[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Equilibrium between Nitric Oxide, Nitrogen Peroxide and Aqueous Solutions of Nitric Acid

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The absorption of nitrogen oxides by water to produce nitric acid involves the principal reactions

$$2NO + O_2 = 2NO_2 \rightleftarrows N_2O_4 \qquad (1)$$

$$3NO_2 + H_2O = 2HNO_3 + NO \qquad (2)$$

The first proceeds slowly and probably determines the rate of nitric acid formation in dilute solution. The importance of the readily displaceable equilibrium (2) was first pointed out by Burdick and Freed,[1] who were able to give a rational explanation of the relatively low nitric acid strengths obtainable on the absorption by water of gases produced by the oxidation of ammonia.

Burdick and Freed also reported data on the equilibrium for the second reaction, expressing their results in the form of the equilibrium constant

$$K = \frac{(P_{NO})\,(P_{HNO_3})^2}{(P_{NO_2})^3\,(P_{H_2O})}$$

which they considered to be the product of the two parts

$$K_1 = \frac{(P_{NO})}{(P_{NO_2})^3} \qquad K_2 = \frac{(P_{HNO_3})^2}{(P_{H_2O})}$$

Determinations of the gas compositions in equilibrium with aqueous solutions of nitric acid led to values of K_1 for various acid strengths for temperatures from 10 to 75°. Separate determinations of the vapor pressures of water and of nitric acid over similar solutions led to values of K_2 covering a similar range. Since the publication of their results Taylor[2] has presented a summary of the available vapor pressure data, from which values of K_2 may be calculated.

More recently Abel, Schmid and Stein[3] have studied the equilibrium of reaction (2) and report values of K differing by roughly 10-fold from those of Burdick and Freed. From 35 to 60% nitric acid the discrepancy is relatively constant, the values of K reported by Abel, Schmid and Stein being about five times those of Burdick and Freed. At lower acid strengths the discrepancy is in the same direction but much greater. At low acid strengths, however, the accuracy is poor because of the difficulty of measuring the corresponding low pressures of nitrogen peroxide. Since this pressure enters as the third power in K_1 any errors in its measurement become greatly magnified.

The discrepancies between the results of Burdick and Freed and of Abel, Schmid and Stein suggested the present attempt to measure the equilibrium by a new method. Since the solution activities used[4] by Abel, Schmid and Stein in evaluating K_2 were consistent with the vapor pressure determinations of Burdick and Freed and with the correlation of vapor pressure data given by Taylor, it seemed clear that the discrepancy lay in the determination of K_1. Consequently, the present investigation was restricted to a measurement of gas compositions in equilibrium with acids of various strengths.

Burdick and Freed passed nitrogen dioxide diluted with nitrogen through an absorption train containing nitric acid solution. The nitrogen oxides in the gas leaving were absorbed in alkali, the resulting solution analyzed for nitrate and nitrite, and the amounts of absorbed nitric oxide and nitrogen dioxide then calculated. The equilibrium was approached only from the nitrogen peroxide side. Abel, Schmid and Stein employed a static method wherein they measured the total pressure of the undiluted nitrous gases over a solution of nitric acid, and determined the partial pressure of nitrogen peroxide and tetroxide by comparing the spectrum of the equilibrium gas with that of a standard gas system. The present investigation also employed a static method but involved a chemical rather than spectrographic analysis of the equilibrium gas mixture. The measurements covered the range of acid strengths from 37 to 59% nitric acid, and temperatures from 15 to 35°. In this range the equilibrium partial pressures of nitric oxide and nitrogen peroxide are of the same order of magnitude and the analytical procedure employed is believed to be reliable. Data were obtained by approaching the equilibrium from both directions.

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(1) Burdick and Freed, THIS JOURNAL, **43**, 518 (1921).

(2) Taylor, *Ind. Eng. Chem.*, **17**, 633 (1925).

(3) Abel, Schmid and Stein, *Z. Elektrochem.*, **36**, 692 (1930).

(4) Abel, Redlich and Lengyel, *Z. physik. Chem.*, **132**, 189 (1928).

Experimental Procedure

The nitric acid used was C. P. grade (sp. gr. 1.42). This was diluted to the strengths used in the experiments with distilled water and analyzed by titration with standard alkali. Nitrogen dioxide was prepared by thermally decomposing lead nitrate. The nitrogen dioxide evolved was condensed and further purified by oxygen distillation. Nitric oxide was made by allowing sulfuric acid to react with sodium nitrite.[5] The nitrogen used as diluent was from cylinders and was of purity of 99.85% or better.

