between the results of widely different methods is to be considered reassuring rather than otherwise.

The outcome of the investigation may be summarized as follows.

1. Nickelous oxide prepared by ignition of the nitrate at about 1000° is found to contain 0.11% of occluded gases.
2. After a correction for the gas content is made, the oxide is found by reduction in hydrogen to contain 0.78582% of nickel, whence the atomic weight of nickel is 58.70.
3. The atomic weight of meteoric nickel is found by an exactly similar method to be 58.68, a difference within the experimental error.

We are greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in carrying out this investigation.

CAMBRIDGE, MASS.

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THE EQUILIBRIUM BETWEEN NITRIC OXIDE, NITROGEN PEROXIDE AND AQUEOUS SOLUTION OF NITRIC ACID.

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1. Introduction.

The absorption and conversion into nitric acid of the nitrous gases, such as are produced by the processes of ammonia oxidation or arc fixation of nitrogen, have been found to be attended with considerable difficulty, making necessary the installation of large and expensive systems of reaction chambers and absorption towers in order to accomplish the oxidization and absorption of these nitrous gases. The mechanism of this process and the conditions controlling it seem not to have been made the subject of any very precise or careful study, so in accordance with a suggestion of Prof. A. A. Noyes, at the time Consulting Chemist to the Ordnance Department, an investigation, part of the results of which are here presented, was carried out.

It was hoped that the careful study of the mechanism of the absorption process would yield information which would enable more favorable conditions for the carrying on of the reactions to be established. Early it was seen that the reactions of importance were limited to two, namely, (1) $2NO + O_2 = 2NO_2$; (2) $3NO_2 + H_2O = 2HNO_3 + NO$.

The first of these reactions under ordinary conditions, that is, with dilute gases, progresses very slowly and the second, although it goes on with great rapidity, comes to an equilibrium considerably short of completed reaction.

Reaction 2, namely, the absorption of nitrogen peroxide in water to form nitric acid with the simultaneous liberation of nitric oxide is the fundamental reaction taking place in the absorbing tower. The complete reversibility of this reaction within the range of concentrations of nitric acid encountered in the absorption process is indicated in the comparative data calculated from experiments of Lewis and Edgar[1] who found the pressures of nitrogen peroxide and nitric oxide to be 10^{-5} and 1 atmospheres, respectively, when the concentration of nitric acid was 1.1%, and of Foerster and Koch[2] who found 1 and 10^{-7} atmospheres respectively at 65.3% concentration of nitric acid.

With dil. nitric acid the reaction of absorption of nitrogen peroxide, it is seen, progresses substantially to completion with the liberation of a third of a volume of nitric oxide whereas in the presence of concentrated acid, the presence of only minimal amounts of nitric oxide completely inhibits the progress of the reaction. The importance technically of the determination of this limiting state of absorption for various concentrations of nitric acid is obvious. Likewise the information gained in useful in evaluating the equilibrium constants for nitric acid as well as free energy values derived therefrom.

The equilibrium constant for the reaction under investigation is

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

which may be considered to be the product of 2 partial constants,

$$K_1 = \frac{(P_{\mathrm{NO}})}{(P_{\mathrm{NO_2}})^3}, \text{ and } K_2 = \frac{(P_{\mathrm{HNO_3}})^2}{(P_{\mathrm{H_2O}})},$$

the first relating to the composition of the nitrous gases and the second relating only to the partial pressures of the nitric acid and water vapor over the solutions. Since the partial constants K_2 involve only the vapor pressures of the solution, it is evident that the experimental problem lies in the determination of a series of the partial constants $K_1 = (P_{\mathrm{NO}})/(P_{\mathrm{NO_2}})^3$ for nitric acid at different concentrations and temperatures. The direct determination of these partial constants was limited to solutions containing between 10 and 55% nitric acid, because in the case of solutions below 10% and above 55% the partial pressures of nitrogen peroxide and nitric oxide, respectively, became too small for accurate determination. In order to extend the series of partial constants K_1 to nitric acid solutions more dilute than 10%, it was assumed[3] that for

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[1] Lewis and Edgar, This Journal, **33**, 292 (1911).

[2] Foerster and Koch, *Z. angew. Chem.*, **21**, 2161, 2209 (1908).

[3] At very low concentrations of nitric acid a small fraction of the nitrous gases react to produce nitrous acid according to the equation $2NO + HNO_3 + H_2O = 3HNO_2$.

The assumption that at 0% concentration the conversion of nitrogen peroxide (NO_2) to nitric acid is 66.7 was made to enable us to determine the direction of the curves for K_1 for acids lower than 10% but not at extreme dilution.

