however, takes place when the light is cut off. Due to the erratic behavior of ozone decompositions, the alternate dark and light reactions were necessarily tried within the same experiment. An inter-experiment comparison as in the case of nitrous oxide decomposition is not practical.

Summary

A simple, homogeneous, high temperature reaction, the decomposition of nitrous oxide, has been investigated from the point of view of the radiation hypothesis and found unresponsive to an increase in the radiation density of frequencies corresponding to the infra-red.

A heterogeneous low temperature reaction, the decomposition of ozone, has similarly been found to be uninfluenced by infra-red radiation.

In view of the somewhat similar experiments with nitrogen pentoxide, hydrogen chloride and alcohol,[3,4] together with the failure of predicted activating frequencies to correspond with absorption bands,[2,3] molecular activation through the absorption of single or multiple frequencies seems improbable.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF PRINCETON UNIVERSITY]

II. THE LOW PRESSURE DECOMPOSITION OF NITRIC AND NITROUS OXIDES

BY JAMES H. HIBBEN[1]

RECEIVED AUGUST 18, 1927 PUBLISHED APRIL 5, 1928

In a previous publication[2] the various radiation and collision theories of molecular activation were mentioned, together with some experimental data. Of the most significance to the present publication, which deals with collisions in chemical gas reactions, however, is the original theory of Lindemann.[3] This has been amplified by Hinshelwood[4] and others.[5] Lindemann has accounted for the existence of unimolecular reactions by the assumption that dissociation does not take place instantly on collision but only after a time which, on the average, is greater than that necessary to reëstablish Maxwellian distribution. Otherwise the rate of dissociation would depend on the rate by which this distribution was reëstablished or upon the collision frequency. At high pressures, the concentration of active molecules is therefore maintained constant and the

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[1] National Research Fellow.

[2] Hibben, *Proc. Am. Acad. Sci.*, August, 1927.

[3] Lindemann, *Trans. Faraday Soc.*, **17**, 598 (1922).

[4] Hinshelwood, *Proc. Roy. Soc.* (*London*), **113A**, 230 (1926).

[5] (a) Fowler and Rideal, *ibid.*, **113A**, 570 (1926); (b) Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); (c) Lewis and Smith, *ibid.*, **47**, 1514 (1925). Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.*, **13**, 188 (1927).

reaction unimolecular. But at low pressures, when the time between collisions is of the same order as the average life of a molecule after attaining its critical velocity, the apparent unimolecular reaction will become dependent on collision frequency, or bimolecular. Experimental verification of this phenomenon has been obtained by Hinshelwood,[6] who has noted that the decomposition of propionic aldehyde changes from unimolecular toward a bimolecular reaction at a pressure of approximately 80 mm. of Hg, and the decomposition of diethyl ether similarly changes at 150 mm. of Hg. To the contrary, however, Hirst and Rideal[7] have noted that in the decomposition of nitrogen pentoxide, instead of changing from unimolecular to bimolecular at very low pressures, the reaction actually increased in velocity until the decomposition followed the Rideal-Dushman equation. The decomposition at high pressures[8] follows the equation

$$-\mathrm{d}c/\mathrm{d}t = 4.98 \times 10^{13}\, e^{-24.700/RT}C$$

while at low pressures this becomes, according to Rideal

$$-\mathrm{d}c/\mathrm{d}t = 2.59 \times 10^{14}\, e^{-24.700/RT}C$$

corresponding to the Rideal-Dushman equation

$$-\mathrm{d}c/\mathrm{d}t = v\, e^{-Nhv/RT}C$$

Lindemann's theory presupposes that for a unimolecular reaction the rate of activation must exceed the rate of decomposition. For simple bimolecular reactions the rate of reaction may be expressed as a function of the collision frequency of activated molecules.[9] The number of molecules reacting per cc. per second is

$$[\text{Equation 1}]\ N = 2\sqrt{2}\,\pi\,\sigma^2\bar{u}\,n^2\,e^{-Q/RT}$$

where σ is the molecular diameter, $\bar{u}$ the root mean square velocity, n the number of molecules per cc. and $e^{-Q/RT}$ the fraction of the total number activated. In the case of apparently unimolecular reactions, however, it seems that the decomposition rate is in excess of the activation rate thus calculated, which is incompatible with Lindemann's theory. To account for this divergence[10] Hinshelwood makes the assumption that the total energy E could be made up by any distribution among a considerable number of degrees of freedom instead of two as generally used. This leads to the following expression.