Figure 1 is a diagrammatic sketch of the reaction vessel and sampling apparatus. The reaction vessel (A) consisted of a 2-liter round-bottomed flask into which were sealed two capillary gas sampling tubes (B,B), a tap for measuring pressure (C), and a tube for introduction and removal of the liquid (D). The stopcocks on these taps were lubricated with vaseline, which withstood the actions of nitric acid and nitrogen dioxide very well. Air was removed by filling the flask with acid to be used in the experiment. About a liter of this acid was displaced with nitrogen and 400 to 500 cc. more with either nitric oxide or nitrogen dioxide. About 500 cc. of acid was left in the flask, this quantity being sufficient to ensure no appreciable change in the composition of the solution during the experiment. The reaction vessel was then immersed and shaken in a constant temperature bath controlled to ±0.02°. As a result of check runs it was found that equilibrium was attained within a period of four hours at all temperatures reported.

Samples were taken by means of the two modified Gaillard bulbs[6] (E,E). Prior to sampling, the first bulb containing 25 to 50 cc. of distilled water was evacuated and weighed. A measured amount of standard potassium permanganate solution made slightly acidic with sulfuric acid was added to the second. This bulb was evacuated and swept out with nitrogen several times to ensure complete removal of oxygen before weighing.

A mercury manometer (F) was connected to (C) to determine the pressure in the reaction vessel. The Gaillard bulbs were then connected to (B,B) and the tube from the bottle (H) to (D). Acid of the same strength as that in the reaction vessel was allowed to flow from (H) at such a rate that the samples would be obtained at constant pressure. The pressure was maintained constant by regulating cock (G). After sampling the Gaillard bulbs were again weighed, the increase in weight being a direct measure of the amount of sample obtained.

In the analysis of the gas phase, one is confronted with the problem of determining six constituents: water vapor, nitric acid vapor, nitric oxide, nitrogen dioxide, nitrogen tetroxide and nitrogen. Water was neglected, and the inert gas assumed to be only nitrogen. The error from this simplifying assumption affected the calculated value of K less than 1% in the worst case. From the analysis of the first bulb, the total nitrous oxides plus the nitric acid were determined. In this analysis the oxides were converted to nitric acid and determined as such. This method is a modification of that advanced by Gaillard[6] for determination of conversion efficiencies in the commercial oxidation of ammonia to nitric acid. The second or permanganate bulb gave a measure of the ratio of nitrogen dioxide plus tetroxide to nitric oxide. That permanganate will convert nitrous oxides to nitrate has been demonstrated by several investigators.[7] This procedure was checked experimentally by analyzing a mixture consisting of nitrogen and nitric oxide only. In accordance with theory, the equivalents of nitric acid per gram of sample formed in the first bulb were a third of the equivalents of permanganate per gram of sample reduced in the second.

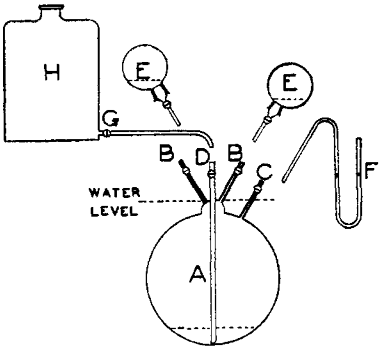

Fig. 1.

Oxygen was admitted to the first bulb with shaking until no further gas was taken up. This was taken as an indication that all the nitrous oxides had been converted to nitric acid. The solution in this bulb was then titrated with standard sodium hydroxide using methyl red as an indicator.

The bulb containing the permanganate was shaken for several hours to ensure completion of the reaction with nitric oxide. An excess of standard ferrous sulfate was added and the solution titrated to pink with permanganate. In this determination it was found that a large excess of potassium permanganate was necessary, as nitric oxide seemed to reduce it only as far as manganese oxide.

Taylor's data on the vapor pressure of nitric acid were used to calculate the amount of nitric acid taken in with the first sample, which value was applied as a correction to the titration of this sample. The ratio of dioxide to tetroxide was computed from Bodenstein's later values for the equilibrium constant.[8]

Results

The results are summarized in Table I and the calculated values of K_1 at 25° are plotted *vs.* acid strength in Fig. 2. In each case the pressures employed are in atmospheres and the logarithms are base 10. It is evident from the table that the results obtained starting with nitrogen peroxide check within the experimental error those obtained when starting with nitric oxide. Figure 2 also shows the results of Burdick and Freed and of Abel, Schmid and Stein. The vertical arrows indicate the extreme deviations of the results at a constant acid strength. It is evident that the

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(5) W. A. Noyes, THIS JOURNAL, **47**, 2170 (1925).

