mixture the hydrogen soon catches fire, and the catalyst becomes incandescent.

3. The effects on the efficiency of the catalyst of temperature, space velocity, carbon dioxide, hydrogen sulfide, and the concentration of the carbon monoxide have been studied.
4. Formulas for the temperature rise in the catalyst, the factor limiting the permissible concentration of the carbon monoxide, have been derived and have been experimentally verified at different space velocities, and in tubes of different diameters.
5. On the basis of these results, the proper conditions for the technical application of this method of removing carbon monoxide from hydrogen have been outlined.
6. Our results have been shown to be in agreement with the computations of Rideal, relative to the simultaneous oxidation of carbon monoxide and hydrogen.
7. A method for the analysis of small amounts of carbon monoxide in the presence of hydrogen has been worked out.

CAMBRIDGE 38, MASSACHUSETTS

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

THE THERMAL DECOMPOSITION OF NITROGEN PENTOXIDE IN SOLUTION

BY ROGER H. LUECK

Received January 23, 1922

The problem of reaction velocity is one of paramount interest to chemists. Attempts which have been made to explain the tremendous temperature coefficients of reaction velocities solely on the basis of the kinetic theory have not been verified by experimental data. For a 10° rise in temperature, reaction velocities are known to increase from 200 to 400%, whereas the number of collisions between the molecules increases by not more than 2%.

Arrhenius[1] early investigated the problem and found that the dependence of the velocity constant on the temperature could be satisfactorily expressed by the formula

$$\frac{d\,ln\,k}{dT} = \frac{E}{RT^2} \qquad (1)$$

where E is a quantity possessing the dimensions of energy, and which is found to vary but slightly with the temperature. Arrhenius sought an explanation of the huge temperature coefficients in postulating the existence of an equilibrium between "active" and "passive" molecules

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[1] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

in which only those in the "active" form are in a condition to react. These "active" molecules are produced from the "passive" form by the absorption of a quantity of energy, corresponding to the E of the preceding equation, from their environment. The treatment of Arrhenius is unable to give any information concerning the internal processes involved in the absorption of this activating energy and, as Tolman[2] points out in a recent review, the physical significance of the quantity E is the subject of many conflicting opinions among investigators in this field.

Trautz,[3] Perrin[4] and Lewis[5] have attempted to correlate the value of E with the radiant energy available to a system undergoing chemical change. Their fundamental assumption is that $E = Nh\nu$ where N is Avogadro's number, h the universal quantum constant, and ν the frequency of the radiation which is absorbed by the reacting substance. The Arrhenius expression shows the natural logarithm of the reaction velocity to be a linear function of the reciprocal of the absolute temperature, and according to the Wien radiation law an exactly similar relation holds between the intensity of any monochromatic black-body radiation and the absolute temperature. From this very striking analogy Perrin has developed the following expression for the calculation of reaction velocity

$$k = se^{-\frac{Nh\nu}{RT}} \tag{2}$$

Here s is a constant having the dimensions of a frequency. This formula rendered in the logarithmic form leads to an equation exactly similar in form to that of Arrhenius.

References to the works of W. C. M. Lewis, Dushman and Tolman who have studied the question and arrived at similar expressions may be found in the excellent review of the last named.

Any problem of this nature offers a wide field of opportunity to the theoretical chemist and quite naturally the major portion of the literature on the subject is of a theoretical character. The amount of experimental data for checking up the various theories is at present unduly limited.

Cox[6] has recently published a paper in which the problem is attacked experimentally. It follows from the Perrin-Lewis radiation hypothesis that any reaction medium which increases the velocity of a given reaction, *i. e.*, by increasing the density of the particular radiation frequency which is absorbed by the reacting molecules, should decrease the temperature

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[2] Tolman, This Journal, **43**, 269 (1921).

[3] Trautz; for summary of earlier papers see *Z. anorg. allgem. Chem.*, **102**, 81 (1918) and **106**, 149 (1919).

[4] Perrin, *Ann. phys.*, **11**, 5 (1919).