That this fraction of the nitrous gases, which react to produce nitrous acid, is really dilute concentrations of acid, where K_1 approaches infinity, the conversion of nitrogen peroxide to nitric acid becomes 66.7%, corresponding to complete reaction. By plotting the nitric acid concentration against the percentage conversion of a 1.0% nitrogen peroxide gas, as calculated from the constants obtained for acids above 10%, and extending the curve to zero acid concentration, where the conversion is 66.7%, the values of K_1 for the dilute solutions may be evaluated. In order to extend the series of partial constants K_1 to acids above 55% it was necessary to employ vapor-pressure data. These, when properly substituted in the expression for the complete equilibrium constant $K_1K_2 = K$ give at once K_1 if K is known. The constant K was obtained by combining the partial constants K_1 and K_2 independently determined for the solutions between 25 and 50% nitric acid.

Substitution of the value of K in the thermodynamic equation $- \Delta F = RT \log K$ gives the free energy decrease attending the reaction under investigation and with the aid of this value together with the vapor pressure data and previously determined free-energy values for nitric oxide, nitrogen peroxide, and water the free energy of nitric acid as vapor and in solution has been calculated.

II. Description of the Experiments.

The general plan of the experiments was the following. Nitrogen peroxide gas diluted with 90 to 95% nitrogen was bubbled through nitric acid solutions maintained at constant temperature. The issuing gases were analyzed for nitric oxide and nitrogen peroxide and from the quantities of nitric oxide, nitrogen peroxide, and nitrogen which issued in a given time the partial pressures of each of these gases were computed and the partial constant $K_1 = (P_{NO})/(P_{NO_2})^3$ calculated.

In a like manner, air was bubbled through the nitric acid solutions, and from the mol quantities of air, water vapor and nitric acid vapor which issued in a given time the partial pressures of each of these gases were computed and the partial constant $K_2 = (P_{HNO_3})^2/(P_{H_2O})$ calculated.

The nitrogen peroxide used in the experiments was made by heating dry lead nitrate and condensing the nitrogen peroxide evolved in a tube immersed in a freezing mixture. The peroxide condensed either as a white solid or straw colored liquid.

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very small may be shown by calculating the ratio of nitrous acid to nitric acid in equilibrium with nitrogen peroxide and nitric oxide. The calculations may be made by considering the equilibrium constants, computed from available free-energy data and free-energy data given in this article, for the reactions $2NO + HNO_3 + H_2O = 3HNO_2$, and $3NO_2 + H_2O = 2HNO_3 + NO$. From these equilibrium constants, it can be shown that if a 5.0% (0.82 formal) nitric acid solution reacts with a 1.0% nitrogen peroxide gas, the resulting concentration of nitrous acid at equilibrium will be 0.0034 formal. The ratio of the concentrations of the nitrous acid and nitric acid is 0.004, which represents a 0.4% conversion of the nitrogen peroxide to nitrous acid.

The apparatus used for the measurements of K_1 is shown in Fig. 1.

The bulb A when heated gave gaseous nitrogen peroxide in a continuous stream, the constancy of flow of which was maintained by observance of the flowmeter C. Paraffin oil was used in the arms of the gage. In the mixing chamber D the gas was diluted with 90 to 95% of nitrogen from the tank E. The nitrogen was scrubbed in the towers F filled with copper turnings and ammoniacal ammonium chloride, the ammonia removed with dil. sulfuric acid and the gas dried with soda lime and calcium chloride. The flow of nitrogen was measured by means of the carefully calibrated gage I.

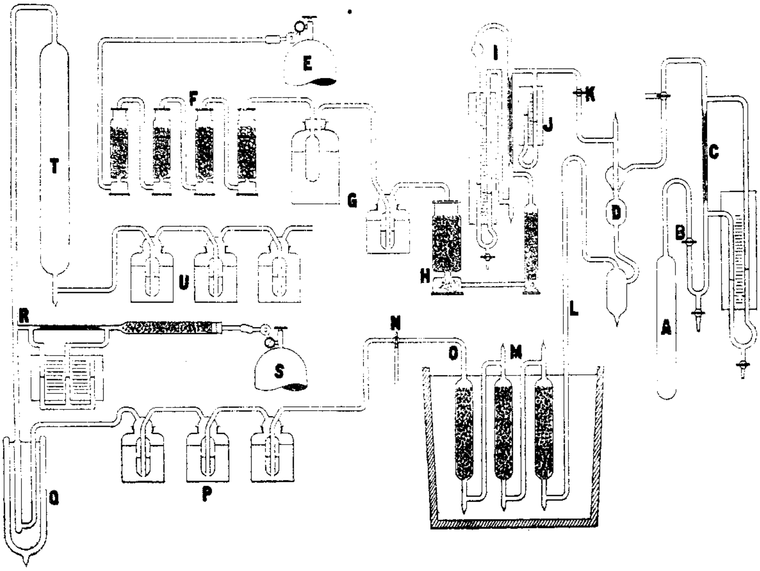

Fig. 1.

During the experiments, which were from 15 to 20 minutes in length, the gage was read every minute and an average value taken. The reading of the gage served to give the mols of nitrogen passed at the given temperature and the pressure given by the manometer at J.

