

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

THE DISSOCIATION CONSTANTS OF NITROGEN TETROXIDE AND OF NITROGEN TRIOXIDE

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It was found necessary to redetermine the dissociation constants of nitrogen tetroxide and nitrogen trioxide accurately as part of a larger program dealing with the kinetics of the decomposition of nitrogen pentoxide.

Although the dissociation of nitrogen tetroxide is used as a classical example of an equilibrium, the data are unsatisfactory and no attempts have been made to correct for deviations from the simple gas laws. In fact there has not been a sufficiently large number of independent measurements at any single temperature to determine quantitatively how these deviations affect the value of the dissociation constant and how it changes with pressure. Some of the earlier work was rendered inaccurate by the use of stopcock grease, rubber or mercury, but Bodenstein¹ in 1922 described accurate measurements using an all-glass apparatus at different temperatures. He gave two values of the equilibrium constant, one for high pressures and another for low pressures.

The dissociation constant of nitrogen trioxide had not been known with any accuracy and in fact the very existence of nitrogen trioxide in the gas phase was disputed. The earlier work was inaccurate because the apparatus was not chemically inert. Evidence that some nitrogen trioxide exists in a gaseous mixture of nitric oxide and nitrogen tetroxide is offered by the fact that when such a mixture is bubbled through alkali the oxides are absorbed in equivalent amounts to form almost pure nitrite; nitric oxide alone does not react and nitrogen dioxide gives equal quantities of nitrite and nitrate. Wourtz² obtained two good measurements of the equilibrium constant by allowing nitric oxide to mix with an insufficient supply of oxygen. After the work described in this communication was well started a preliminary article on nitrogen trioxide was published by Abel and Proisl.³ Although the apparatus and technique was similar to that of the present authors, the work was not discontinued because it seemed desirable to have measurements of such an uncertain quantity from two different laboratories.

Furthermore, it seemed likely that accurate measurements on these two equilibria might reveal the possible existence of oxides of nitrogen other than the four in question. Such oxides would be of interest in connection with studies on kinetics. To determine the effect of inert gases

¹ Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

² Wourtz, *Compt. rend.*, **170**, 109 (1920).

³ Abel and Proisl, *Z. Electrochem.*, **35**, 712 (1929).

on the equilibrium and the rate of dissociation, measurements were made in the presence of such gases.

Experimental Procedure

The apparatus is shown in Fig. 1. It is so constructed that the reacting gases come in contact with no material other than glass. Each gas is sealed off in a one-liter Pyrex flask and its pressure is measured by means of the glass manometer developed in this Laboratory.⁴ A measured air pressure is balanced against the pressure in the flask through a glass diaphragm which is provided with an electrical contact. The air can be evacuated rapidly through K or slowly through the capillary J or the pressure may be allowed to increase rapidly through H or slowly through G, thus facilitating the rapid and exact adjustment of the balancing pressure. Calcium chloride tubes are used to keep the manometer system dry. A trap L and an automatic check valve N, consisting of a glass bead seated on a small rubber tube inside a glass tube, were used to prevent water running back from the aspirator.

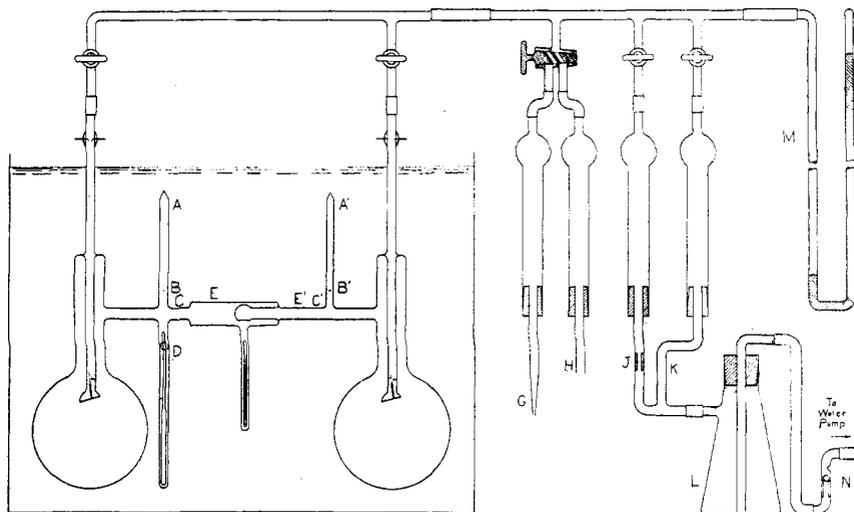


Fig. 1.