[6] Hinshelwood, *Proc. Roy. Soc.* (*London*), **113A,** 221 (1926); *ibid.*, **114A,** 84 (1927).

[7] Hirst and Rideal, *ibid.*, **109A,** 526 (1925).

[8] Daniels and Johnston, THIS JOURNAL, **43,** 53 (1921).

[9] (a) W. C. McC. Lewis, *J. Chem. Soc.*, **113,** 471 (1918); (b) Hinshelwood and Burk, *Proc. Roy. Soc.* (*London*), **106A,** 284 (1924).

[10] See references 3 and 4. It might be mentioned that here the postulates of Fowler and Rideal, of Rice and Ramsperger, and of Hinshelwood differ from one another chiefly in approximations and simplifications.

$$[\text{Equation 2}]\ N = \frac{Z\, e^{\left(\frac{-Q + (1/2n' - 1)RT}{RT}\right)} \left[\left(\frac{Q + (1/2n' - 1)RT}{RT}\right)^{1/2n' - 1}\right]}{1/2n' - 1}$$

where N is the number of molecules which react per second per cc., Z the total number of collisions calculated from the equation $Z = 2\sqrt{2}\, \pi\, \sigma^2 \bar{u}\, n^2$ and n' is the number of degrees of freedom. The number of degrees necessary to satisfy the experimental conditions for propionic aldehyde decomposition is 12 to 14, and for diethyl ether 8 degrees of freedom. The equation may be applied only when the pressure is known where the assumption can be made that there are just enough collisions to account for the number of molecules which react, that is, at the beginning of the transitions between unimolecular and bimolecular reaction.

In view, therefore, of the fundamental theoretical importance attached to the behavior of unimolecular reactions at low pressures not only from the point of view of Lindemann's theory but also from that of any proposed chain, quantum chain, or ternary collision hypotheses,[11] it seemed pertinent to attempt to provide some experimental data on the behavior of chemical gas reactions at low pressures. For this purpose a unimolecular and a simple homogeneous bimolecular reaction were chosen.

As has been mentioned, Hirst and Rideal studied the decomposition of nitrogen pentoxide down to a total pressure of 4.5×10^{-2} mm. of mercury. Their results were not in accordance with Lindemann's theory. The reaction velocity increased with decreasing total pressure, the transition beginning at approximately 0.25 mm. of mercury. As their results showed considerable inter-experimental variation, it seemed justifiable to repeat this work. The bimolecular reaction selected was the decomposition of nitrous oxide. The results obtained in both cases were somewhat unexpected.

Experimental Part

1. Nitrous Oxide

Apparatus.—The reaction system used for the study of the decomposition of nitrous oxide is pictured in Fig. 1. It consists essentially of a quartz reaction vessel of about 200cc. capacity, a pressure manometer and a pumping system. The latter included one rotary oil pump, one two-stage mercury vapor pump and one Deauvillier type mercury vapor pump. The reaction vessel was connected to the condensation trap, the pumping system and manometer by means of a graded seal. The reaction was followed in two ways (A) by condensing out everything except the products of the reaction, nitrogen and oxygen, and measuring their pressure at definite time intervals, (B) by measuring the total pressure of the system and calculating the decomposition from the increase in pressure. The two methods gave concordant results.

Of the greatest importance was the pressure measuring device. This was a Pirani-

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[11] (a) Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923); (b) Langmuir, THIS JOURNAL, **42**, 2201 (1920); (c) Tolman, *ibid.*, **47**, 1524 (1925); (d) Born and Franck, *Z. Physik*, **31**, 411 (1925).