The nitrogen and nitrogen peroxide after mixing passed to the absorption Bulbs M containing a definite strength of nitric acid. These bulbs were filled with broken glass and were immersed in a thermostat. In each bulb the gases were intimately in contact with the liquid for a period of about 1.2 seconds. That this time of contact was adequate to establish equilibrium conditions in the exit gases is shown by the course of the absorption from the curve in Fig. 2 for 1, 2 and 3 bulbs in series. The gas on entry contained 4.2% nitrogen peroxide and at completion of the reaction 51% was absorbed.

The gases leaving the bulbs consisted of nitrogen, nitrogen peroxide (NO_2 and N_2O_4), nitric oxide (NO) and small amounts of nitric acid and water vapor. After the establishment of steady conditions the gases were diverted to the alkali absorption train P by means of the 3-way Stopcock N. This cock also permitted flushing the absorption train with nitrogen to remove air. In runs made at the higher temperatures it was necessary to keep the exit tube O warm enough to prevent condensation.

In the equilibrium experiments in which the gases contained too large a proportion of nitric oxide relative to their nitrogen peroxide content the alkali absorption train

P is inadequate to secure complete absorption. In this case the exit gases after mixing with oxygen at R and after passing through the large oxidation Chamber T were scrubbed again by the second alkali absorption train U. In order to avoid condensation of nitric acid mist on the walls of the oxidation chamber, the water vapor present in the gas was largely removed before admixture with the oxygen by passing through the tube Q cooled in liquid ammonia. The condensate in Q was scarcely of determinable acidity.

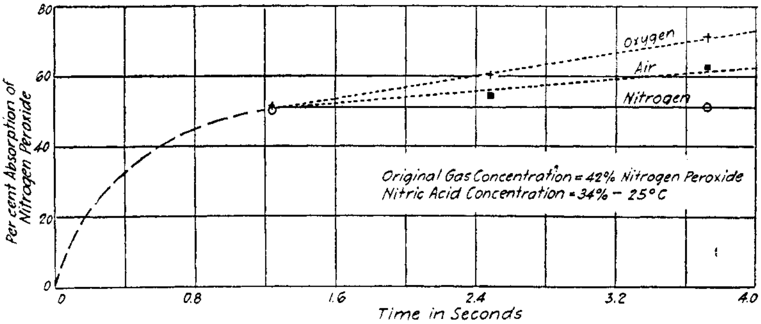

Fig. 2.—Rate of absorption of nitrogen peroxide in aqueous nitric acid with oxygen, air and nitrogen as diluent gases.

The nitrous gases to be determined consist of nitrogen peroxide (NO_2 and N_2O_4), nitric oxide, and nitric acid vapor. Such a mixture reacts with dil. sodium hydroxide solution to form sodium nitrate and sodium nitrite in varying proportions depending on the composition of the gas. The amount of sodium nitrate formed in the alkali solution due to the nitric acid in the gas was calculated from the vapor pressure of nitric acid solutions. The remaining nitrate and nitrite represent a measure of the nitric oxide and nitrogen peroxide in the gas. The nitrogen dioxide and nitrogen tetroxide react alike and cannot be differentiated by analysis. The total nitrate and nitrite formed in the alkali solution in the absorption apparatus was determined by back titration with standard acid using phenolphthalein as an indicator and the nitrite by oxidation with excess permanganate and back titration with ferrous sulfate.

It has been customary to state that the absorption of nitrogen peroxide in alkali gives equimolal mixtures of nitrate and nitrite, that the absorption of equimolal mixtures of nitrogen peroxide and nitric oxide gives pure nitrite, and that excess nitric oxide escapes from solution without absorption. These statements we find are subject to some qualification. Nitrogen peroxide gives equivalent amounts of nitrate and nitrite only when the absorption takes place in the absence of oxygen, and for this reason the air in the absorbers was displaced by nitrogen. It was also found that when nitrogen peroxide was mixed with a less than equivalent amount of nitric oxide some of the nitric oxide escaped from the solution unabsorbed and, furthermore, when the gases are in equivalent proportions, or even when nitric oxide is in excess, some nitrate is produced.

Our study of the absorption of nitrous gases in dilute alkali has shown that its accomplishment can be represented by the following equations: (*a*) $3NO_2 + H_2O = 2HNO_3 + NO$; (*b*) $NO_2 + NO + H_2O = 2HNO_2$; (*c*) $HNO_3 + NaOH = NaNO_3 + H_2O$; (*d*) $HNO_2 + NaOH = NaNO_2 + H_2O$. In words, according to Reactions *a* and *b*, the water and nitric oxide compete with each other for a reaction with the nitrogen peroxide. These equations permit the explanation of the fact that when mixtures of nitrogen peroxide and nitric oxide react with alkali solutions some nitrate is always formed; and, also, with gases containing not too great an excess of nitrogen peroxide some of the nitric oxide is unabsorbed. By considering these reactions, it is evident that $^3/_2$ the nitrate plus $^1/_2$ the nitrite in the first absorption train is a measure of the nitrogen peroxide (in mols as NO_2); and the total nitrate and nitrite, expressed in equivalents, minus the nitrogen peroxide (in mols as NO_2) is a measure of the nitric oxide absorbed from the original gas.

