a}{a+b} \simeq \frac{1}{1+\dfrac{K_{\text{dis}}}{K_{\text{w}}}(H^+)} \qquad (10)$$

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* This study has been done in the Chemistry Department of the University of Arkansas, Arkansas, U. S. A.

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It is assumed that $a \simeq a + a'$ and $b \simeq b + b'$ are held since nitrogen with natural isotopic abundance is used and the ^{15}N content is about 0.36%[5]. The numerical value of K_{dis}/K_w is 1.04×10^9 at 30°C[6].

If the pH of the solution phase is less than 5, the concentration of $NH_{3(aq)}$ is negligibly small. Hence,

$$K = K_2 \tag{11}$$

for the low pH. The value of K_1 can be calculated from Eq. 8, using the values of K_2, K and pH value.

If the value of K is measured at high pH, the concentration of ammonium ion is very low: $b \ll a$. Hence, Eq. 8 can be written as

$$K_1 = K/K_2 \tag{12}$$

for the value of K at high pH of the solution. This relation gives approximately the value of K_1. Spedding, Powell and Svec[4] have evaluated the fractionation factor, K, in the above-mentioned condition.

Experimental

The ammonia solution was purified by distillation. The other chemicals were of analytical grade. The cation exchange resin used was Dowex 50, X-8.

The conventional water bath for a constant temperature was used. The temperature was controlled within ±0.2°C at the vicinity of the room temperature. The air bath was used to keep the elevated temperatures constant at 200°C to 275°C within ±2°C.

The mass spectrometer used was a Nier type, 60° sector, double collecter instrument designed to measure small differences in isotopic ratio as described by McKinney et al.[7] and Dole[8]. Measurements were made on the ions of mass 28 and 29 ($^{14}N^{14}N^+$ and $^{15}N^{14}N^+$). The result of each isotopic analysis is estimated to have a precision of ±0.0003 in the quantity of δ.

A solution of ammonium chloride and ammonia was added to the cation exchange resin of the ammonium ion form. This mixture was allowed to stand for ten to twelve hours in the constant temperature bath with shaking and brought to isotopic equilibrium. Then, the solution phase was pipetted and acidified with sulfuric acid solution. The resin was separated from the solution by suction filtration. In each experiment, the solution or resin phase contained one to two milligram equivalents of nitrogen. Ammonium ion was converted to nitrogen gas by the oxidation with sodium hypobromite[9]. The resulting nitrogen gas was purified by repeatedly passing the gas over copper oxide at 800°C and through the liquid air[10]. A set of nitrogen gases from the solution and resin phase was analyzed with a mass spectrometer.

The isotopic equilibrium between gaseous ammonia and solid ammonium chloride was measured. The containing vessel was made of Pyrex glass and had two 200 ml. bulbs (Bulbs A and B). A vacuum stopcock (Stopcock 1) connected Bulbs A and B. On the opposite side of Stopcock 1, Bulb A had a well to insert a thermometer and Bulb B had another vacuum stopcock (Stopcock 2). The silicon grease used in the stopcocks was satisfactory at 200 to 275°C. Water vapor and gaseous ammonia were added, at 20 to 25 mmHg and 200 to 275 mmHg, respectively, to 50 to 100 mg. ammonium chloride in Bulb A and allowed to stand for 13 to 62 hr.

It was difficult to know whether or not isotopic equilibrium had been established. The equilibrium was considered to be established if the equilibrium constant did not increase with a longer period of standing at the same temperature. The vapor pressure of ammonium chloride is 117 mmHg at 275°C and 6 mmHg at 200°C[10]. Extra gaseous ammonia was added to get a large enough sample of gas phase for analysis. Water vapor was added to help isotopic equilibrium to be established[11].

After the establishment of isotopic equilibrium, the gas phase was collected in the evacuated Bulb B through Stopcock 1. The stopcock was turned through the window of the air bath. The vessel was taken out of the air bath and cooled with water. A sufficient amount of sulfuric acid was introduced into Bulb B through Stopcock 2 and gaseous ammonia was collected as ammonium ion in aqueous solution. Bulb A was disconnected and the ammonia gas in it was evacuated and replaced with air. Then, the solid ammonium chloride was dissolved with water.

Experimental Results

The experimental fractionation factors between resin and the solution phase are listed in Table I with the pH values of the solution phases. The value of K_1 is calculated by Eq. 8 using the values of the experimental fractionation

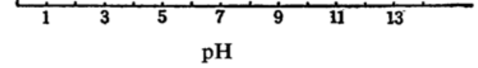

Fig. 1. Fractionation factor and pH.