The device for keeping the gases separate and later allowing them to mix consists of a glass bulb blown from 12-mm. tubing and flattened on one side; this is sealed into 20-mm. tubing, and a side tube attached opposite the flat place. This central piece is now sealed onto the side arms of the two flasks at E and E', and the flasks clamped in position on the ring stand which is later to be set into the thermostat. An iron nail enclosed in glass tubing of such a size that it moves easily inside the side tube is now inserted in the latter and the tube sealed off so as to leave about two centimeters in which the hammer may move. When it is desired to break the bulb, a solenoid is placed around the side tube and the hammer driven up into the bulb when a current is sent through the solenoid. It is imperative that the bulb be flattened; the keystone effect of a spherical bulb is so marked that the glass of the hammer breaks instead of the bulb. The most durable hammers are those made of soft glass padded with asbestos at each end of the nail. The asbestos serves to keep the iron from scratching the glass and to equalize the pres-

⁴ Daniels, *THIS JOURNAL*, 50, 1115 (1928).

sure of the nail on the end of the tube as it is bumped against the bulb. The glass must be worked quickly in the flame and at some distance from the nail, to prevent the temperature strains which would result if the metal were allowed to become heated. In these experiments, small finishing nails ground round on the ends and sealed inside four millimeter tubing moving in seven millimeter tubing, were used as hammers.

The solenoid was made by winding 400 ft. of No. 24 double cotton covered copper wire on a brass tube about 6 cm. long. It was connected in series with a rheostat to a 55 v. direct current circuit and operated at a current of five amperes or less.

A similar device was used at D for breaking the file-scratched capillary of a bulb containing nitrogen tetroxide.

The volumes of the flasks were obtained by filling with distilled water to marks at B, C and B', C' and weighing. After the center piece was inserted, the volumes on each side of the bulb were obtained by tipping to one side or the other and running in water from a standardized buret through A and A' to C and C'.

The outside volume of the filled nitrogen tetroxide bulb was found from the volume of water displaced by it and the inner volume of the broken bulb was determined after the completion of an experiment by running in water from a buret. The difference between the two gives the volume of glass in the bulb. The volumes of the side arms A and A' were obtained at the end of the run by inverting the flasks and filling the arms to the marks B and B' from a buret.

A second apparatus using 500-cc. flasks connected by 20-mm. tubing was also used. No difference could be detected in the results obtained with the different apparatus. The larger connecting tube decreased the time necessary for complete diffusion of the two gases.

The gas for the right-hand flask was prepared and stored over concentrated sulfuric acid in a two-liter flask with a three-way stopcock. When the gas was needed, the stopcock was sealed to the filling tube A'. The inorganic stopcock lubricant described by Stephens⁶ was used. It was prepared by heating a mixture of 85% phosphoric acid and metaphosphoric acid to 300°.

The two flasks of known volume are sealed to the center piece and the whole clamped in position. After setting in the hammer, the flasks are dried and evacuated thoroughly and the zero points of the diaphragms are determined. A bulb of known volume containing a weighed amount of nitrogen tetroxide is dropped in through A and the left-hand flask evacuated thoroughly while being heated with a luminous flame to drive out adsorbed water. It is then sealed off at A and the side arm A' is sealed to the gas holder and evacuated through the three-way stopcock, while the flask is heated. Some gas is allowed to enter the flask and then it is re-evacuated; finally it is filled with gas to approximately the desired pressure and sealed off. The nitrogen tetroxide bulb is broken, the apparatus immersed in the thermostat, and the pressure in the two flasks determined. The separating bulb is then broken and the pressures determined at intervals until there is no further change, showing that diffusion has been complete and equilibrium has been reached. The flasks are next opened to the atmosphere and the zero points re-determined. The broken center piece is cut off at E and E' and the volumes of the arms A and A' and of the nitrogen tetroxide bulb determined. After sealing in a new central piece the apparatus is ready for a second determination.

The apparatus was completely immersed in a large water thermostat the temperature of which was kept constant to within 0.05° and measured with a calibrated thermometer. The closed-end manometer agreed with a standard barometer within 0.2 mm. and the glass diaphragm gave readings reproducible to within 1 mm. All manometer readings were corrected to 0°.

⁶ Stephens, *THIS JOURNAL*, 52, 635 (1930).

The nitrogen tetroxide was prepared by heating lead nitrate and condensing the gas in a flask containing phosphorus pentoxide, from which it was redistilled after several days into weighed bulbs, in the manner described by Daniels, Mathews and Williams.⁶

There was some possibility that this method of procedure might allow the nitrogen tetroxide to become contaminated with moisture, due to diffusion of air down the tube while being filled. To eliminate this uncertainty, several experiments were made with nitrogen tetroxide sealed off in the following manner. A tube of the shape shown in Fig. 2 was weighed, and the bulb Q filled with phosphorus pentoxide. Nitrogen tetroxide was now distilled into the bulb and the tube sealed off at R. The nitrogen tetroxide was allowed to dry for a few days and then distilled over into the right-hand arm, which was then sealed off at S. All the glass was then thoroughly cleaned and dried, and reweighed; the difference between the original and final weights gave the weight of nitrogen tetroxide sealed in the bulb. Experiments using this technique gave results in agreement with those of the simpler technique described in the reference, whence the conclusion was drawn that the simpler procedure was satisfactory.

