The author wishes to thank Professor Worth H. Rodebush for his help on this problem, and also to thank E. I. du Pont de Nemours and Company of Wilmington, Delaware, under whose Fellowship this work was done.

Summary

1. An attempt has been made to calculate the entropy of carbon dioxide from thermal data and from equilibrium data in an effort to furnish another check on the third law of thermodynamics.

2. The best values of the specific heats, heat contents and free energies of the components and reactions have been selected from the literature.

3. Experimental data on the heat of sublimation of carbon dioxide have been obtained with an accuracy of ±35 calories.

4. The results show a discrepancy of 2.64 entropy units between the value as calculated from thermal and equilibrium data on carbon, oxygen and carbon dioxide, and the value as calculated directly from the thermal data for carbon dioxide itself.

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THE RATE OF DECOMPOSITION OF NITROGEN PENTOXIDE AT LOW CONCENTRATIONS

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The study of unimolecular reactions comprises an important branch of chemical kinetics. The specific decomposition rates of these reactions have been supposed to be independent of concentration, and on the basis of this assumption Perrin[1] has maintained that they must be independent of molecular collision. Lindemann[2] has pointed out, however, that we do not possess sufficient evidence to conclude that the specific reaction rate of a unimolecular reaction is independent of the concentration at low concentrations. The purpose of this investigation was to determine, if possible, whether or not there is ground for believing that a reaction of the first order may behave differently at low concentrations than at ordinary concentrations.

Recently a new importance has become attached to the study of unimolecular reactions. In a keen analysis, Rice[3] has denied the very existence of slow reactions of this type, maintaining that reactions which satisfy the equation for a unimolecular reaction and have been classed as unimolecular are in reality bimolecular, catalytic reactions. While admitting

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[1] Perrin, *Trans. Faraday Soc.*, **17**, 546 (1922).

[2] Lindemann, *ibid.*, **17**, 598 (1922).

[3] Rice, THIS JOURNAL, **46**, 2405 (1924).

the truth of much of Rice's argument the authors are not yet willing to admit that the decomposition of nitrogen pentoxide is other than unimolecular. At present, this reaction appears to stand as the sole survivor of the group of truly unimolecular reactions. Whether it, too, will fall or whether new reactions will come to its aid, is a question for the future to decide. There seems to be no *a priori* reason for the non-existence of a unimolecular reaction.

The decomposition of gaseous nitrogen pentoxide has been investigated by Daniels and Johnston[4] at pressures from 56 mm. to 696 mm., and in solution it has been investigated by Lueck[5] up to a calculated osmotic pressure of nearly ten atmospheres.[6] The specific reaction rate was found to be the same for all of these concentrations. In carrying the study to lower concentrations it was necessary to abandon the pressure and volume measurements used previously, because they were not sufficiently accurate under these conditions. Fortunately, the course of the reaction may be followed by analytical methods of high sensitivity. The reaction velocity constant and its temperature coefficient have been determined by this means at pressures ranging from 280 mm. to 0.01 mm.

Experimental Procedure

The apparatus with which the determinations were made is shown in Fig. 1.

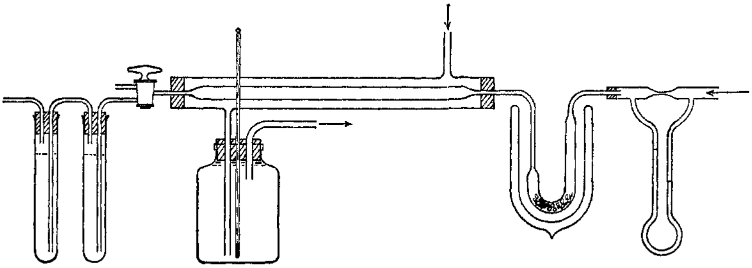

Fig. 1.—Apparatus for measuring by chemical analysis the decomposition rate of nitrogen pentoxide at low concentrations.