Hale manometer with some modifications. As the temperature in the quartz bulb was considerably above that of the gage the volume of the latter could not exceed a few cubic centimeters. The platinum wire, as in the usual design, was strung vertically up and down in the same manner as the vacuum electric light bulbs. However, the distance from the wire to the sides of the gage was only a few millimeters. This results in increased sensitivity per unit volume. The gage can now function as a resistance thermometer, so is extremely sensitive to fluctuations in the temperature of the walls. It was found necessary to place the gage in the interior of a large aluminum block, both gage and block being immersed in an accurately controlled thermostat. The heat capacity of the block compensates for fluctuations in the temperature of the circulating water of the thermostat. The second departure from the usual design of a Pirani gage was in the size of the platinum wire used. This was about 50 cm. of 0.1 mm. pure platinum wire, or three times the diameter generally employed. It must be wound tight enough so that there is no give, but not so tight that there is a strain on the wire. An important feature in the preparation of this manometer is the fact that the wire is heated at atmospheric pressure to a dull red for several hours before using. This con-

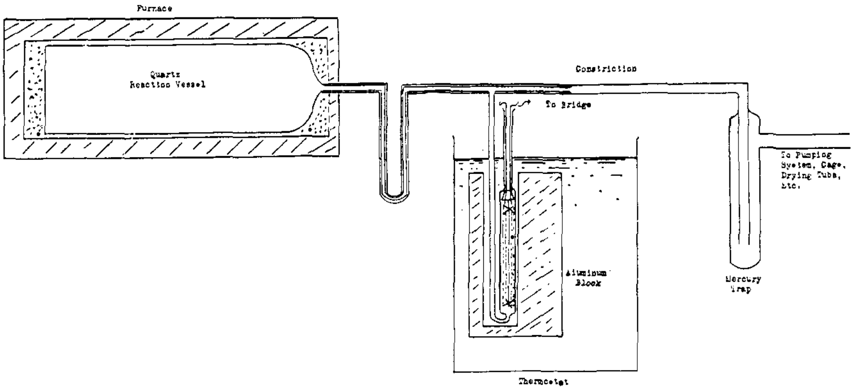

Fig. 1.—Apparatus for nitrous oxide decomposition.

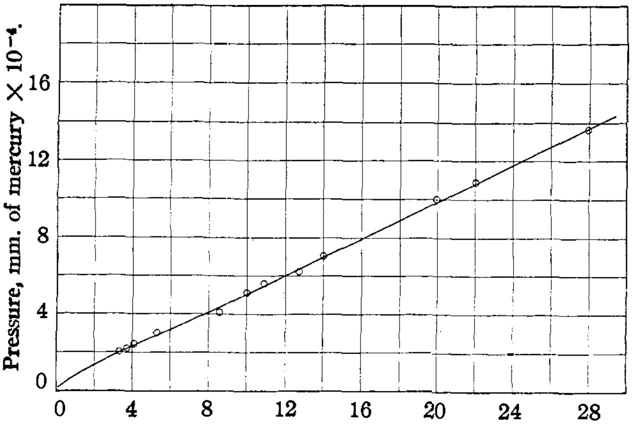

Fig. 2.—Calibration curve for Pirani type gage.

verts the wire to a stable, crystalline structure of constant resistance. With these precautions the manometer will give constant readings for months at a time, in spite of repeated baking and repeated changes in pressure from a vacuum to one atmosphere. The wire was maintained at constant temperature by means of a Callender and Griffiths bridge and the electromotive force input into the bridge measured with a potentiometer. This is Campbell's method.[12] The usual exponential formula $(V^2-V_0^2)/V_0^2$ (where V is the electromotive force at pressure read and V_0 electromotive force at best vacuum) was not necessary, as the direct electromotive force calibration against pressure was practically a linear function. Sample calibration curves are given in Figs. 2 and 3. The platinum wire was kept at 17.76° above the bath temperature, 30.1°.

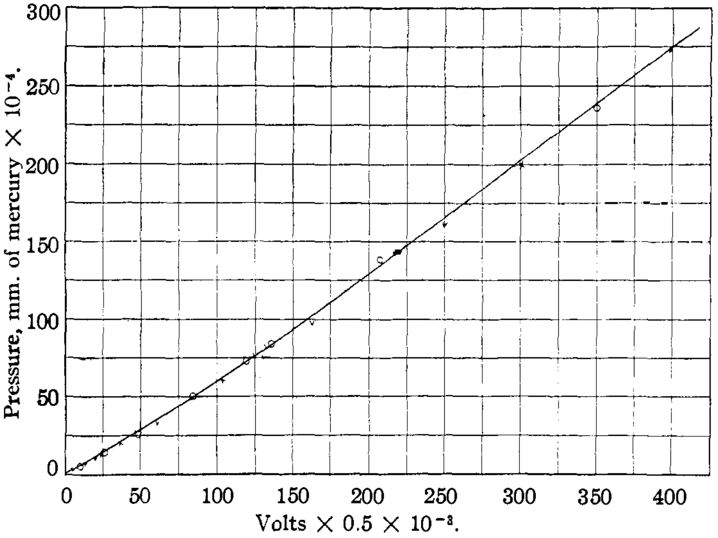

Fig. 3.—Calibration curve for Pirani type gage.