[5] W. C. M. Lewis. See particularly *J. Chem. Soc.*, **111**, 389, 457, 1086 (1917); **113**, 471 (1918); *Phil. Mag.*, **39**, 26 (1920); This Journal, **43**, 1288 (1921).

[6] Cox, *J. Chem. Soc.*, **119**, 142 (1921).

coefficient of the reaction velocity. With this in mind, Cox has studied the reaction of bromo-acetophenone with aniline in a number of organic solvents and also the reaction between sodium β-naphtho-oxide and ethyl iodide in some of the liquid alcohols. His results in general do not corroborate the theories of Perrin and Lewis. It should, however, be observed that a number of disturbing influences enter into these reactions which might readily explain the observed discrepancies. Since both reactions are of the second order there are the varied complications arising from molecular collision, viscosity of the solvent, the absorption of radiant energy by more than one species of molecule, and, in addition, in the second named reaction the ionization of the sodium β-naphtho-oxide. It should be mentioned that Cox himself has pointed out some of these possibilities.

Since any true monomolecular reaction does not depend upon molecular collision, information concerning the velocity constant should throw light on the mechanism of this absorption of radiant energy, provided however, that some of the other factors which may have influenced the work of Cox are likewise absent. The ideal system for this study is a monomolecular reaction, uncatalyzed by the walls of the containing vessel, taking place in solvents where there is little likelihood of any loose solvent-solute complexes or of any ionization of the solute. The reaction in solution possesses an advantage over a gas phase reaction in that it offers a wider variation of conditions under which the reaction may take place, *e. g.*, the concentration of reacting substance, and also enhances the opportunities for varying the reaction medium.

Daniels and Johnston[7] have studied the decomposition of nitrogen pentoxide in the gas phase and have found it to follow the course of a true monomolecular reaction and to be entirely uncatalyzed by the vessel walls of glass. The present paper presents the results of some experiments in which this same reaction has been studied in solution and its velocity followed by measuring the volume of oxygen evolved. It is preliminary to a research being conducted by Dr. Farrington Daniels of this laboratory in an attempt to uncover some definite relationship between the reaction velocity and the absorption of radiation within the solution.

Preparation and Purification of Materials

The nitrogen pentoxide was prepared as described by Daniels and Bright[8] in their study of the vapor pressure of the substance.

Uncombined water was removed from nitric acid by two distillations from conc. sulfuric acid and this 100% product was dehydrated with phosphorus pentoxide. The nitrogen pentoxide thus formed was distilled from the phosphoric acid, through phosphorus pentoxide, and condensed in a U-tube surrounded by a freezing mixture, at −20°. A second distillation through phosphorus pentoxide in a current of ozonized air sufficed

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[7] Daniels and Johnston, THIS JOURNAL, **42,** 1131 (1920).

[8] Daniels and Bright, *ibid.*, **43,** 53 (1921).

to produce snow-white, anhydrous crystals of nitrogen pentoxide. The ozone prevents the formation of nitrogen peroxide. Immediately before use the product was again distilled through phosphorus pentoxide into a second, smaller U-tube which was then sealed off and the material thus preserved on ice until required.

Sulfur was removed from the carbon tetrachloride used as a solvent by allowing to stand over mercury for a week with frequent shaking. After drying with phosphorus pentoxide the liquid was fractionated through a 5-bulb column. Only the middle portion, distilling off over a range of 0.03°, was used in the experiments. The final product gave no test for chloride ion.

The chloroform was purified by shaking thrice with a solution of sodium carbonate to remove alcohol and traces of hydrochloric acid. After washing thoroughly with distilled water the material was dried over calcium chloride and distilled from phosphorus pentoxide through a fractionating column. The final product gave no test for moisture, alcohol or chloride ion.

The solution of the nitrogen pentoxide in the solvents was effected in such a way as to prevent the access of atmospheric moisture. Placed in a desiccator immersed in a freezing mixture these solutions could be kept for several days without any marked deterioration.

Experimental

Apparatus.—The velocity of the decomposition was determined by the gasometric method in the apparatus shown in Fig. 1, the whole being set up in duplicate. Reaction flasks, similar to those used by Walton[9] and his students in their hydrogen peroxide studies, were supported by a shaking cradle in a thermostat maintained constant to ±0.015° and connected by means of capillary tubing to the tops of jacketed 100cc.