Nitric oxide was prepared from sodium nitrite and sulfuric acid according to Noyes,⁷ bubbled through sulfuric acid and stored over concentrated sulfuric acid in the gas holder.

Measurements of $N_2O_4 \rightleftharpoons 2NO_2$.—In every experiment of this investigation liquid nitrogen tetroxide was weighed out and the pressure and volume of the gas were measured in the left-hand flask. In several experiments the right-hand flask was evacuated and a second determination of the dissociation constant was made at a lower pressure after breaking the connecting bulb.

In all cases the dissociation constant, $K_{N_2O_4}$, was calculated from the formula

$$K_{N_2O_4} = \frac{4\alpha^2 P}{1 - \alpha^2}$$

where P is the measured pressure in atmospheres and α is the degree of dissociation as defined by the expression

$$\alpha = \frac{P - p_{N_2O_4}^0}{p_{N_2O_4}^0}$$

$p_{N_2O_4}^0$ is the pressure which would be exerted by undissociated nitrogen tetroxide, *i. e.*

$$p_{N_2O_4}^0 = \frac{g}{M} \frac{RT}{V}$$

⁶ Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1929, p. 115.

⁷ W. A. Noyes, THIS JOURNAL, 47, 2170 (1925).

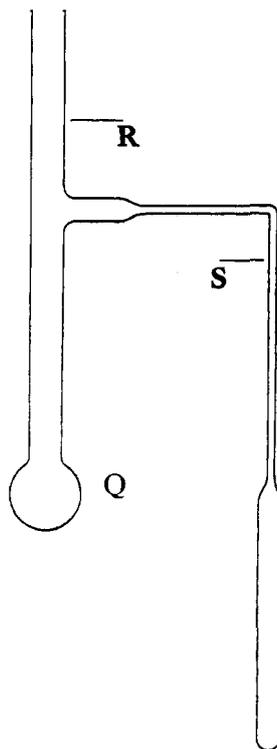


Fig. 2.

in which g is the weight of nitrogen tetroxide, M is the molecular weight, and R , T and V have their usual significance.

In these and all subsequent calculations a lower case p with subscript referring to the gas in question indicates the partial pressure of that gas; a superscript zero indicates the idealized pressure which the gas would exert if it did not dissociate nor react with other gases; and a capital P represents the total, measured pressure.

TABLE I
EQUILIBRIUM $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ AT 25.0°

$C_{\text{N}_2\text{O}_4}^0$ moles N_2O_4 /liter $\times 10^3$	P , atm.	$K_{\text{N}_2\text{O}_4}$	$C_{\text{N}_2\text{O}_4}^0$ moles N_2O_4 /liter $\times 10^3$	P , atm.	$K_{\text{N}_2\text{O}_4}$
4.49	0.1566	0.1380	14.18	0.4369	0.1265*
6.28	.2118	.1419*	14.93	.4588	.1294
6.51	.2172	.1323	14.98	.4598	.1278
7.65	.5129	.1384†	15.39	.4743	.1381
8.90	.2889	.1378	15.85	.4843	.1290*
8.98	.6543	.1325‡	16.67	.5107	.1393
9.33	.5699	.1359†	17.31	.5254	.1295
9.87	.3150	.1287*	18.01	.5435	.1261
10.15	.3271	.1470*	18.02	.5443	.1274
10.54	.3357	.1349	18.40	.5554	.1290
11.62	.3660	.1318*	18.99	.5719	.1292
12.10	.3793	.1310	19.84	.5996	.1412*
12.26	.3841	.1318*	20.07	.6007	.1272
12.59	.3941	.1340*	20.90	.6214	.1218
12.59	.3942	.1340*	21.40	.6349	.1205
12.89	.4021	.1319	21.62	.6373	.1121
13.59	.4213	.1303	27.72	.8081	.1236
			29.68	.8623	.1261*

TABLE II
EQUILIBRIUM $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$

$C_{\text{N}_2\text{O}_4}^0$ moles/liter $\times 10^3$	35.0°			45.0°		
	P , atm.	$K_{\text{N}_2\text{O}_4}$	ΔH (25-35°)	P , atm.	$K_{\text{N}_2\text{O}_4}$	ΔH (35-45°)
6.28	0.2382	0.3174	14700	0.2662	0.6771	14760
9.87	.3533	.2950	15140			
10.15	.3649	.3163	13990	.4064	.6491	14010
11.62	.4086	.2937	14640	.4554	.6103	14250
12.26	.4287	.2953	14730			
12.59	.4391	.2949	14400	.4889	.6104	14180
12.59	.4400	.3007	14670	.4903	.6266	14320
14.18	.4871	.2877	15010	.5446	.6230	15050
15.85	.5378	.2859	14540	.5985	.5993	14420
16.67	.5659	.3016	14110	.6295	.6290	14340
17.31	.5823	.2860	14470	.6484	.6068	14660
19.84	.6623	.3032	13950	.7349	.6280	14190
21.62	.7065	.2644	15670	.7834	.5567	14510
27.72	.8902	.2806	14950	.9814	.5718	13850
29.68	.9470	.2792	14520	1.0474	.5934	14700

The experimental results are summarized in Tables I and II and in Fig. 3. In each case the ideal concentration, $C_{N_2O_4}^0$, is given assuming no dissociation. In Table I the values marked (*) were determined with the special drying precautions described above. The two marked (†) were obtained in the presence of 0.2608 and 0.2689 atmosphere of oxygen and the experiment marked (‡) was made in the presence of 0.3643 atmosphere of carbon dioxide. These determinations are designated with triangles in Fig. 3. In these experiments the right-hand flask was filled with the foreign gas before breaking the connecting bulb.