Procedure.—The general procedure in an experiment was to bake out the entire reaction system at 300°, allow the requisite amount of previously purified nitrous oxide to enter, seal off the pumping system and then follow the reaction by pressure measurements. Inasmuch as the reaction is bimolecular, the first experiments were carried out at a very elevated temperature to obtain any decomposition in a reasonable time at low pressures. This, incidentally, led to the observation that above 1000° K. the quartz vessel may be permeable to carbon dioxide and water vapor. No amount of superheating or pumping would reduce the enormous quantities of these gases admitted. It was observed, however, that the decomposition at these temperatures was instantaneous. At 600° K. the quantity of carbon dioxide was negligible and the pressure of the water vapor kept at 10^{-3} mm. of mercury by means of a carbon dioxide-ether trap constantly present.

Results.—The results are given in Table I (see Fig. 4).

Interpretation of Results.—The reaction velocity is approximately *1000 times faster* than the calculated value for the bimolecular decomposition of nitrous oxide at these temperatures and pressures, using the equation of Hinshelwood and Burk.[9b] The velocity constants calcu-

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[12] Campbell, *Proc. Phys. Soc.*, **33**, 257 (1921).

TABLE I

THE DECOMPOSITION OF NITROUS OXIDE

Partial pressure of N_2O. 1/100 mm. Hg	Time. minutes	K. unimolecular constant
Curve 1. 625° K.		
2.68	...	....
1.85	6.5	0.023
1.36	30	.021
.80	78	.0155 (total pressure method)
.60	90	.0166
.26	170	.0138
Curve 2. 550° K.		
3.17	...	....
1.81	16.8	.033
1.71	28.0	.022 (total pressure method)
1.31	64.0	.0137
.51	172.0	.011
Curve 3. 605° K.		
7.53	...	....
5.20	23.4	.0161 (condensation method)
2.60	66.6	.0159
.53	132.0	.019

lated as a unimolecular reaction are in fair agreement, particularly in the latter half of each reaction. The initial part of the reaction is somewhat complicated by the adsorption of appreciable quantities of the gas. The

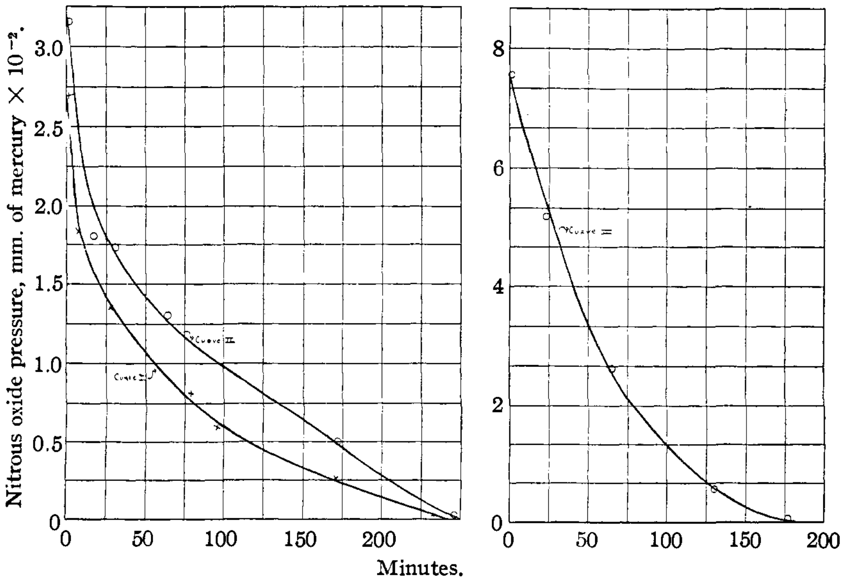

Fig. 4.—Nitrous oxide decomposition.

most logical explanation of this phenomenon seems to be that the reaction at low pressures is entirely heterogeneous.