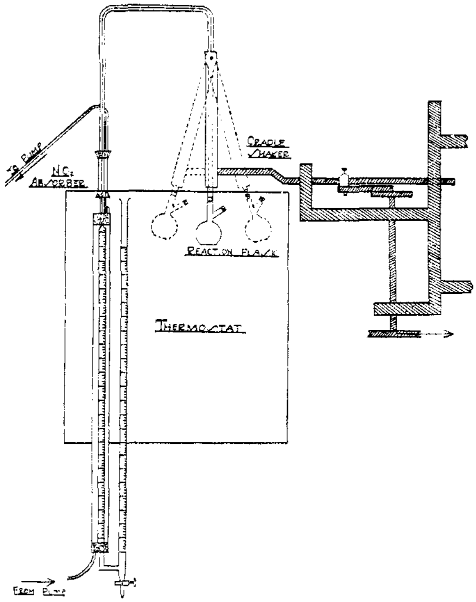

Fig. 1.

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[9] Walton, *Z. physik. Chem.*, **47**, 185 (1904).

burets in which the oxygen evolved was collected. Thorough shaking was insured by the addition of glass beads to the reaction flasks. The outside of the flasks was painted with several coats of black shellac to exclude light.

The greatest difficulty was experienced with the indispensable rubber connection between the reaction flasks and the capillary tubing which carried the oxygen over into the burets. The action of the oxides of nitrogen on rubber is very vigorous. Of all forms, pressure tubing functioned the worst. The problem was ultimately solved by inserting one length of red rubber tubing inside another just large enough to take it with a very thin layer of vaseline between the two. A 20cm. length of capillary tubing was fused to the reaction flasks so that the rubber connection was made at some distance from the flasks and at the axis of rotation of the shaking cradle.

The reaction was assumed to take place the same as in the gas phase in accordance with the following equation

$$\begin{array}{c} 2N_2O_5 = 2N_2O_4 + O_2 \\ \downarrow\uparrow \\ 4NO_2 \end{array}$$

Most of the nitrogen dioxide formed remained dissolved in the solvent. However, some always passed into the gaseous state and tended to pass over into the burets, rendering the readings erroneous. To prevent this, 15 cm. of 12mm. glass tubing, filled with glass wool wet with conc. sulfuric acid and water-jacketed, was interposed between the burets and the reaction flasks. The free space above the solution in the flasks was always maintained as small as possible in order to render negligible the errors introduced by the passage of some nitrogen dioxide into the gas phase.

It was essential to know whether the actual decomposition was occurring in solution as desired or in the free space above the solution. The following considerations proved the invalidity of the latter possibility. The total amount of nitrogen pentoxide present in the system, as measured by the total volume of oxygen evolved, would have to be initially present in the free space if the velocity constants were to remain regular. Such a condition would necessitate an initial pressure of several atmospheres in almost every case, whereas the experiments were all carried out under atmospheric pressure. A second proof was obtained by direct experiment. When the shaking device was at rest no increase in volume was registered in the burets, provided the rest period was not excessively long. If, after such a stationary period, the shaking was commenced, oxygen was rapidly evolved, equilibrium attained within a minute, and the volume of oxygen thus obtained with intermittent shaking was exactly equal to that which would have been evolved with continuous shaking over an equal interval of time under the same conditions. This is conclusive proof that the decomposition occurs entirely in the solution, the oxygen which is formed when the shaker is not in action being retained in the solvent as a supersaturated solution.

The evolved gas was collected in gas burets and measured over the liquid which was being used as a solvent in the reaction flasks. A leveling tube connected with the bottom of the burets made possible the rapid adjustment of liquid levels. Water at constant temperature was forced through the buret jackets, thus obviating a variable temperature correction.