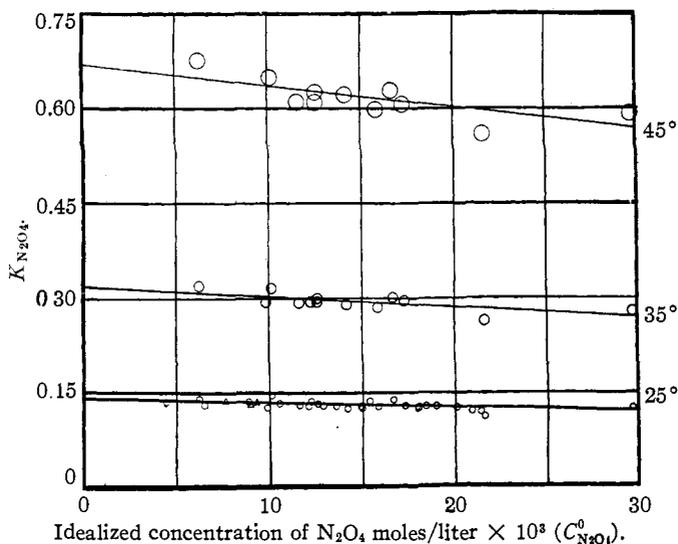


Fig. 3.

The calculation of the dissociation constant is such that an error of 1 mm. in the pressure measurements introduces a larger error in the value of the equilibrium constant at 45° than at 25° and the circles have been drawn larger. In each case the radius is a measure of the experimental accuracy.

The heat of dissociation, ΔH , as calculated from the van't Hoff equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H (T_2 - T_1)}{2.303 R T_1 T_2}$$

is included for each experiment in Table II. Although the equilibrium constant is markedly affected at the higher pressures by the deviations from the perfect gas laws, the heat of dissociation remains nearly constant.

Measurements of $N_2O_3 \rightleftharpoons NO_2 + NO$.—When nitrogen tetroxide expands into an evacuated space the resulting pressure is greater than that calculated by the ideal gas laws on account of the greater dissociation into nitrogen dioxide at the lower pressures. When it expands into

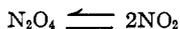
an inert gas the partial pressures of nitrogen tetroxide and nitrogen dioxide are still the same as when expanding into an evacuated space, but when it expands into nitric oxide the pressures are smaller on account of the reaction



The calculation of the equilibrium constant for this reaction is complicated by the fact that as soon as nitrogen dioxide is used up more nitrogen tetroxide dissociates. However, the following relations between the partial pressures of the gases present must hold under any conditions

$$\begin{aligned} K_{\text{N}_2\text{O}_4} &= p_{\text{NO}_2}^2 / p_{\text{N}_2\text{O}_4} \\ p_{\text{NO}}^0 &= p_{\text{NO}} + p_{\text{N}_2\text{O}_3} \\ 2p_{\text{N}_2\text{O}_4}^0 &= 2p_{\text{N}_2\text{O}_4} + p_{\text{NO}_2} + p_{\text{N}_2\text{O}_3} \\ P &= p_{\text{N}_2\text{O}_4} + p_{\text{NO}_2} + p_{\text{NO}} + p_{\text{N}_2\text{O}_3} \end{aligned}$$

At equilibrium, these four equations must be simultaneously satisfied. The four values on the left are experimentally measured quantities. $K_{\text{N}_2\text{O}_4}$ is the value of the equilibrium constant for the reaction



obtained from the curves in Fig. 3 for the particular concentration of nitrogen tetroxide existing in the final volume, as calculated from the original weight of nitrogen tetroxide. A very slight approximation is being made here, because the concentration of nitrogen tetroxide will decrease on account of the formation of some nitrogen trioxide; the resulting change in K , however, will cause no change in the results within the experimental error. p_{NO}^0 is the pressure which would be exerted by the original quantity of nitric oxide if present alone in the final volume. $p_{\text{N}_2\text{O}_4}^0$ is the pressure exerted by the original weight of nitrogen tetroxide if present alone and undissociated in the final volume. P is the total pressure as measured at the end of the experiment.