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TABLE I. EFFECT OF pH OF THE SOLUTION PHASE ON THE FRACTIONATION FACTOR BETWEEN THE RESIN AND SOLUTION PHASE, *K*, AT 30°C

Run	pH	Concentration of solution ($NH_3+NH_4^+$) mol./l.	Fractionation factor *K*
1	11.3	0.496	1.0255
2	11.3	0.496	1.0250
3	11.2	0.196	1.0257
4	11.2	0.196	1.0253
5	10.3	0.196	1.0210
6	10.3	0.196	1.0208
7	9.76	0.496	1.0163
8	9.76	0.496	1.0156
9	9.72	0.496	1.0160
10	9.34	0.196	1.0112
11	9.28	0.516	1.0125
12	8.66	0.516	1.0029
13	7.47	0.196	1.0010
14	7.46	0.196	1.0010
15	4.30	0.483	0.9997
16	2.75	0.196	1.0007
17	2.72	0.196	0.9997
18	2.35	0.196	0.9992
19	2.34	0.196	0.9992
20	1.17	0.516	0.9999

TABLE II. EFFECT OF THE CONCENTRATION OF THE SOLUTION ON THE FRACTIONATION FACTOR BETWEEN RESIN AND SOLUTION PHASE AT 30°C

Run	pH	Concentration of solution ($NH_3+NH_4^+$) mol./l.	Fractionation factor *K*
15	4.30	0.483	0.9997
21	4.40	0.0966	1.0000
22	5.40	0.0097	1.0000
23	basic	3.23	1.0279
24	basic	1.29	1.0269
25	basic	0.515	1.0265
26	basic	0.208	1.0257

" basic " shows that pH value is larger than 11.2.

factor of Run 1 to 4:

$$K_1 = 1.0256 \pm 0.0006 \text{ at } 30°\text{C}$$

The error shown is the average deviation. The fractionation factors of Run 1 to 20 are plotted against their pH values of the solution phase in Fig. 1, on which the calculated line is drawn by Eq. 8 using the K_1 and K_2 obtained.

The effects of the concentration of the solution phase are shown in Table II.

TABLE III. EFFECT OF TEMPERATURE ON THE FRACTIONATION FACTOR BETWEEN RESIN AND SOLUTION PHASE, *K*

T°C	Acidic solution (pH less than 6) ($NH^+_{4(aq)}$)=0.107 M			Basic solution (pH=11.2) ($NH_{3(aq)}$)=0.196 M		
	Run	$\delta \times 1000$	*K*	Run	$\delta \times 1000$	*K*
50	27	0		32	−21.9	
	28	−0.5	1.0002	33	−21.9	1.0224
40	29	0	1.0000	34	−22.3	
				35	−23.1	1.0232
30	*		0.9997	36	−24.7	
				37	−25.0	1.0255
0.2	30	−0.8		38	−25.0	
	31	+0.3	1.0003	39	−25.8	
				40	−25.2	1.0260

* Average of Run 15 to 20 in Table I.

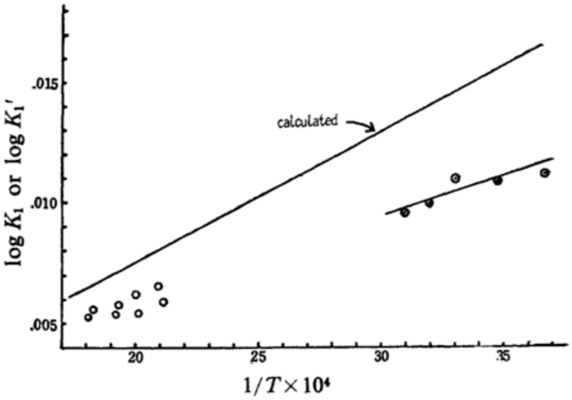

Fig. 2. Equilibrium constant and $1/T$.

○ Represents the equilibrium constant measured for the exchange reaction between gaseous ammonia and solid ammonium chloride.

⊙ Represents the average value of the equilibrium constant measured for the exchange reaction between ammonia and ammonium ion in an aqueous solution.