For computing the gas composition the further data required are the volume of nitrogen used in the given period of time and the proportion of the nitrogen peroxide existing as NO_2 and as its polymer N_2O_4. From the flow meter, temperature and pressure readings the nitrogen passed through the apparatus was determined. The quantities of nitrogen dioxide and tetroxide were calculated from the equation for the equilibrium constant given by Bodenstein,[1] which expressed in terms of partial pressures in atmospheres is

$$\log \frac{(P_{N_2O_4})}{(P_{NO_2})^2} = \frac{2866}{T} - \log T - 6.251$$

For the various temperatures at which experiments were performed, namely, 10°, 25°, 50° and 75°, the values taken for the constant expressed in atmospheres are 26.5, 7.81, 1.30, and 0.276, respectively.

III. Results of the Equilibrium Measurements.

Table I presents the results of the equilibrium measurements. In the first, third, and seventh columns are given the number of the experiment, the temperature, and pressure at which these experiments were made. In the fourth, fifth and sixth columns are given the mol per cents. of nitrogen tetroxide, nitrogen dioxide and nitric oxide in the gas which was in equilibrium with the nitric acid at the concentration given in the second column. In the eighth column is given the logarithm of the partial constant K_1 calculated from these mol per cents. and pressure data, and in the last column is recorded the mean of these values. Values indicated by the asterisk were omitted from the mean.

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[1] Bodenstein, *Z. physik. Chem.*, **21**, 2161, 2209 (1908).

TABLE I.
The Equilibrium Data.

Expt.	Conc. HNO_3. % by wt.	Temp. ° C.	Mol. % N_2O_4.	Mol. % NO_2.	Mol. % NO.	Press. mm.	Log of $\frac{(P_{NO})}{(P_{NO_2})^3}$.	Mean log of $\frac{(P_{NO})}{(P_{NO_2})^3}$.
71	5.94	50	0.0005	0.189	1.00	798	6.13	..
72	5.94	50	0.0011	0.284	2.06	798	5.91	..
73	5.94	50	0.0015	0.326	2.58	798	5.88	5.97
74	5.94	75	0.0004	0.465	1.60	798	5.16	..
75	5.94	75	0.0004	0.446	1.57	798	5.21	..
76	5.94	75	0.0004	0.444	1.08	798	5.05	5.14
62	11.50	10	0.004	0.118	3.73	792	7.32	..
63	11.50	10	0.004	0.127	4.38	792	7.30	..
64	11.50	10	0.004	0.127	5.20	792	7.37	7.33
59	11.50	25	0.001	0.117	1.92	792	7.04*	..
60	11.50	25	0.005	0.251	8.08	792	6.67	..
61	11.50	25	0.004	0.218	3.57	792	6.50	6.59
65	11.50	50	0.0015	0.340	1.99	796	5.66	..
66	11.50	50	0.002	0.379	2.87	796	5.68	..
67	11.50	50	0.002	0.386	2.60	796	5.62	5.65
68	11.50	75	0.001	0.671	1.37	796	4.61	..
69	11.50	75	0.001	0.574	0.568	796	4.44	..
70	11.50	75	0.001	0.709	1.86	796	4.67	4.57
51	21.7	10	0.0125	0.213	2.02	786	6.29	..
52	21.7	10	0.0125	0.210	2.32	786	6.37	6.33
48	21.7	25	0.003	0.196	0.894	786	6.04*	..
49	21.7	25	0.012	0.377	2.47	786	5.64	..
50	21.7	25	0.014	0.412	2.99	786	5.59	5.62
53	21.7	50	0.008	0.764	1.32	784	4.44	..
54	21.7	50	0.012	0.969	3.08	784	4.50	..
55	21.7	50	0.013	0.989	2.76	784	4.43	4.46
56	21.7	75	0.005	1.30	0.740	784	3.50	..
57	21.7	75	0.010	1.71	2.50	784	3.67	..
58	21.7	75	0.005	1.51	0.990	784	3.43	3.53
39	31.4	10	0.056	0.455	2.64	782	5.42	..
40	31.4	10	0.040	0.383	2.87	782	5.68	..
41	31.4	10	0.039	0.377	3.10	782	5.74	5.61
36	31.4	25	0.027	0.576	0.894	784	4.64	..
37	31.4	25	0.057	0.843	2.00	784	4.50	..
38	31.4	25	0.037	0.676	2.05	784	4.79	4.64
42	31.4	50	0.027	1.42	0.816	777	3.44	..
43	31.4	50	0.057	2.05	2.05	777	3.36	..
44	31.4	50	0.052	1.96	1.71	777	3.34	3.38
45	31.4	75	0.01	1.45	0.284	776	2.95*	..
46	31.4	75	0.03	3.24	1.16	776	2.51	..
47	31.4	75	0.03	3.17	0.860	776	2.41	2.46
27	40.2	10	0.102	0.610	1.27	790	4.71	..
28	40.2	10	0.154	0.753	1.80	790	4.59	..
29	40.2	10	0.154	0.754	2.39	790	4.71	4.67

TABLE 1 (*continued*).
The Equilibrium Data.