Solving these four equations simultaneously

$$\begin{aligned} p_{\text{NO}_2} &= \frac{-K_{\text{N}_2\text{O}_4} + \sqrt{K_{\text{N}_2\text{O}_4}^2 + 4K_{\text{N}_2\text{O}_4}(P - p_{\text{NO}}^0)}}{2} \\ p_{\text{NO}} &= 2P - p_{\text{N}_2\text{O}_4}^0 - p_{\text{NO}}^0 - p_{\text{NO}_2} \\ p_{\text{N}_2\text{O}_3} &= p_{\text{NO}}^0 - p_{\text{NO}} \end{aligned}$$

whence $K_{\text{N}_2\text{O}_3}$ can be calculated from

$$K_{\text{N}_2\text{O}_3} = \frac{p_{\text{NO}} \times p_{\text{NO}_2}}{p_{\text{N}_2\text{O}_3}}$$

The results are shown in Tables III, IV and V and in Fig. 4, in which the values of $K_{\text{N}_2\text{O}_3}$ are plotted against the concentration of nitrogen trioxide assuming no dissociation; that is against $C_{\text{N}_2\text{O}_3}^0$, where

$$C_{\text{N}_2\text{O}_3}^0 = 1/2(p_{\text{NO}_2} + p_{\text{NO}} + 2p_{\text{N}_2\text{O}_3}) \frac{1}{RT}$$

In the determination of $K_{N_2O_3}$ there is a large accumulation of errors such that the experimental error amounts to about 10%. The curves for the three different temperatures are plotted on different scales, such that the

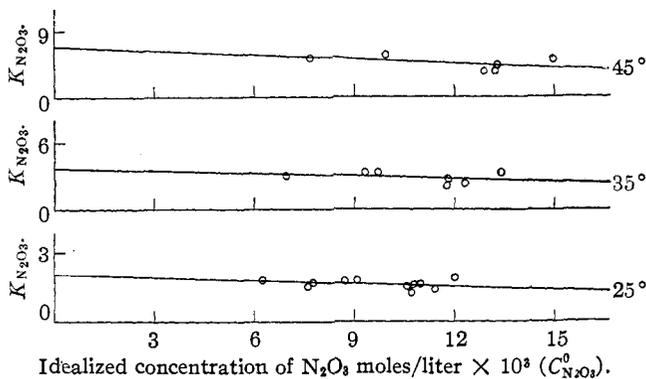


Fig. 4.

radius of the circles drawn around the points represents in each case the experimental error.

The data and calculations for the first experiment in Table III are given to illustrate the details of the method. Here the weight of nitrogen

TABLE III
EQUILIBRIUM $N_2O_3 \rightleftharpoons NO + NO_2$ AT 25°

$C_{N_2O_4}^0 \times 10^3$	p_{NO}^0	P	$C_{N_2O_3}^0 \times 10^3$	$K_{N_2O_3}$
6.24	0.1834	0.3868	6.26	1.87
6.76	.2397	.4551	7.62	1.59
8.96	.2246	.5046	7.76	1.74
5.77	.3048	.4902	8.72	1.83
6.12	.3177	.5131	9.09	1.86
9.45	.3477	.6346	10.58	1.54
11.03	.3351	.6638	10.71	1.28
14.15	.3057	.7261	10.77	1.63
9.99	.3614	.6631	10.98	1.59
8.58	.3955	.6540	11.44	1.42
15.18	.3736	.8205	12.02	1.98

TABLE IV
EQUILIBRIUM $N_2O_3 \rightleftharpoons NO + NO_2$ AT 35°

$C_{N_2O_4}^0 \times 10^3$	p_{NO}^0	P	$C_{N_2O_3}^0 \times 10^3$	$K_{N_2O_3}$
6.24	0.1900	0.4199	6.99	2.99
5.77	.3144	.5257	9.34	3.26
6.12	.3287	.5509	9.74	3.26
11.03	.3466	.7173	11.77	2.09
14.15	.3160	.7868	11.82	2.65
8.58	.4093	.7027	12.32	2.30
15.18	.3862	.8866	13.43	3.26

TABLE V
EQUILIBRIUM $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO} + \text{NO}_2$ AT 45°

$C_{\text{N}_2\text{O}_4}^0 \times 10^3$	p_{NO}^0	P	$C_{\text{N}_2\text{O}_4}^0 \times 10^3$	$K_{\text{N}_2\text{O}_4}$
6.24	0.1958	0.4544	7.69	5.36
5.77	.3243	.5625	9.97	5.66
11.03	.3576	.7753	12.89	3.38
8.58	.4226	.7530	13.23	3.46
14.15	.3263	.8540	13.25	4.22
15.18	.3989	.9605	14.98	5.07

tetroxide introduced into the left-hand flask was 1.2798 g., the volume of the flask was 1.1042 liters, the pressure, P , at 25° , 299.6 mm. From these data, $K_{\text{N}_2\text{O}_4}$ is calculated.