Dry, oxygen-free nitrogen was passed through a flowmeter and thence into a U-tube containing solid nitrogen pentoxide kept at a constant temperature in a vacuum vessel. The nitrogen pentoxide was made by dehydrating 100% nitric acid with phosphorus pentoxide and redistilling the product at least twice in a stream of dry ozone to remove traces of nitrogen dioxide. It was condensed in the U-tube from an ozone current just before using. The nitrogen, together with the nitrogen pentoxide which it had picked up, passed through a capillary tube into the decomposition chamber. The latter, a glass tube about 1 cm. in diameter and 75 cm. long, was kept at a definite temperature (35°, 45° or 55°) by rapidly pumping water from a large thermostat into a

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[4] Daniels and Johnston, This Journal, **43,** 53 (1921).

[5] Lueck, *ibid.,* **44,** 757 (1922).

[6] Unpublished data.

glass jacket surrounding the decomposition chamber. This jacket was covered with tin foil to prevent photochemical decomposition, and wound with asbestos to minimize heat losses. The temperature of the exit was taken as the temperature of the decomposition chamber, although it was about 0.1° colder than the thermostat. Glass wool was inserted at the inlet of the decomposition chamber for the purpose of breaking up eddy currents in the gas stream.

Within the decomposition chamber a portion of the nitrogen pentoxide underwent decomposition and the exit gases passed directly into absorption tubes containing 50 cc., each of 0.1 N sodium hydroxide solution. Practically all of the nitrogen oxides were absorbed in the first tube and only traces were found in a third tube. Usually two tubes were employed. A three-way stopcock at the end of the decomposition chamber made it possible to pass the exit gases through a second set of tubes at the beginning of an experiment, until the rate of flow, as indicated by the flowmeter, was uniform. This arrangement also made possible a continuous series of runs.

The decomposition was assumed, for analytical calculations, to take place according to the scheme, $2N_2O_5 \longrightarrow 2N_2O_4\ (+\ O_2) \rightleftharpoons 4NO_2$. An aliquot portion of the solution was titrated with standard acid to obtain a measure of the total number of moles of nitrogen pentoxide absorbed either as the pentoxide or as tetroxide or the dioxide. Another aliquot portion was titrated for nitrites with 0.002 M potassium permanganate by the method of Laird and Simpson.[7] Each mole of nitrogen tetraoxide (or two moles of the dioxide) absorbed in the alkaline solution gave one mole of sodium nitrite and one mole of sodium nitrate.

In a sample calculation the alkali neutralized in 0.4 of the solution was 25.5 cc., corresponding to 0.00319 mole of nitrogen pentoxide entering the decomposition chamber (fifth experiment, Table IV). The permanganate titration for a 0.4 aliquot portion was 10.1 cc., corresponding to 0.000126 mole of nitrogen pentoxide decomposed. The flowmeter indicated a current of 34.5 cc. of nitrogen per minute, or a total of 1104 cc. for 32 minutes, the duration of the run. This was the volume of the nitrogen under conditions existing at the flowmeter, namely, 21°, the temperature of the room, and 757 mm., the pressure within the system. The latter value was obtained by adding to the observed barometric pressure the hydrostatic pressure due to the liquid in the absorption tubes. On entering the decomposition chamber heated to 45°, the above volume of gas expanded to 1194 cc. The 0.00319 mole of nitrogen pentoxide at 45° and 757 mm. occupied a calculated volume of 83.5 cc. making a total of 1277.5 cc. of gas. Since this volume passed through in 32 minutes, the rate per minute was 39.9 cc. The volume of the decomposition chamber was 60.55 cc.; hence, each molecule remained in the heated chamber 1.517 minutes. The specific reaction rate was calculated in the usual manner:

$$K = \frac{2.303}{1.517} \log \frac{0.00319}{0.00319 - 0.000126} = 0.027$$

Since a total of 1177.5 cc. contained 83.5 cc. of nitrogen pentoxide, the

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[7] Laird and Simpson, THIS JOURNAL, **41**, 525 (1919).

partial pressure must have been $\frac{83.5}{1177.5} \times 757 = 49.5$ mm. In this experiment the crystals of nitrogen pentoxide were kept at 0°, at which temperature they were found in a previous investigation[8] to exert a sublimation pressure of 51 mm. The close agreement increases confidence in both measurements and proves further that nitrogen pentoxide exists in the gas phase as N_2O_5.