(6) Gaillard, *Ind. Eng. Chem.*, **11**, 745 (1919).

(7) Mellor, "Inorganic Chemistry," Longmans, Green and Co., New York, Vol. III.

(8) Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

TABLE I

SUMMARY OF RESULTS

Run	Temp., °C.	Nitric acid, %	Original gas	Equilibrium Pressures P_{NO_2}, atm.	P_{NO}, atm.	log K_1	log K'_2	K	Mean K
37	15	54.5	NO	0.0348	0.0272	2.81	−4.59	0.017	0.019
38	15	54.5	NO_2	.0301	.0214	2.89	−4.59	.020	
35	20	54.7	NO	.0255	.0081	2.71	−4.40	.020	.018
36	20	54.5	NO_2	.0303	.0109	2.59	−4.40	.016	
15	25	37.2	NO_2	.0095	.0235	4.44	−6.20	.017	
17	25	37.1	NO_2	.0132	.0430	4.27	−6.20	.012	
18	25	37.1	NO	.0144	.0568	4.28	−6.20	.012	
30	25	40.7	NO_2	.0096	.0097	4.04	−5.80	.017	
31	25	40.7	NO	.0133	.0214	3.96	−5.80	.014	
32	25	40.7	NO_2	.0099	.0111	4.06	−5.80	.018	
19	25	48.5	NO_2	.0175	.0100	3.27	−4.91	.023	.017
20	25	48.4	NO	.0204	.0131	3.19	−4.91	.019	
21	25	48.4	NO_2	.0280	.0252	3.06	−4.91	.014	
22	25	58.8	NO	.0450	.0110	2.08	−3.74	.022	
23	25	58.8	NO	.0440	.0078	1.96	−3.74	.017	
24	25	58.8	NO_2	.0350	.0042	1.99	−3.74	.018	
39	30	54.6	NO	.0437	.0089	2.03	−4.03	.010	.011
40	30	54.5	NO_2	.0535	.0190	2.10	−4.03	.012	
33	35	54.8	NO	.0490	.0080	1.83	−3.86	.009	.010
34	35	54.7	NO	.0495	.0094	1.89	−3.86	.011	

present data support the results of Abel, Schmid and Stein rather than those of Burdick and Freed.

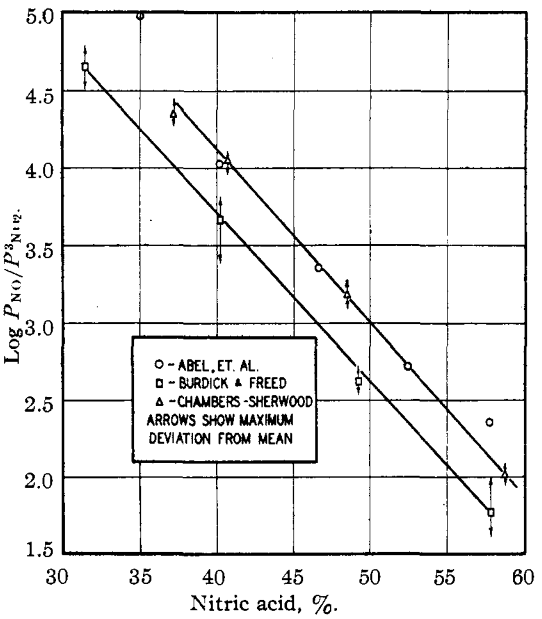

Fig. 2.

The mean value of K at 25° over the range of acid strengths studied is 0.017, which may be compared with 0.0046 from the results of Burdick and Freed and 0.019 obtained from the data of Abel, Schmid and Stein over the same range. The value of K reported by Abel, Schmid and Stein is 0.046, but this value was based only on two determinations at low acid strengths, where the partial pressures of nitrogen peroxide were very low.

It may be concluded that the results of Burdick and Freed are inaccurate, and that the data of Abel, Schmid and Stein, and those of the present investigation, serve as a more reliable basis for calculation of the equilibrium of this important reaction. It is difficult to suggest the source of error in the procedure used by Burdick and Freed, although it may be pointed out that they approached the equilibrium only from the peroxide side, and that failure to attain equilibrium would result in low values of K_1, as found.

It may be noted from Table I that K decreases with increased temperature, being 0.018 at 15° and 0.010 at 35°. The temperature range covered and the accuracy of the determinations are probably not great enough to justify a quantitative analysis of the trend of K with temperature, but it may be noted that the apparent temperature effect is considerably greater than that reported by Burdick and Freed, who found a 12% decrease in K on increasing the temperature from 25 to 75°.