$$p_{\text{N}_2\text{O}_4}^0 = \frac{1.2798 \times 0.08206 \times 298}{92.02 \times 1.1042} = 0.3080$$

$$\alpha^2 = \left(\frac{P - p_{\text{N}_2\text{O}_4}^0}{p_{\text{N}_2\text{O}_4}^0} \right)^2 = \left(\frac{\frac{299.6}{760} - 0.3080}{0.3080} \right)^2 = 0.0783$$

$$K_{\text{N}_2\text{O}_4} = \frac{4\alpha^2}{1 - \alpha^2} P = \frac{4 \times 0.0783}{0.9217} \times 0.3942 = 0.1340$$

$$C_{\text{N}_2\text{O}_4}^0 = \frac{1.2798}{92.02 \times 1.1042} = 12.59 \times 10^{-3}$$

The volume of the right-hand flask was 1.1254 liters and the pressure of nitric oxide in it was 276.2 mm. The final pressure measured at equilibrium after breaking the connection was 294.0 mm. From these data and those above, $K_{\text{N}_2\text{O}_4}$ is calculated as follows.

$$p_{\text{NO}}^0 = \frac{276.2}{760} \times \frac{1.1254}{(1.1254 + 1.1042)} = 0.1834$$

$$C_{\text{N}_2\text{O}_4}^0 = \frac{1.2798}{92.02 \times 2.2296} = 6.236 \times 10^{-3}$$

From an equation given below for the curve in Fig. 3

$$K_{\text{N}_2\text{O}_4} = 0.1426 - 0.7588 \times 6.236 \times 10^{-3} = 0.1379$$

$$p_{\text{N}_2\text{O}_4}^0 = \frac{1.2798}{92.02} \times \frac{0.08206 \times 298}{2.2296} = 0.1525$$

$$P = \frac{294.0}{760} = 0.3868$$

These values for $p_{\text{N}_2\text{O}_4}^0$, p_{NO}^0 , P , and $K_{\text{N}_2\text{O}_4}$ are to be substituted in the solutions of the simultaneous equations already given, to give

$$p_{\text{NO}_2} = \frac{-0.1379 + \sqrt{(0.1379)^2 + 4 \times 0.1379(0.3868 - 0.1834)}}{2} = 0.1122$$

$$p_{\text{NO}} = 2 \times 0.3868 - (2 \times 0.1525 + 0.1834 + 0.1122) = 0.1730$$

$$p_{\text{N}_2\text{O}_4} = 0.1834 - 0.1730 = 0.0104$$

$$K_{\text{N}_2\text{O}_4} = \frac{0.1122 \times 0.1730}{0.0104} = 1.87$$

$$C_{\text{N}_2\text{O}_4}^0 = 1/2(0.1122 + 0.1730 + 2 \times 0.0104) \frac{1}{0.08206 \times 298} = 6.27 \times 10^{-3}$$

Discussion

The number of independent measurements at a single temperature is sufficiently great to permit reliable calculations of the influence of pressure on the equilibrium constants. The three curves of Fig. 3 are reproduced by the following equations obtained by the method of least squares.

TABLE VI

Temp., °C.	Equilibrium constants ($C_{N_2O_4}^0 = \text{total weight}/92.02 \times \text{volume in liters}$)
25	$K_p = 0.1426 - 0.7588 \times C_{N_2O_4}^0$
35	$K_p = .3183 - 1.591 \times C_{N_2O_4}^0$
45	$K_p = .6706 - 3.382 \times C_{N_2O_4}^0$

The idealized equilibrium constants extrapolated to zero pressure are 0.1426 at 25°, 0.3183 at 35° and 0.6706 at 45°. These values are important for they give the equilibrium constants for perfect gases and the laws of thermodynamics may be applied with exactness. They correspond to values obtained with fugacities or activities rather than pressures. Then

$$-\Delta F^\circ = RT \ln K_p$$

and $\Delta F_{298}^\circ = 1154$ calories, $\Delta F_{308}^\circ = 700$ calories and $\Delta F_{318}^\circ = 252$ calories. ΔF° is the increase in free energy necessary to convert one mole of nitrogen tetroxide at a fugacity of 1 atmosphere into 2 moles of nitrogen dioxide at a fugacity of 1 atmosphere. From the free energy of formation of nitrogen dioxide⁸ the free energy of formation of 1 mole of nitrogen tetroxide from nitrogen and oxygen at 25° and 1 atmosphere is 23,836 calories.

The heat of dissociation, ΔH , calculated from the values of the equilibrium constant extrapolated to zero pressure gives from 25–35° 14,670 cal., from 35–45° 14,530 cal. The entropy change, ΔS , may be calculated from the equation

$$\Delta F = \Delta H - T\Delta S$$

using the average value of the heat of dissociation $\Delta H = 14,600$. ΔS is constant over this range of temperature and equal to 45.1 entropy units.