Method.—All connections between the burets and the reaction flasks rendered gas-tight, a measured volume of the solution to be investigated was pipetted into the reaction flasks which had previously been thoroughly cleaned and dried. The flasks were stoppered with the accurately fitting glass stoppers, the shaking cradle lowered and set in motion. After waiting until 15–20 cc. of gas had been evolved, in order to allow for thermal lag and the disruption of an initial condition of supersaturation of oxygen in the solvent, volume readings were taken at measured intervals. All readings were corrected to 0° and 760 mm. pressure in order that the velocity constants obtained would be independent of the barometric pressure. Time readings were taken on a stop-watch. The final observation, which was a measure of the quantity of nitrogen pentoxide initially present, was made when no further increase in volume was noticed after a long period of time.

Experiments were not carried out above 55°, for in so doing accuracy would be sacrificed for speed in observation and the reaction would be well-nigh complete before the shaking had effected a regular evolution of gas. Likewise, nothing was done below 25° because of the long time involved in the completion of an experiment at lower temperatures.

Calculations.—Fig. 2 represents a graphical grouping of the results obtained where the volume of oxygen evolved is plotted against time. Duplicates are not shown. Graphical interpolation over equal intervals of time on these same curves, plotted individually on a far larger scale, gave the values for time, t, and the total volume of oxygen liberated, $V_t - V_0$, between the starting point V_0 and any time t. To follow the course

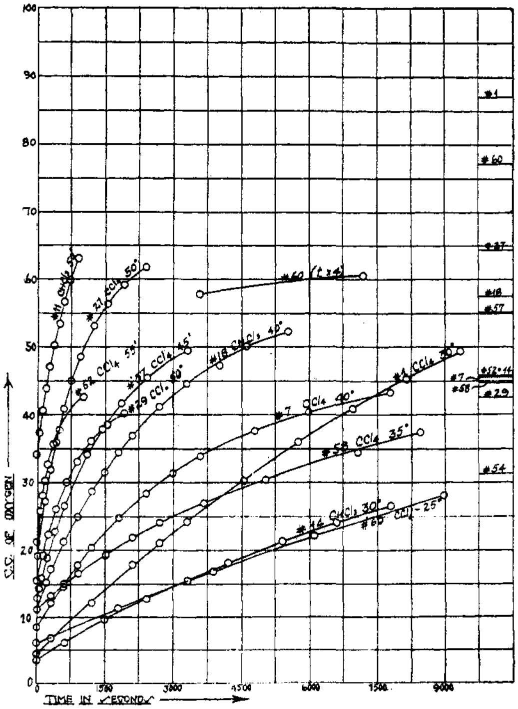

Fig. 2.

of the reaction only the total volume of gas evolved and the differences between successive readings are necessary.

TABLE I

Carbon Tetrachloride. 40°

$V_0 = 10.75$ cc. V_∞ 45.50 cc.

t Sec.	$V_t - V_0$ Cc.	$V_\infty - V_t$ Cc.	$K \times 10^{-4}$
0	0.00	34.75	..
300	3.42	31.33	..
600	6.30	28.45	3.21
900	8.95	25.80	3.26
1200	11.40	23.35	3.32
1500	13.55	21.25	3.14
1800	15.52	19.23	3.33
2100	17.30	17.45	3.24
2400	18.90	15.85	3.20
2700	20.35	14.40	3.20
3000	21.70	13.05	3.28
3600	23.95	10.80	3.15
4200	25.65	9.10	..
4800	27.25	7.50	3.22
6000	29.55	5.20	3.05
∞	34.75	0.00	..
		Av.	3.22
		Duplicate Av.	3.22
		Mean	3.22

Table I presents a typical calculation of the velocity constants from the data. The column headed $V_\infty - V_t$ gives the difference between the final volume V_∞ and the volume at any time V_t. The reaction-velocity constants shown in the last column were calculated directly from the data in the first and third columns with the aid of the familiar formula

$$k = \frac{2.302}{t_2 - t_1} \log \frac{V_\infty - V_{t_1}}{V_\infty - V_{t_2}}$$

The values of t_2 and t_1, chosen for the calculations, are successive times shown in the first column; all times are expressed in seconds.