Expt.	Conc. HNO_3. % by wt.	Temp. ° C.	Mol. % N_2O_4.	Mol. % NO_2.	Mol. % NO.	Press. Mm.	Log of $\frac{(P_{NO})}{(P_{NO_2})}$.	Mean log of $\frac{(P_{NO})}{(P_{NO_2})^3}$.
24	40.2	25	0.163	1.42	0.744	789	3.38	..
25	40.2	25	0.170	1.45	2.07	789	3.79	..
26	40.2	25	0.170	1.45	2.17	789	3.82	3.66
30	40.2	50	0.080	2.44	0.694	789	2.64	..
31	40.2	50	0.075	2.41	0.694	789	2.66	..
32	40.2	50	0.090	2.59	0.700	789	2.57	2.63
33	40.2	75	0.03	3.46	0.627	780	2.15	..
34	40.2	75	0.05	4.15	1.02	780	2.13	..
35	40.2	75	0.015	2.30	0.507	780	2.59*	2.14
4	49.4	10	0.58	1.45	1.30	775	3.61	..
5	49.4	10	0.32	1.08	0.570	775	3.64	..
6	49.4	10	0.36	1.16	0.794	775	3.69	3.65
1	49.4	25	0.495	2.50	1.02	770	2.80	..
2	49.4	25	0.295	1.93	0.356	770	2.68	..
3	49.4	25	0.650	2.87	1.41	770	2.76	2.75
7	49.4	50	0.07	2.25	0.233	784	2.29*	..
8	49.4	50	0.27	4.50	0.428	784	1.65	..
9	49.4	50	0.17	3.52	0.319	784	1.84	1.75
10	49.4	75	0.02	2.88	0.493	771	2.30*	..
11	49.4	75	0.04	3.61	0.624	771	2.11*	..
12	49.4	75	0.05	4.42	0.754	771	1.93*	..
13	49.4	75	0.35	11.20	1.12	771	0.89	..
14	49.4	75	0.25	9.35	1.79	771	1.35	1.11
18	57.8	10	1.39	2.27	0.400	770	2.52	..
19	57.8	10	1.15	2.07	0.267	770	2.47	..
20	57.8	10	1.16	2.08	0.226	770	2.39	2.46
15	57.8	25	1.99	5.00	0.781	774	1.78	..
16	57.8	25	2.77	5.91	0.882	774	1.62	..
17	57.8	25	2.53	5.64	0.868	774	1.67	..
21	57.8	25	0.54	2.63	0.185	769	2.00	1.77
22	57.8	50	0.70	7.19	0.448	774	1.07	..
23	57.8	50	1.05	8.75	0.374	774	0.73	0.90

IV. Vapor Pressure Measurements for Evaluating K_2.

The method of measurement consisted in passing a known volume of air through the nitric acid bulbs in the thermostat and absorbing the nitric acid and water vapor in 2 weighed potash bulbs. The first contained dil. alkali for the removal of the nitric acid vapors, and was cooled in an ice-bath to collect the greater part of the water vapor. The second bulb contained sulfuric acid for removing the remaining water vapor. From the volume of air passed, the increased weight of the absorption bulbs, and the acid titration, the partial vapor pressures were calculated. The issuing gases were colorless, indicating little or no dissociation of nitric acid. The results of the vapor pressure measurements are given in Table II.

TABLE II.

Vapor Pressure of Aqueous Solutions of Nitric Acid.

Conc. HNO_3.	P (mm.) HNO_3.			P (mm.) H_2O.			Total pressure (mm.).		
% by wt.	° C. 25.	50.	75.	25.	50.	75.	25.	50.	75.
24.1	0.0158	0.103	0.645	19.5	78.0	251.0	19.5	78.1	252
33.8	0.0471	0.330	1.88	16.3	63.7	214.0	16.4	64.0	216
40.2	0.110	0.752	3.77	13.1	53.6	175.0	13.2	54.3	179
45.1	0.167	1.17	6.15	12.2	49.8	158.0	12.4	51.0	164
49.4	0.253	1.97	9.28	11.1	42.9	145.0	11.4	44.9	154
69.9	4.14	16.6	53.1	3.62	17.7	69.5	7.76	34.3	123

V. Treatment of Results.

Graphical presentation of the experimental measurements is made in Fig. 3, in which the logarithms of the partial constants K_1 are shown plotted against the acid concentration. The points indicated by O are the experimentally determined values, the points by + those for dilute solutions determined by the method of extrapolation previously mentioned, and the points by 0 the values for concentrated acid calculated from the mean value of the complete equilibrium constant K and the observed vapor pressure measurements. In Table III are shown the observed and calculated values of these latter quantities.