The values of the equilibrium constant are somewhat lower than those calculated for corresponding pressures from the equations of Bodenstein.¹

By weighing out the samples of nitrogen tetroxide, a more direct evaluation of the amount of material present is obtained than by the method of Bodenstein, who determined the concentration of nitrogen dioxide from the pressures existing at temperatures in the neighborhood of 150°, making corrections for the nitrogen tetroxide and nitric oxide and oxygen present at those temperatures. Further, this communication reports a large number of separate determinations made on different samples of

⁸ "International Critical Tables" ("revised" data of Randall and White), McGraw-Hill Book Co., Inc., New York, Vol. VII, 1930, p. 239.

tetroxide, whereas Bodenstein used one original sample and obtained results at lower pressures by progressively removing portions of this original material from the reaction flask. On the other hand, Bodenstein's manometer was more sensitive and the temperature range studied was considerably greater.

The decrease in the equilibrium constant with increase in pressure is due to the deviation of the gases from the ideal gas laws. Although the critical data for the gases are inaccessible to experimental measurement, it is reasonable to assume that they are similar to those of sulfur dioxide, which has a structure somewhat like that of nitrogen dioxide and a boiling point near that of nitrogen tetroxide. Assuming that the mixture of gases in the reaction vessel acts like sulfur dioxide, as far as its non-ideal properties are concerned, it is possible to idealize the total pressure and recalculate α and $K_{N_2O_4}$. Using Berthelot's equation of state and the critical data of sulfur dioxide ($T_c = 430^\circ\text{K.}$ and $P_c = 78 \text{ atm.}$), the values of $K_{N_2O_4}$ calculated from the idealized pressures agree with those obtained by extrapolating to zero pressure.⁹

In spite of the fact that the change of K with pressure seems to be explained by the deviation of nitrogen tetroxide and nitrogen dioxide from the gas laws, there was a further possibility that it might be due to increased adsorption of the gases on the glass walls at higher pressures, complicated by a preferential adsorption of the nitrogen tetroxide over the nitrogen dioxide. From the start it seemed unlikely that the decrease of K could be explained in this way, because calculation showed that at a concentration of 0.030 mole/liter, the unlikely amount of 0.037 g. of material would have to be adsorbed in the liter flask at 25° in order to account for the drop from $K = 0.1426$ at zero concentration to $K = 0.1198$ at a concentration of 0.030 mole/liter. To investigate this point, scales of Pyrex glass made by breaking up thin bulbs, with a total surface at least twice as great as the inner surface of a flask, were put into a U-tube, covered with water overnight in order partially to etch the surface, dried by heating in a stream of dry air, and then weighed. Liquid nitrogen tetroxide was poured into the tube, the liquid allowed to evaporate and the U-tube re-weighed. An increase in weight of only 0.0013 g. was observed. In another experiment, gaseous nitrogen tetroxide was passed through the weighed U-tube; no increase in weight could be detected.

⁹ The fact that one constituent of the gas mixture may show a deviation from the gas laws different in degree from that of the other does not alter this result. Any idealization whatsoever must increase the total pressure and, consequently, the degree of dissociation; the equilibrium constant is thus increased in every case, in spite of the fact that, as is probably true, a greater correction is to be applied to nitrogen tetroxide than to nitrogen dioxide. The assumption made above is that the combined effect of the deviations of the two gases is such as to give a resultant non-ideality, over the temperature range in consideration, like that of sulfur dioxide.

Finally, glass scales having an area over twenty times as great as that of the inner surface of a liter flask, were treated overnight with chromic acid, washed and dried. A regular determination of the equilibrium constant with this extra glass in the apparatus showed that any adsorption of nitrogen tetroxide or nitrogen dioxide is entirely negligible.

The fact that inert gases such as oxygen and carbon dioxide do not affect the equilibrium constant is of interest in kinetics. The decomposition of nitrogen tetroxide is probably unimolecular and its formation is a bimolecular reaction. If a large increase in the number of collisions affects either reaction more than the other, the equilibrium constant should be shifted. However, no influence of this kind was found.

An interesting observation regarding diffusion was made during the course of the experiments. When the nitrogen tetroxide in the left-hand flask was allowed to expand into a vacuum the equilibrium was reached quickly. When the right-hand flask was filled with a gas, such as oxygen, carbon dioxide or nitric oxide, twenty hours or more were necessary to insure complete mixing of the gases. The rate of diffusion was determined qualitatively by observing the decrease in red color in the left-hand flask and its increase in the right-hand flask. It was measured more quantitatively by observing the pressure increase on standing. As the nitrogen tetroxide diffuses to regions of lower concentrations it dissociates to a greater extent and increases the total pressure. In many experiments involving the mixing of gases there is no simple indicator to tell when the mixing is complete. With a smaller connecting tube or with a stopcock in the tube, the rate of mixing would be very much lower.

The curves of Fig. 4 are reproduced by the following equations obtained by the method of least squares.