For the experiments at the lowest concentrations, the titration methods were not applicable. When the crystals were kept at —80°, the vapor pressure was only 0.01 mm. and it would have taken several days to accumulate sufficient material for an accurate titration. It was necessary then to resort to colorimetric methods. The nitrogen tetroxide was determined in one part of the solution by adding sulfanilic acid solution and α-naphthylamine solution[9] and comparing the pink color with that of a solution of known nitrite content in a colorimeter of the Duboscq type.

The total amount of nitrogen pentoxide was determined in a second portion of the sodium hydroxide solution by adding sufficient hydrogen peroxide to oxidize the nitrite completely to nitrate. The solution was evaporated to dryness, phenoldisulfonic acid was added and enough potassium hydroxide added to make the solution alkaline.[9,10] The yellow color was matched in the colorimeter with that of a known nitrate standard.

A test was made to compare the colorimetric method with the titration method in which the former showed 0.00300 mole of nitrogen pentoxide and 0.000260 mole of the tetroxide, while the latter showed 0.00309 and 0.000332 mole, respectively. Irregularities in calculated constants are probably due to inaccuracies in the colorimetric analyses.

In all the experiments described above, the nitrogen pentoxide had been mixed with a large excess of nitrogen, and it was thought advisable to conduct further experiments with the nitrogen pentoxide at very low concentrations in the absence of nitrogen. For these experiments a large bulb, 5475 cc. in volume, was connected through stopcocks with a vacuum pump and with a tube of nitrogen pentoxide crystals, kept at —18°. The bulb was exhausted and nitrogen pentoxide vapor at about 10 mm. pressure admitted. The bulb was again exhausted to a pressure less than 1 mm., and kept in a thermostat at 35° for two hours, after which time dil. sodium hydroxide solution was drawn in, sufficient to absorb all the nitrogen oxides. The partial vacuum was then relieved with nitrogen and the solution analyzed colorimetrically for nitrites and nitrates.

In Table I are given the constants obtained at different temperatures,

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[8] Daniels and Bright, THIS JOURNAL, **42**, 113 (1920).

[9] "Standard Methods for the Examination of Water and Sewage," American Public Health Association, **1920.**

[10] Chamot, Pratt and Redfield, THIS JOURNAL, **33**, 366 (1911).

and the detailed measurements from which they are calculated are given in Tables II, III, IV and V.

TABLE I

CONSTANTS OBTAINED AT DIFFERENT TEMPERATURES

Approximate partial pressure N_2O_5 Mm. of mercury	Specific reaction rates 35°	45°	55°
280	0.0103	0.027	. . .
280	.0104	.027	0.110
120	.0092	.026	.080
120	.0085	.027	.083
50	.0073	.027	.079
50	.0084	.026	.085
10	.0084	.023	.084
10	.0075	.026	.084
0.01	. . .	.020	.059
.01	. . .	.021	(.037)
Av.	.0088	.025	.083
Values of Daniels and Johnston[4]	.00808	.0299	.0900

TABLE II

THE DECOMPOSITION OF NITROGEN PENTOXIDE AT 35°

Duration of expt. Min.	Vol. of N_2 Cc.	Total N_2O_5 Milli-moles	Vol. of N_2O_5 Cc.	Pressure of N_2O_5 Mm.	Velocity chamber Cc. per min.	Time in chamber Min.	Total N_2O_4 Milli-moles	Specific reaction rate Min.
5	157	3.64	90.5	283	49.4	1.226	0.0459	0.0103
5	107	3.50	87.0	346	38.9	1.557	.0563	.0104
20	478	3.91	98.8	137	28.8	2.102	.0746	.0092
30	716	6.39	161.4	140	29.3	2.067	.1116	.0085
40	1194	3.49	88.3	52.2	32.0	1.893	.0476	.0073
40	1241	3.65	92.4	52.5	33.3	1.817	.0550	.0084
120	2865	1.94	49.0	12.8	24.3	2.492	.0399	.0084
120	2840	1.53	38.7	10.2	24.0	2.529	.0288	.0075

TABLE III

DECOMPOSITION OF NITROGEN PENTOXIDE IN EVACUATED BULB AT 35°

120	..	0.400	...	1.4	..	...	0.182	0.0051
120	..	.611	...	2.1	..	...	.417	.0096
120	..	.322	...	1.1	..	...	.167	.0061

Table IV includes experiments covering a twenty-eight-thousand-fold range of concentration and the agreement between constants is well within the limit of experimental error. One must conclude that the specific reaction rate is independent of molecular concentration, at least within the range studied. If one includes an unpublished constant of Lueck,[6] the specific reaction rate remains constant from 0.01 mm. to 10 atmospheres, a range of concentration of three quarters of a million.