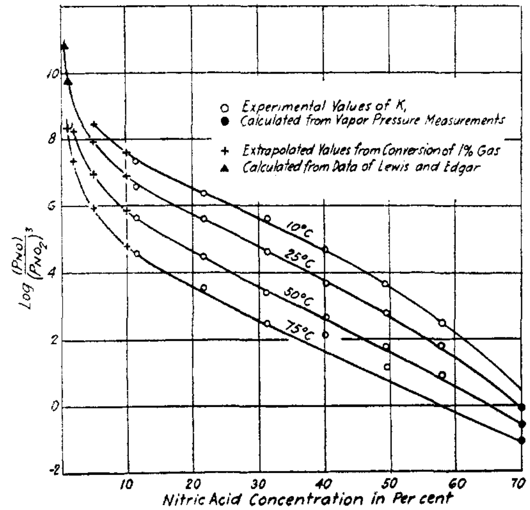

Fig. 3.—Variation of the partial constant K_1 with the acid concentrations and temperature.

TABLE III.

Constants Expressed in Atmospheres Calculated from Equilibrium Data and Vapor Pressures.

Conc. HNO_3.	$\text{Log}\ \frac{(P_{HNO_3})^2}{(P_{H_2O})}$.			$\text{Log}\ \frac{(P_{NO})}{(P_{NO_2})^3}$.			$\text{Log}\ \frac{(P_{NO})(P_{HNO_3})^2}{(P_{NO_2})^3(P_{H_2O})}$.		
% by wt.	° C. 25.	50.	75.	25.	50.	75.	25.	50.	75.
24.1	—7.77	—6.75	—5.66	+5.37	+4.20	+3.17	—2.40	—2.55	—2.49
33.8	—6.75	—5.65	—4.66	+4.36	+3.18	+2.19	—2.39	—2.47	—2.47
40.2	—5.91	—4.86	—3.97	+3.70	+2.58	+1.63	—2.21	—2.28	—2.35
45.1	—5.52	—4.44	—3.50	+3.20	+2.10	+1.18	—2.30	—2.34	—2.32
49.4	—5.12	—3.93	—3.11	+2.75	+1.67	+0.77	—2.38	—2.26	—2.34
69.9	—2.12	—1.69	—1.27	—0.13	—0.69	—1.12	..	..	..
					Mean,		—2.34	—2.38	—2.39

With the aid of the free energy data given by Lewis and Edgar[1] the 25° curve for K_1 may be extended to very dilute solutions. Using the values of 0.72 and 0.66 for the ionization of 0.1 and 0.2 N nitric acid as assumed by Lewis, the following free energies at 25° have been calculated.

$3NO_2$ (1 atm.) + H_2O (liq.) = $2HNO_3$ (0.1*f*) + NO (1 atm.) + 14,720 cal.

$3NO_2$ (1 atm.) + H_2O (liq.) = $2HNO_3$ (0.2*f*) + NO (1 atm.) + 13,280 cal.

Substitution of these values of the free energy in the equation $-\Delta F = RT \log K$, gives for the logarithm of the constant $(P_{NO})/(P_{NO_2})^3$ at 0.1*f* and 0.2*f* nitric acid the values 10.80 and 9.72, respectively. These points are shown on the plot at 0.6 and 1.2% nitric acid.

The results of the equilibrium measurements serve further for the evaluation of 2 quantities of importance, namely, the free energy of nitric vapor and the free energy of nitric acid in its strong solutions. From the values of the constant log K given in Table IV and using 2.32 as the corresponding figure at 10° the free energy decreases for the reaction $3NO_2$ (1 atm.) + H_2O (1 atm.) = $2HNO_3$ (1 atm.) + NO (1 atm.) at the temperatures 10°, 50° and 75° become —3000 cal., —3200 cal., —3520 cal., and —3810 cal., respectively. These figures combined with values for the other quantities in the equation from the free energy expressions given by Lewis and Randall[2] and Lewis and Adams[3] give for the free energies of nitric acid vapor (1 atm.) at the specified temperatures the values —16750 cal., —16240 cal., —15490 cal. and —14,720 cal.

These free energies may be expressed by the equation[4]

$$\Delta F = -25{,}510 + 31T.$$

For the calculation of the free energy of nitric acid in solution the free energy value for the gas at one atmosphere must be converted to that of nitric acid at the vapor pressure of the given solution. The values for the vapor pressure of the acid were calculated from the equation $K_2 = (P_{HNO_3})^2/(P_{H_2O})$, the values of K_2 being obtained by the division of the mean value for the complete constant K by the values of K_1 selected from Fig. 1 using as values for the term (P_{H_2O}) those selected from a plot of the experimental vapor-pressure data.

Since for strong solutions there is lacking a standard basis to which free-energy values may be reduced, Table IV is presented showing the free energies and nitric acid vapor pressures for the range of concentration and temperature studied.

[1] *Loc. cit.*

[2] Lewis and Randall, THIS JOURNAL, **36**, 1969 (1914).

[3] Lewis and Adams, *ibid.*, **37**, 2316 (1915).

[4] By assuming in our calculations from the vapor pressure measurements complete dissociation to equilibrium of the nitric acid in the vapor phase we obtain for the free energy of nitric acid gas, the expression —25170 + 30 T, which gives results substantially the same as those calculated from the corresponding expressions in the text.