2. Nitrogen Pentoxide

Nitrogen pentoxide was selected as the unimolecular reaction to be investigated at low absolute pressures, partially because of the effect observed by Hirst and Rideal, as mentioned, and partially because the reaction has been found to remain truly unimolecular throughout a series of rigid experimental investigations.[7,13]

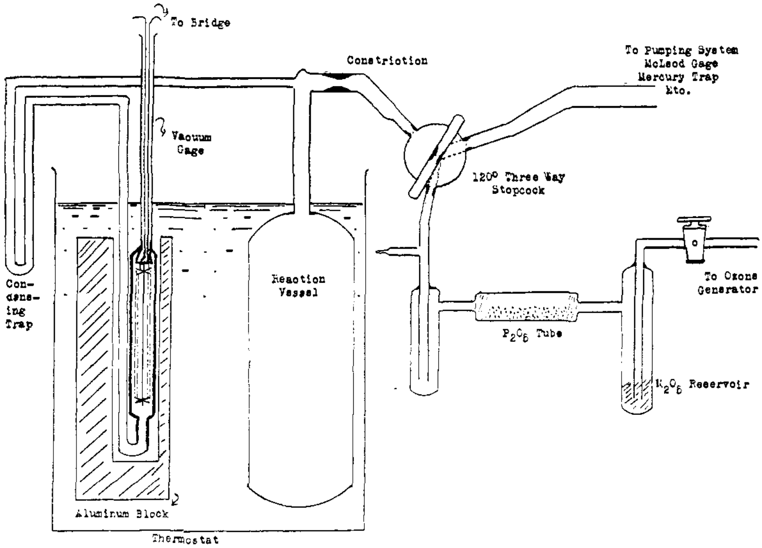

Fig. 5.—Apparatus for nitrogen pentoxide decomposition.

The experimental arrangement for this investigation was substantially that developed to study the nitrous oxide decomposition. The reaction vessel in this case, however, was immersed in the same thermostat as the vacuum gage. The latter, as before, was inside an aluminum block but was connected across to a one and one-half liter bulb by means of a short piece of tubing containing a small condensation trap outside the thermostat. A "T" insertion in this same tubing led to the same evacuating system previously used. This was constricted for sealing off after the pentoxide admission. A three way 120° stopcock permitted an interchangeable connection between the pumping system and reaction system, between the former and the pentoxide reservoir, and between the reservoir and the reaction system. This is illustrated in Fig. 5.

Procedure.—The thermostatic system was so designed, after the manner of Hirst and Rideal, that it could be removed and the entire reaction system baked out at 300°. The nitrogen pentoxide in the reservoir at −78° had previously been prepared from nitric acid and phosphorus pentoxide and purified by repeated distillations in ozone at −10°. As many as ten distillations were necessary to remove all visible traces of ni-

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[13] (a) Daniels, Wulf and Karrer, THIS JOURNAL, **44**, 2402 (1922); (b) White and Tolman, *ibid.*, **47**, 1240 (1925); (c) Hunt and Daniels, *ibid.*, **47**, 1602 (1925); (d) Busse and Daniels, *ibid.*, **49**, 1257 (1927).

trogen dioxide. This product was then distilled into the nitrogen pentoxide reservoir of the experimental system proper, where it could be washed with an ozone stream before using. It was then evacuated and distilled *in vacuo* from the reservoir into the first trap and then the surplus distilled back again and kept in liquid air. The reservoir-trap stopcock was then closed and the pentoxide allowed to distil from the first trap into the reaction system, where it was condensed with liquid air in the condensing trap just outside the thermostat. Pressure measurements at this point indicated an entirely negligible decomposition on admission. Pressure measurement of the total pressure at the end of the reaction as compared with the calculated total pressure from the pentoxide decomposition indicated possibly a trace of nitrogen dioxide originally present or decomposed stopcock grease vapor. The pressure of the pentoxide is practically identical with the total pressure of the system.

After the pentoxide was entirely condensed, the pumping system was connected to the reaction system and the constriction sealed off with pumping. The pentoxide was then reëvaporated. At intervals it was condensed and the residual oxygen pressure measured. The nitrogen pentoxide decomposed is twice the oxygen pressure. The experiments were carried out in the dark.