TABLE II

VALUES OF THE VELOCITY CONSTANT ($k \times 10^{-4}$)

Temperature °C.	Carbon tetrachloride 1	2	Mean	Chloroform 1	2	Mean
55	21.1	21.3	21.2			
50	11.5	11.7	11.6	12.7	12.6	12.8
					13.0	
45	6.37	5.95	6.11			
	6.13	5.97				
40	3.22	3.22	3.22	3.74	3.89	3.81
35	1.62	1.62	1.62			
30	0.841	0.842	0.8415	1.03	1.02	1.025
25	0.421	0.398	0.409			

In order to conserve space the other results have not been tabulated in this form but are shown condensed in Table II.

Results

The matter of the temperature coefficient of the reaction velocity is of considerable interest. It has been previously mentioned that those agencies which increase the reaction velocity decrease the temperature coefficients. Skrabal[10] has arrived at the very general conclusion that the "relations between reaction velocity, temperature effects, influence of solvent, added catalyst and photochemical action are all essentially the same; accordingly, change in the reaction velocity effected by any one of these factors diminishes as the magnitude of the velocity constant increases." Table III shows how well the data obtained in this investigation agree with this deduction from the theories of Perrin and Lewis. It will be observed that the temperature coefficients in the case of chloroform, in which the reaction proceeds more rapidly than in carbon tetrachloride, are smaller than those in carbon tetrachloride for corresponding temperature intervals. Similarly with increasing temperature the values of the temperature coefficients show a uniform decrease.

Table III

Temperature Coefficients of the Reaction Velocity

Temp. interval ° C.	Carbon tetrachloride	Chloroform
55/45	3.47	..
45/35	3.77	..
35/25	3.96	..
50/40	3.60	3.33
40/30	3.83	3.73

Dushman[11] has proposed a formula for monomolecular reactions by which the magnitude of the velocity constant at any temperature may be calculated from its value at one particular temperature. He assumes with Perrin and Lewis that $E = Nh\nu$ but does not specify any mechanism for the interaction of radiant energy. His equation is of the same form as that of Arrhenius and Perrin (see Equations 1 and 2) but Dushman ingeniously postulates that the unknown quantity s, which has the dimensions of a frequency, is the same frequency already introduced in the expression $E = Nh\nu$. This leads him to the equation

$$k = \frac{E}{Nh} e^{\frac{-Nh\nu}{RT}} \tag{3}$$

which for purposes of calculation may be written

$$\log k = 10.0203 + \log E - (E/4.571\ T) \tag{4}$$

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[10] Skrabal, *Monatsh.*, **37,** 495 (1916).

[11] Dushman, This Journal, **43,** 397 (1921).

Dushman has tested this equation with the experimental data obtained by Trautz and Bhandarkar[12] for the monomolecular decomposition of phosphine above 920° K. and finds excellent agreement within the limit of experimental error.

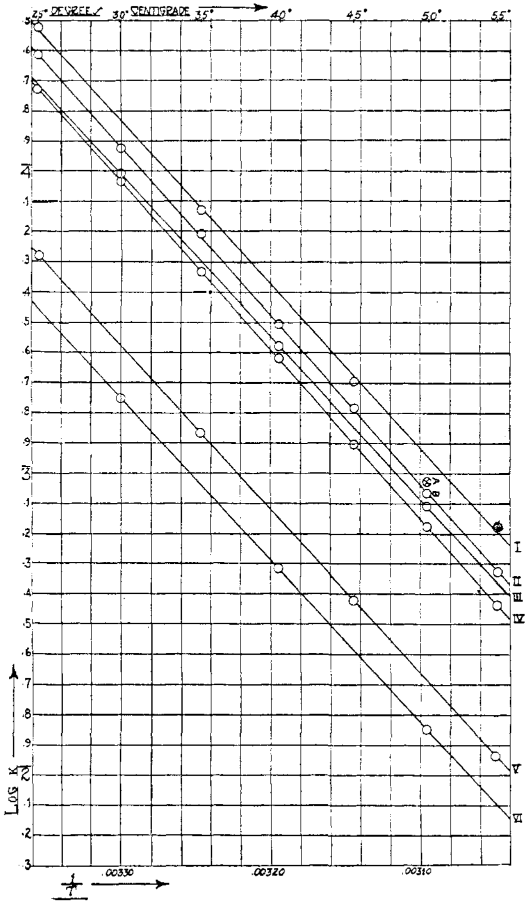

Fig. 3.—I. Gas phase; II. Carbon tetrachloride; III. Chloroform; IV. Carbon tetrachloride (calculated); V. Gas phase (calculated); VI. Chloroform (calculated).