TABLE IV.

Vapor Pressures and Free Energy of Nitric Acid Solutions.

Conc. acid. % by wt.	Log of HNO_3 press. (atm.). °C. 25.	50.	75.	Free energy of HNO_3 solutions. F_{298}.	F_{323}.	F_{348}.
5	—5.88	—5.10	—4.37	—24250	—23040	—21700
10	—5.37	—4.58	—3.80	—23560	—22270	—20770
15	—5.07	—4.27	—3.48	—23150	—21810	—20270
20	—4.83	—4.00	—3.20	—22820	—21410	—19820
25	—4.59	—3.73	—2.95	—22500	—21010	—19420
30	—4.36	—3.48	—2.73	—22190	—20640	—19070
35	—4.14	—3.28	—2.52	—21880	—20340	—18730
40	—3.91	—3.07	—2.33	—21570	—20040	—18440
45	—3.66	—2.84	—2.12	—21230	—19690	—18100
50	—3.42	—2.62	—1.92	—20900	—19370	—17780
55	—3.18	—2.40	—1.71	—20580	—19040	—17440
60	—2.90	—2.17	—1.50	—20190	—18700	—17110
65	—2.66	—1.93	—1.30	—19870	—18350	—16790
70	—2.28	—1.70	—1.12	—19350	—18000	—16500

VI. Practical Interpretation of Results.

The previous considerations have shown that when nitrogen peroxide reacts with water in aqueous solutions of nitric acid in the absence of oxygen the accomplishment of the reaction may be represented by the equation

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

The proportion of the nitrogen peroxide converted to nitric acid depends upon the concentration of the nitrogen peroxide in the gas, the proportion of nitric oxide already present, the concentration of the acid, and the temperature. In the presence of oxygen at concentrations such as are met with in gases from ammonia combustion or arc processes of fixation the progress of the reaction of re-oxidation of the nitric oxide progresses at a very much slower rate than the progress of the absorption reaction, so slow in fact that under conditions of efficient contact of the gases with the liquid, the nitrous gases are at all times substantially at equilibrium with the liquid and the concentration of the absorption may only proceed as the nitric oxide present in the gas re-oxidizes. It is therefore of considerable importance to know what per cent. of the nitrogen peroxide in a given gas can be converted to nitric acid when in contact with a given solution at a given temperature.

In Table V, a series of such values has been calculated using the constant $(P_{NO})/(P_{NO_2})^3$ evaluated for each acid and temperature. In the table the nitrogen peroxide in the original gas is given as the volume per cent. of nitrogen peroxide. It is seen that the percentage conversion for nitrogen peroxide gases of strengths such as are produced by fixation processes will vary with the dilution of the acid from 0%, representing no reaction, to approximately 66.7%, representing complete reaction. It is also seen that nitric acid above 50% in strength is a very poor medium for the absorption and conversion of the oxides. In fact if there is even a small proportion of nitric oxide in the gas the absorption will not occur at all and may only progress as the nitric oxide is re-oxidized by the excess oxygen of the gases.

TABLE V.

Per Cent. Conversion of Nitrogen Peroxide Gases to Nitric Acid by Absorption in Aqueous Solutions of Nitric Acid at Atmospheric Pressure.