Results.—The results are as shown in Table II.

TABLE II

DECOMPOSITION OF NITROGEN PENTOXIDE

Time, minutes	Decomposed $N_2O_5 \times 10^{-2}$ mm. of Hg	*K*, unimolecular vel. const.
Experiment I. 30.1°		
32	2.54	0.0047
110	7.0	.0042
170	9.4	.0042
275	12.8	.00422
442	15.8	.00427
∞	18.6	
Experiment II. 30.1°		
18	1.0	0.005
44	2.32	.005
88	4.20	.0051
139	5.6	.0048
259	8.0	.0046
499	10.3	.0045
∞	11.5	
Experiment III. 30.1°		
20	1.2	0.0056
17	2.1	.0056
67	3.3	.0052
130	5.4	.00506
277	8.2	.00476
412	9.6	.0048
877	11.0	.0046
∞	11.2	

Time, minutes	Decomposed $N_2O_5 \times 10^{-2}$ mm. of Hg	*K*, unimolecular vel. const.
Experiment IV. 30.1°		
11	0.18	0.00562
58	.82	.0054
94	1.12	.00496
196	1.84	.00486
311	2.30	.00468
471	2.64	.0045
931	2.95	.0044
∞	2.955	
Experiment V. 40.0°		
18	2.5	0.0168
60	6.0	.0166
105	7.8	.0165
139	8.5	.0162
259	9.35	.0160
∞	9.5	
Experiment VI. 30.1°		
147	0.16	0.010
∞	.18	...
Experiment VII. 30.1°		
45	1.20	0.00473
135	2.84	.00450
205	3.81	.00451
335	4.84	.00450
∞	6.20	

The initial pressures utilized in the study of the nitrogen pentoxide decomposition were (in 10^{-4} mm. of mercury) 18, 295, 620, 950, 1120, 1150 and 1860.

Discussion of Results

The final velocity constant values are probably nearest to the correct value since traces of any foreign matter such as stopcock grease vapor and mercury oxide would tend to make the initial decomposition greater. This is borne out by Experiment VII in which excessive precautions were taken to keep the grease vapor at a minimum and by Experiment I. In the latter, the initial decomposition due to such vapor would be less noticeable because of the greater total initial pressure. Furthermore, a similar increase of the same magnitude in the case of the nitrous oxide decomposition indicates that a small variation in the constant is possibly inherent in low pressure systems due to initial adsorption on the glass walls. In the sixth experiment the larger value found for the constant is without great significance, as the error in the oxygen pressure measurement and the effect of foreign matter is comparatively large at this pressure. *The essential fact is that the velocity constant shows no variation in excess of the experimental errors.* This is further substantiated by the following comparison. Taking 25,000 as the critical increment, this gives at 30.1° $K = 0.0044$, found; $K = 0.00424$, calcd., the second value being calculated from Daniels and Johnston's data.

Taking, furthermore, the velocity constant values of $K = 0.0044$ at 30.1° and $K = 0.0162$ at 40°, as found, and calculating the critical increment from the temperature coefficient, the following result is obtained: critical increment, calcd., 24,775; critical increment, Daniels and Johnston, 24,700. This is better agreement than the experimental error justifies.

Outside of three qualitative preliminary experiments and one final confirmatory experiment (Experiment VII), Experiments I–VI, inclusive, represent all those carried to completion. The three preliminary ones demonstrated the presence of nitrogen dioxide initially in the system to the extent of one to two hundredths of a millimeter unless extreme precaution was taken to have as pure nitrogen pentoxide as possible in the reservoir, to wash this with ozone and finally to distil at −10° before using. Excessive precautions were taken in Experiment VII to reduce the possible influence of grease and other vapors by means of a baking out at higher temperatures and the use of traps between the last stopcock and the reaction system. As a result there is a small reduction in the total variation of the velocity constant.

Notwithstanding, therefore, a hundred-fold variation in pressure, from 0.18 to 18×10^{-4} mm. of mercury, the reaction velocity of the nitrogen pentoxide decomposition remains substantially constant and in excellent agreement with the values found by Daniels and Johnston at much higher pressures.