Summary

The equilibrium of the reaction $3NO_2 + H_2O = 2HNO_3 + NO$ has been studied at 25° over the range of acid strengths from 37 to 59% nitric acid, and over the temperature range from 15 to

35° for an acid strength of 54–55% nitric acid. The results expressed in the form of the constant $K_1 = (P_{NO})/(P_{NO_2})^3$ agree well with the data of Abel, Schmid and Stein, deviating considerably from those of Burdick and Freed.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 17, 1936

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The Infra-red Absorption of Heavy Acid Solutions

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A previous study[1] has revealed the presence of intense absorption bands at 2.4 μ and near 5.5 μ in the spectra of aqueous solutions of a number of acids. These bands were attributed to the effects of hydration. As the position of the band near 5.5 μ varied slightly with the solute, this absorption was identified with a characteristic frequency of an associational group containing undissociated acid molecules, while the 2.40 μ band was attributed to a hydrate in which the H^+ ion is involved. An investigation of the spectra of solutions of hydrolyzing salts gave additional support to this conclusion.[2]

The present work was undertaken in order to determine the changes in the positions of these bands caused by the substitution of deuterium for the hydrogen in the aqueous solutions. The deuterium oxide used as a solvent was a Norwegian product containing only a trace of ordinary water. The DCl solution was obtained from the California Isotope Company of Berkeley and contained about 0.5% H_2O. The D_2SO_4 and D_3PO_4 solutions were prepared by dissolving known amounts of the anhydrides in deuterium oxide. The sulfur trioxide used in this process was obtained by heating fuming sulfuric acid and the gas was allowed to pass through two drying tubes containing phosphorus pentoxide before entering the solvent. From specific gravity determinations it is estimated that the D_2SO_4 solution was approximately four normal and a D_3PO_4 solution of equal concentration was prepared. The spectroscopic methods have been described in a previous paper.[3] A rock-salt prism was used in the region from 2.5 to 12.0 μ, additional measurements being made in the 2.0–3.8 μ region with a fluorite prism. The absorbing layers used in the region of longer wave lengths were 0.02 mm. in thickness, while the layers in the 2.0–3.8 μ region were 0.05 mm. thick.

The infra-red absorption of deuterium oxide has been studied previously by Ellis and Sorge,[4] by Casselman,[5] and by the authors.[3] Intense bands have been observed at 2.85, 4.00, 6.80 and 8.20 μ. Although the broad band at 4.00 μ has three maxima, it was impossible to resolve this band into its components with the rock-salt prism used in the present work. The results obtained with deuterium oxide in the present study are given by the upper curve of Fig. 1. In addition to the bands shown in the figure, another band appeared at 10.4 μ. This band probably corresponds to the band recently observed at 8.6 μ in the spectrum of ordinary water.[6]

The transmission of the DCl solution is shown in the lower curves of Fig. 1. It will be noted that there is a marked increase in absorption near 5.5 μ. The dotted curve shows the transmission of a more concentrated solution of DCl in this region. There is also a slight increase in absorption near 3.4 μ, and this absorption may be seen more clearly when thicker absorbing layers are used. The results obtained in the 3 μ region with thicker cells are shown in another figure. With the exception of the increased absorption in the 3.4 and 5.5 μ regions of the solution spectrum, the transmission curve for the DCl solution bears a close resemblance to the D_2O curve. The curves are practically identical from 9 to 12 μ, and for this reason the transmission curves obtained in this region are omitted from the figure. The results obtained with the D_2SO_4 and D_3PO_4 solutions are the same as those obtained with the DCl except for the appearance of bands near 9 and 4.8 μ which are characteristic of the sulfate and phosphate

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[1] E. K. Plyler and E. S. Barr, *J. Chem. Phys.*, **2**, 306 (1934).

[2] E. K. Plyler and W. Gordy, *ibid.*, **2**, 470 (1934). Recent unpublished work, however, seems to indicate that the hydrated H^+ ion absorbs also in the region of 5.4 μ and the hydrated acid molecules absorb at slightly longer wave lengths.

[3] E. K. Plyler and D. Williams, *ibid.*, **4**, 157 (1936).

[4] J. W. Ellis and B. W. Sorge, *ibid.*, **2**, 559 (1934).

[5] A. L. Casselman, *Phys. Rev.*, **45**, 221 (1934).

[6] D. Williams, *ibid.*, **49**, 869 (1936).