Conc. HNO_3 % by wt.	Temp. ° C.	Log $\frac{(P_{NO})}{(P_{NO_2})^3}$.	% nitrogen peroxide in the gas.								
			0.1.	0.6.	1.0.	2.0.	4.0.	6.0.	8.0.	10.	20.
5	10	8.45	59.8	64.5	65.1	65.7	66.1	66.2	66.3	66.3	66.4
	25	7.90	57.1	63.3	64.4	65.3	65.7	65.9	66.1	66.2	66.3
	50	6.90	48.8	60.0	61.8	63.7	64.8	65.2	65.4	65.6	66.0
	75	5.93	32.6	53.0	56.8	60.2	62.7	63.6	64.2	64.6	65.3
10	10	7.58	54.0	62.5	63.6	64.9	65.5	65.7	65.9	66.0	66.2
	25	6.87	47.0	59.8	61.6	63.6	64.7	65.1	65.4	65.6	66.0
	50	5.85	27.8	52.2	56.0	60.1	62.3	63.5	64.1	64.5	65.3
	75	4.77	7.8	37.0	44.3	53.0	57.2	58.8	60.8	62.0	63.1
15	10	7.00	48.0	60.3	61.6	64.0	64.8	65.2	65.4	65.6	66.0
	25	6.25	35.6	55.8	58.7	61.7	63.5	64.1	64.7	65.0	65.5
	50	5.20	14.9	43.9	49.8	56.2	59.4	61.2	62.3	63.0	64.3
	75	4.12	2.4	24.2	32.6	44.0	51.5	55.0	57.1	58.4	61.5
20	10	6.50	40.0	57.0	59.2	62.3	63.8	64.5	64.8	65.1	65.7
	25	5.75	26.3	51.3	55.0	59.4	62.1	63.1	63.7	64.2	65.0
	50	4.64	6.3	34.5	42.1	51.4	56.2	58.6	60.0	61.0	63.1
	75	3.55	0.7	13.1	21.7	35.0	44.4	49.0	52.0	54.0	58.7
25	10	6.07	31.3	53.7	57.0	60.5	62.7	63.8	64.1	64.5	65.3
	25	5.25	17.7	44.2	50.0	56.4	59.6	61.2	62.1	62.9	64.2
	50	4.09	2.2	23.7	32.4	44.8	51.2	54.6	56.4	57.7	61.3
	75	3.03	0.2	5.9	11.8	23.6	35.0	41.8	45.2	48.2	54.8
30	10	5.62	24.4	48.4	53.3	57.6	60.8	62.1	62.9	63.5	64.6
	25	4.75	7.6	35.8	43.0	51.6	56.4	58.5	60.0	60.9	62.8
	50	3.55	0.7	13.1	21.2	34.6	44.2	48.8	51.7	53.6	58.3
	75	2.55	...	2.3	5.8	14.0	25.6	32.8	38.0	41.2	49.6
35	10	5.17	14.6	41.8	47.6	53.8	57.8	59.8	61.0	61.8	63.4
	25	4.25	3.0	26.8	34.0	44.4	51.0	54.4	56.4	58.0	61.0
	50	3.08	0.3	6.3	12.3	25.6	35.8	41.8	45.2	48.2	54.8
	75	2.09	...	0.8	2.2	8.0	16.5	23.4	28.8	32.4	43.6
40	10	4.68	6.1	32.4	39.5	47.6	53.4	56.1	57.6	58.7	61.4
	25	3.73	1.0	16.3	23.0	35.4	43.5	48.0	51.0	52.6	57.6
	50	2.60	0.1	2.6	5.6	15.6	26.0	32.0	37.0	40.4	49.6
	75	1.65	...	0.3	0.8	3.4	9.0	14.4	19.6	23.4	36.2
45	10	4.15	2.2	20.4	28.2	38.0	45.8	49.7	52.0	53.5	57.6
	25	3.18	0.4	7.4	12.0	22.5	33.3	38.4	42.1	44.6	52.0
	50	2.10	...	0.8	2.1	7.2	16.6	21.6	26.0	29.6	41.2
	75	1.17	...	...	0.3	1.1	4.0	7.1	10.5	13.6	25.7

TABLE V (*continued*).

Conc. HNO_3 % by wt.	Temp. ° C.	Log $\frac{(P_{NO})}{(P_{NO_2})^3}$.	% nitrogen peroxide in the gas.								
			0.1.	0.6.	1.0.	2.0.	4.0.	6.0.	8.0.	10.	20.
50	10	3.55	0.6	9.7	14.8	26.0	35.0	39.4	42.2	44.2	50.0
	25	2.66	...	2.8	5.0	9.6	20.8	26.6	30.7	34.3	42.0
	50	1.60	...	0.3	0.7	2.6	7.0	11.6	15.8	19.6	31.1
	75	0.71	...	...	...	0.4	1.5	3.0	4.8	6.7	15.9
55	10	2.92	...	2.7	5.2	11.5	17.9	22.0	26.2	27.7	32.6
	25	2.08	...	0.7	1.5	4.1	9.3	13.3	16.7	19.5	28.1
	50	1.10	...	...	0.2	0.9	2.8	5.0	8.4	9.4	18.9
	75	0.24	...	...	...	...	0.5	1.1	2.0	2.6	8.0
60	10	2.20	...	0.6	1.1	2.8	5.5	7.8	9.2	10.4	15.0
	25	1.42	...	...	0.2	1.0	2.6	4.1	5.5	6.8	12.2
	50	0.55	...	...	...	0.3	0.9	1.6	2.5	3.6	8.5
	75	—0.25	...	...	...	...	...	0.3	0.6	0.8	1.6
65	10	1.37	...	...	0.2	0.4	0.8	1.2	1.6	1.9	3.2
	25	0.70	...	...	...	...	0.5	0.8	1.1	1.5	3.0
	50	—0.05	...	...	...	...	...	...	0.6	0.8	1.5
	75	—0.75	...	...	...	...	...	...	...	...	...

VII. Summary of Results.

The chief reaction in the process of absorption of the nitrous gases, such as are produced by processes of ammonia oxidation or arc fixation, is

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO.$$

The rate of attainment of equilibrium in this reaction is very rapid, but in acids of even moderate concentration it is halted at a state far short of complete absorption of the nitrogen peroxide. The study of the equilibrium conditions of this reaction over a range of temperatures has established accurately the degree of absorption which will occur and the concentration of acid which may be produced with nitrous gases of any concentration and degree of oxidation.

The data from the study of the above equilibrium in combination with measurements of the vapor pressures of aqueous solutions of nitric acid has permitted the calculation of the free energies of nitric acid vapor and nitric acid in aqueous solutions.

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