As has been previously mentioned, Hirst and Rideal studied the decomposition of nitrogen pentoxide between total pressures in the system of 0.045 to 1.45 mm. of mercury. Beginning with a total pressure of 0.25 mm., their velocity constant increased as the total pressure decreased until a limiting value of five times the original was approximately reached at a few hundredths of a millimeter total pressure. The reaction velocity then followed the Rideal-Dushman equation. This was explained by the assumption that one-fifth of the molecules undergo decomposition irrespective of pressure, but that four-fifths undergo decomposition only if they do not suffer collisions with other molecules for a period of 10^{-6} seconds after activation. This permits the energy in one oscillator to pass to another in the same molecule, a process requiring something of the order of 10^{-6} seconds.

It is immediately apparent that the results obtained by the writer are not in agreement with those of Hirst and Rideal. Certainly no alteration in the velocity constant of the same order of magnitude as observed by them was present. From an examination of their data it may be briefly pointed out here that the change in the velocity constant during an experiment as noted by them, due to the pressure change in the course of the reaction, is not in agreement with a corresponding velocity constant change due to different initial pressures in different experiments as it should be. Furthermore, the actual pentoxide present in the beginning of their reactions was generally only 50% and occasionally only 25% of the total pressure. This was due to decomposition on admission and no doubt was a complicating factor.

It is also apparent that no evidence of initial transition between unimolecular and bimolecular reaction is present. At 0.01 mm. pressure about 10^{-10} more molecules react than is explainable from the simple collision theory (Equation 1). It is interesting to note that the modified form (Equation 2) will not account for this discrepancy even with the assumption of 30 or more degrees[4,14] of freedom and a transition point at 0.01 mm., which is not the case.

It might also be mentioned that the average time interval between collisions of activated molecules at these pressures is about 10^{-5} seconds. In view of the fact that the average life of an activated molecule is of the order of 10^{-6} seconds, some deactivation by radiation might be expected.

[14] Fowler and Rideal calculate by means of their special equation sufficient energy to account for the reaction at the lowest total pressure measured by Rideal but questionably enough for the total pressures herein obtained. Since this article was submitted for publication A. C. Ramsperger, *Proc. Nat. Acad. Sci.*, **13**, 849 (1927), has found that azo*iso*propane decomposition shows no evidence of a transition point at pressures down to 0.025 cm. of mercury.

Rideal[7] has already pointed out that a modification of reaction velocity should take place at these low pressures if simple collision, quantum chain or chain theories of molecular activation are applicable to the decomposition of nitrogen pentoxide.

The author takes this opportunity to express his appreciation of the assistance given by Professor Hugh S. Taylor.

Summary

The decomposition of nitrous oxide has been studied at low pressure. The reaction changes from bimolecular to unimolecular. The most probable explanation seems to be that the reaction is entirely heterogeneous when the pressure is at a few hundredths of a millimeter.

The decomposition of nitrogen pentoxide was studied between the total pressure limits of 0.18 and 0.0018 mm. of mercury. The velocity constant remained essentially constant throughout this hundred-fold variation of initial pressure and was in excellent agreement with the values found by Daniels and Johnston at high pressures. This was in contradiction of the observations of Hirst and Rideal.

No evidence of a transition from a unimolecular to a bimolecular reaction as predicted from Lindemann's theory was present. Not even the assumption of 30 degrees of freedom in the nitrogen pentoxide molecules would account for the rate of activation found at low pressures.

An undisturbed life for active molecules of approximately 10^{-5} seconds seems to be without effect.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS. XXVII. I. FRACTIONAL PRECIPITATION OF THE CERIUM GROUP EARTHS BY ELECTROLYSIS. II. SOLUBILITY OF RARE EARTH OXALATES IN NITRIC ACID[1]

BY J. W. NECKERS WITH H. C. KREMERS

RECEIVED AUGUST 19, 1927 PUBLISHED APRIL 5, 1928

I. Fractional Precipitation of the Cerium Group Earths by Electrolysis

Electrolysis of neutral salt solutions of the rare earths will cause the formation of hydroxide at the cathode. Due to difference in basicities of the rare earth elements, a fractionation may be effected in this manner. Dennis and his co-workers[2] electrolyzed solutions of the rare earths using

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[1] Part of a thesis submitted by J. W. Neckers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

[2] Dennis and others, THIS JOURNAL, 37, 131 (1915); 37, 1963 (1915); 40, 174 (1918).