The fact that some of the constants are high at the high concentrations may be explained by the fact that in these experiments the temperature of

TABLE IV

THE DECOMPOSITION OF NITROGEN PENTOXIDE AT 45°

Duration of expt. Min.	Vol. of N_2 Cc.	Total N_2O_5 Milli-moles	Vol. of N_2O_5 Cc.	Pressure of N_2O_5 Mm.	Velocity chamber Cc. per min.	Time in chamber Min.	Total N_2O_4 Milli-moles	Specific reaction rate Min.
5	142	3.13	81.5	278	44.6	1.358	0.112	0.027
5	151	3.39	88.2	281	47.9	1.264	.114	.027
12	519	3.50	91.7	114	50.9	1.190	.108	.026
12	511	3.46	90.6	114	50.1	1.209	.112	.027
32	1194	3.19	83.5	49.5	39.9	1.517	.126	.027
30	1106	3.09	81.0	51.6	39.6	1.530	.121	.026
60	2680	1.18	31.0	8.6	45.2	1.339	.0359	.023
60	2104	1.03	27.2	9.6	35.5	1.705	.0444	.026
180	7360	0.0098	0.256	0.0264	40.9	1.481	.00029	.020
180	7106	.0066	.173	.0185	39.5	1.533	.00021	.021

TABLE V

THE DECOMPOSITION OF NITROGEN PENTOXIDE AT 55°

7	211	2.38	63.5	178	39.2	1.544	0.370	0.110
10	352	2.71	72.2	131	42.4	1.429	.291	.080
10	310	2.46	75.5	141	37.6	1.611	.306	.083
30	1081	3.08	82.0	54	38.8	1.561	.356	.079
30	937	2.68	71.4	55	33.6	1.802	.382	.085
60	3280	1.40	37.0	8.6	55.3	1.095	.123	.084
60	2952	1.59	42.4	10.9	49.9	1.213	.154	.084
180	7430	0.0036	0.097	0.0099	41.3	1.467	.00030	.059
180	6868	.0032	.086	.0095	38.2	1.585	.00018	(.037)

the nitrogen pentoxide crystals was high enough to cause some decomposition before the decomposition chamber was reached. The determinations at the very low concentrations are not so reliable because the colorimetric analysis is less accurate than the volumetric analysis. The last value at 55° is undoubtedly wrong and it was excluded in calculating the average.

The average value of the constants obtained by Daniels and Johnston[4] in an entirely different manner are included in Table I for comparison. The agreement is within the limit of experimental accuracy.

Theoretical Discussion

Perrin[1] has endeavored to show that the life of dissociable molecules does not depend upon the number of collisions occurring among them, but upon the radiation received from the walls of the containing vessel.

Christiansen and Kramers[11] have suggested that if radiation is a factor in a unimolecular reaction, it can be appreciable, only, at very low concentrations. Such a situation should lead to a different specific reaction rate at sufficiently low concentrations.

Rodebush,[12] in proposing a statistical theory for unimolecular reactions.

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[11] Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923).

[12] Rodebush, THIS JOURNAL, **45**, 606 (1923).

postulated that the dissociation of a molecule is caused by a series of collisions fortuitously timed so as to accelerate the oscillation of some part of the molecule to the breaking point. A breakdown of the unimolecular constant might be expected on the basis of this theory at concentrations so low that the time between collisions is greater than the average calculated time between the decomposition of nitrogen pentoxide molecules. No indication of such a breakdown of the constant was obtained, but unfortunately it does not seem possible to obtain accurate results at pressures lower than 0.01 mm. with present analytical methods. Even at this pressure there are many millions of collisions for every molecule of nitrogen pentoxide decomposed. Approximately 2×10^{11} molecules decompose per second per cc. at 45°, while in the same time there are roughly 6×10^{19} collisions per cc. between nitrogen pentoxide molecules and 5×10^{24} collisions of nitrogen pentoxide molecules with nitrogen molecules.