TABLE VII	
$\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2 + \text{NO}$	
Temp., °C.	Equilibrium constants
25	$K_p = 2.105 - 45.63 C_{\text{N}_2\text{O}_4}^0$
35	$K_p = 3.673 - 78.11 C_{\text{N}_2\text{O}_4}^0$
45	$K_p = 6.880 - 196.4 C_{\text{N}_2\text{O}_4}^0$

The heat of dissociation calculated from the van't Hoff equation between 25 and 35° is 10,160 at zero concentration (from extrapolated values of K) and 10,310 at a concentration of 15×10^{-3} moles per liter. Calculating between 35 and 45° the heat of dissociation is 12,210 at zero concentration and 8820 at a concentration of 15×10^{-3} . From the constancy of the value of $\Delta H_{(25-35^\circ)}$ as the pressure changes and from analogy with the results on nitrogen tetroxide, it seems likely that the variation of $\Delta H_{(35-45^\circ)}$ is due to experimental error. At 45° the errors are considerably magnified and the number of determinations is rather small.

The curve is probably slightly too steep. An average of the four values gives $\Delta H = 10,300$.

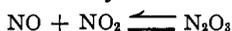
The free energies changes are as follows:

$$\Delta F_{298}^{\circ} = -441 \quad \Delta F_{308}^{\circ} = -796 \quad \Delta F_{216}^{\circ} = -1218$$

and using the data of "International Critical Tables," Vol. VII, p. 238, for the free energy of formation of nitric oxide and nitrogen dioxide, the free energy of formation of nitrogen trioxide from its elements is 33,805 calories.

The values of the equilibrium constant check only fairly well with those of Abel and Proisl.³ For example, at 25° the value of K extrapolated to zero concentration from their curve and translated into the notation used in this communication gives 1.43 as against the value of 2.10 given here.

The straight line relation between $C_{N_2O_3}$ and $K_{N_2O_3}$ seems definitely to indicate that the reaction is actually



No other reaction gives a smooth straight line. If the equilibrium constant is calculated from



the "constant" varies greatly with pressure, even though fairly regularly. If the reaction is considered to be



the equilibrium "constant" shows wide and irregular variations. If the calculations are made from



the "constant" is very irregular.

It is believed that the results of the present investigation show that the dissociation of nitrogen tetroxide is correctly represented by the equation $N_2O_4 \rightleftharpoons 2NO_2$ and that the dissociation of nitrogen trioxide is correctly represented by the equation $N_2O_3 \rightleftharpoons NO + NO_2$. Within the limits of experimental accuracy recorded here it may be concluded that no other oxides of nitrogen are present in appreciable amounts in the partially dissociated gases.

Summary

1. The dissociation constant for gaseous nitrogen tetroxide has been measured at 25, 35 and 45° with special reference to the influence of pressure. The dissociation constant is directly proportional to the pressure and is about 13% greater at 0.1 atmosphere than at 1 atmosphere.
2. The presence of inert gases such as oxygen and carbon dioxide has no effect upon the dissociation constant in the above reaction.
3. The dissociation constant for gaseous nitrogen trioxide has been measured with an all-glass apparatus at 25, 35 and 45° at different pressures.
4. The value of the equilibrium constant is not affected by any adsorption on the glass walls.

5. The influence of pressure on the equilibrium constants can be attributed to deviations from the simple gas laws.

6. The true equilibrium constants for thermodynamical calculations have been determined by extrapolation to zero pressure. Calculations are given for ΔF , ΔH and ΔS .

7. The measurements indicate that the dissociations proceed according to the reactions $N_2O_4 \rightleftharpoons 2NO_2$ and $N_2O_3 \rightleftharpoons NO + NO_2$.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, CAMBRIDGE, ENGLAND]

THE DIELECTRIC PROPERTIES OF ANTIMONY PENTACHLORIDE AND PHOSPHORUS PENTACHLORIDE¹

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The dielectric properties of antimony pentachloride and phosphorus pentachloride were studied in the hope of adding some information on which to consider the structure of these compounds.

The apparatus used has been described by Lowry and Jessop.² The materials used were carefully purified. The carbon tetrachloride was treated with chlorine and allowed to stand in sunlight for several days. It was dried with freshly fused calcium chloride and distilled. The antimony pentachloride was distilled three times in a vacuum and kept sealed in glass. It had a very light color and a sharp melting point. The phosphorus pentachloride used to make the solutions was contained in a small sealed glass vessel into which it had been distilled in vacuum.

In order to test out the apparatus, the dielectric constant of pure dry carbon tetrachloride was determined in it over a range of temperatures. These values and also the molar polarizations calculated from them are given in Table I. These agree very well with published data.³ Pure benzene and chloroform were used to calibrate the cell. The densities

TABLE I

DIELECTRIC CONSTANT AND MOLAR POLARIZATION OF CARBON TETRACHLORIDE

Temp., °C.	Dielectric constant	Density, g./cc.	Molar polarization, cc.
3.5	2.268	1.62638	28.1
16.5	2.239	1.60128	28.1
26.3	2.217	1.58230	28.0
46.4	2.171	1.54264	28.0

¹ Part of this work was done during the time that one of the authors, J. H. Simons, was a National Research Council Fellow.

² Lowry and Jessop, *J. Chem. Soc.*, 782 (1930).

³ Compare Stranathan, *Phys. Rev.*, 31, 653 (1928).