The effects of temperature on the fractionation factor between the resin and solution phase are shown in Table III. The equilibrium constants, K_1, are calculated by Eq. 12 with the fractionation factors at the solution of low pH value, and the logarithms of the equilibrium constants are plotted against the reciprocal of the absolute temperature, $1/T$, to get the heat of the exchange reaction 1 in Fig. 2:

$$\Delta H \doteqdot -13.8 \text{ cal./mol.}$$

The effect of temperature on the fractionation factor between gaseous ammonia and solid ammonium chloride is shown in Table IV with the experimental conditions. In this case, these fractionation factors are the equilibrium constant of the equation:

$$^{15}NH_{3(gas)} + {}^{14}NH_4Cl_{(solid)} = {}^{14}NH_{3(gas)} + {}^{15}NH_4Cl_{(solid)} \qquad K_1' \quad (13)$$

The logarithms of the equilibrium constants are

TABLE IV. EFFECT OF TEMPERATURE ON THE FRACTIONATION FACTOR BETWEEN AMMONIA GAS AND SOLID AMMONIUM CHLORIDE

Run	NH_4Cl[1] mg.	NH_3[2] mmHg	T°C	Period hr.	Fractionation factor, K_1'
41	100	100	275	27	1.0123
42	50	200	274	22	1.0130
43	50	255	245	13	1.0135
44	50	250	248	21	1.0124
45	50	200	247	62	1.0132
46	50	200	227	18	1.0144
47	50	260	224	38	1.0125
48	50	250	203	21	1.0137
49	50	300	206	49	1.0155

1: Amount of ammonium chloride used
2: Pressure of ammonia added at room temperature.

also plotted against the reciprocal of the absolute temperature in Fig. 2. The equilibrium constant between ammonia and ammonium ion, both in the gaseous state, has been calculated by Urey[12]. The calculated values are also plotted in Fig. 2.

Discussion

The equilibrium constant for the equation

$$^{15}NH_{3(gas)}+{}^{14}NH^{+}_{4(aq)}={}^{14}NH_{3(gas)}+{}^{15}NH^{+}_{4(aq)} \tag{14}$$

has been measured and found to be 1.034 at 25°C by Kirshenbaum et al.[3] The equilibrium constant for the equation

$$^{14}NH_{3(aq)}+{}^{15}NH_{3(gas)}={}^{15}NH_{3(aq)}+{}^{14}NH_{3(gas)} \tag{15}$$

has been obtained and found to be 1.005 at 25°C[3]. From the data by Kirshenbaum et al. the equilibrium constant for Eq. 1 is calculated to be 1.029 at 25°C. The value of K_1 obtained by the author compares well with the values reported in literature. Further, Fig. 1 shows that Eq. 8 is well satisfied by the experimental fractionation factors and Eqs. 1 and 2 are enough to represent the equilibria involved in the aqueous ammonia-ammonium ion solution and the exchanger of ammonium ion form.

In the equations which involved ammonia in aqueous solution the unionized ammonium hydroxide, NH_4OH, is assumed not to exist in the aqueous solution. Instead, $NH_{3(aq)}$ is assumed to represent ammonia in the aqueous solution. There is some uncertainity in regard to the interpretation of "ammonium hydroxide". However, the relatively weakly basic character of "ammonium hydroxide" solution is interpreted recently as resulting simply from the fact that the ammonia molecule is a weaker than the hydroxide ion. There must be a hydrogen bond between the nitrogen of ammonia in aqueous solution and hydrogen of solvent water.

The value of the equilibrium constant K_1 is smaller than that of the calculated equilibrium constant with the gaseous partition functions of the isotopic ammonia and ammonium ion as shown in Fig. 2. This difference may be chiefly contributed by the difference of ammonia in the aqueous state from the gaseous state. The equilibrium constant for Eq. 14 by Kirshenbaum et al.[3]: 1.005; is considered to be large enough to explain the difference of the isotopic equilibrium constant K_1 from the calculated values. There may not be a large isotope effect on the difference between the gaseous and aqueous ammonium ions, since the nitrogen atom is surrounded by the hydrogen atoms and the nitrogen isotope effect on the solvation in the aqueous ammonium ion may be very small.

The effect of the concentration of the solution phase on the fractionation factor between resin and solution phase (Table II) shows that there is no effect upon acidic solution or ammonium ion and that the concentration of ammonia in the aqueous solution has the tendency to increase the value of the fractionation factor.

The slope of $\log K_1$ versus $1/T$ gives $\Delta H=-13.8$ cal. per mole for the exchange reaction 1. The measurements of the equilibrium constants K_1' for the gas-solid exchange reaction have some difficulty in separating phases at elevated temperatures. The data are not sufficient to determine the accurate value of the heat of the exchange reaction.

In Fig. 2, it is seen that the equilibrium constants measured are located below the line of the calculated equilibrium constants. However, the differences between the measured and the calculated values at the same temperature are smaller with the measured values of the gas-solid exchange reaction than with those of the exchange reaction in aqueous solution. This fact may be partly understood by the presence of the hydrogen bond of ammonia molecules in aqueous solution.

This work was made possible by the support of the U. S. Atomic Energy Commission. The invaluable advice and encouragement from Dr. T. C. Hoering are acknowledged with thanks.

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