Sir J. J. Thompson[13] has suggested the possibility that the presence of an inert gas may accelerate the decomposition of molecules in a unimolecular reaction. The experiments described above do not support this hypothesis, however, for within the limits of experimental error (which are rather large) the addition of a large excess of nitrogen, even 76,000 to 1, does not alter the specific reaction rate.

There is some evidence that under certain conditions the decomposition of nitrogen pentoxide may be catalyzed by the nitrogen dioxide present.[5,14,15] On the basis of this evidence Rice[3] maintained that the decomposition of nitrogen pentoxide is not unimolecular, but is autocatalytic. It is evident that if the concentration of nitrogen dioxide is very small as compared with the concentration of nitrogen pentoxide, the reaction would appear to be unimolecular, whether of the first or second order. However, the present velocity constants check very well with those obtained by Daniels and Johnston, under conditions of nearly complete decomposition. If the reaction is autocatalytic, its constants should be higher when the reaction proceeds to the point where there is a relatively high concentration of nitrogen dioxide. To make this fact apparent the data of the first and last experiments in Table IV were used in calculating "constants" with the equation for a bimolecular reaction, $K = \frac{2.303}{t\,(a - b)} \log \frac{b\,(a - x)}{a\,(b - x)}$. In this equation b = the number of moles of nitrogen dioxide given in the table and a = the corresponding number of moles of pentoxide; x was taken as the number of moles that would have reacted if the gases had been in the reaction chamber one minute longer (that is,

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[13] Thompson, *Phil. Mag.*, **47**, 337 (1924).

[14] Ref. 4, p. 72.

[15] Daniels, Wolf and Karrer, THIS JOURNAL, **44**, 2402 (1922).

$t = 1$). In the first case $K = 151$ and in the second $K = 88{,}000$. In this calculation the nitrogen tetra-oxide was assumed to be completely dissociated into the dioxide, but the constants were not changed appreciably when the proper correction for the equilibrium, $N_2O_4 \rightleftarrows 2NO_2$, was applied. Since the same data satisfy the equation of the first order, which depends only on concentration of the nitrogen pentoxide, it appears unlikely that the reaction rate is influenced by the nitrogen dioxide. It is to be noticed that the specific reaction rate is maintained even at the beginning of the reaction, when the partial pressure of nitrogen dioxide is less than 0.0013 mm. (last experiment in Table IV).

Bodenstein[16] has suggested that the decomposition of nitrogen pentoxide is not given by the equation, $2N_2O_5 \longrightarrow 2N_2O_4\ (+\ O_2) \rightleftarrows 4NO_2$, as assumed in this investigation, but that it might be better represented by the following: $2N_2O_5 \longrightarrow 2N_2O_3 + 2O_2$. At high concentrations, however, the rate of oxidation of nitrogen trioxide (N_2O_3) is sufficiently rapid to give the tetra-oxide. If this equation is the correct one, the ratio of sodium nitrite to sodium nitrate should be greater at the very low concentrations, where the oxidation of the trioxide is slow, than at high concentrations; for two molecules of nitrogen trioxide yield four molecules of sodium nitrite, while two molecules of the tetroxide yield only two molecules of sodium nitrite. However, since the ratio was not different at various concentrations, as shown by the constancy of the calculated specific reaction rates, it may be assumed that the reaction proceeds according to the former equation.

Summary

1. The decomposition rate of nitrogen pentoxide has been measured at low concentrations by chemical analysis.
2. Its specific reaction rate is independent of its concentration, even at partial pressures as low as 0.01 mm. of mercury.
3. Its specific reaction rate is independent of the amount of nitrogen dioxide, even when its partial pressure is as low as 0.001 mm.
4. The presence of a large excess of nitrogen does not alter its decomposition rate.
5. Theories which have been advanced to explain unimolecular reactions have been discussed.

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[16] Bodenstein, *Z. physik. Chem.*, **104**, 51 (1923).