Tolman[2] has applied this equation to the results obtained by Daniels and Johnston[7] for the decomposition of nitrogen pentoxide in the gas phase and finds a far better agreement with the experimental data than can be obtained using the older expressions developed by Trautz and by Lewis. Table IV and Fig. 3 show a comparison of the results obtained in this investigation with those calculated by means of Dushman's equation.

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[12] Trautz and Bhandarkar, *Z. anorg. allgem. Chem.*, 106, 95 (1919).

By integrating the expression of Arrhenius and converting to common logarithms we obtain

$$E = \frac{1.98\ T_2 \times T_1 \times 2.302 \log k_2/k_1}{T_2 - T_1} \qquad (5)$$

By substituting the values of the reaction velocity constants, k_2 and k_1, corresponding to two different absolute temperatures, T_2 and T_1, the values of E were calculated.

Table IV

Carbon Tetrachloride

Temp. °C.	$1/T$ $\times 10^{-2}$	K (obs.)	Log k (obs.)	E cal.	Log k (calc.)	K (calc.)
55	0.30488	21.2×10^{-4}	$\bar{3}.32634$	25,292	$\bar{3}.438$	27.4×10^{-4}
50	0.30960	11.6	$\bar{3}.06446$	26,070	$\bar{3}.175$	15.0
45	0.31446	6.11	$\bar{4}.78604$	25,242	$\bar{4}.904$	8.02
40	0.31949	3.22	$\bar{4}.50786$	26,218	$\bar{4}.624$	4.21
35	0.32468	1.62	$\bar{4}.20952$	24,222	$\bar{4}.335$	2.16
30	0.33004	0.841	$\bar{5}.92480$	25,770	$\bar{4}.036$	1.09
25	0.33557	0.409	$\bar{5}.61172$		$\bar{5}.728$	0.535
			Av.	25,469		
			Chloroform			
50	0.30960	12.8	$\bar{3}.10721$	24,252	$\bar{3}.848$	70.6
40	0.31949	3.81	$\bar{4}.58092$	24,648	$\bar{3}.318$	20.8
35	0.33004	1.02	$\bar{4}.01072$		$\bar{4}.754$	5.68
				Av. 24,450		

Theoretical

In Fig. 3 these same results are graphically expressed. It will be observed that in every case the line representing the results calculated by the Dushman equation for any particular solvent lies exactly parallel to that representing those experimentally determined and plotted according to the Arrhenius expression. It is apparent, however, that no physical significance can be attached to this fact since both expressions are equations for a straight line and their slopes are made numerically equal by setting E equal to $Nh\nu$, as Dushman has done in his derivation.

It is of importance to note that the differences between observed and calculated values for the gas phase and for chloroform are exactly equal while those for carbon tetrachloride are considerably less. The full significance of this fact is at present not quite clear, but if fully understood it might be of assistance in explaining the mechanism of a monomolecular reaction. The magnitude of these differences as compared with those obtained when k is calculated from the equations of Trautz and Lewis, as Tolman has done shows quite conclusively that the work of Dushman is a step in the right direction, but likewise indicates the necessity for the introduction of some *variable* factor into the equation which will account for the variable differences obtained with different reaction mediums. Undoubtedly the form of the equation is correct since it is the same as that of Arrhenius which does give quite satisfactorily the dependence of the velocity constant on the temperature. Likewise the values of N and h are constant and have been checked by a variety of methods. This leaves but the one alternative: that the expression, $\nu = E/Nh$, is not entirely applicable in this connection. The value of ν as calculated from the data obtained in the gas phase reaction is 1.16 μ, when expressed as a wavelength, for carbon tetrachloride 1.13 μ and for chloroform 1.18 μ. In their study of the photochemical decomposition of nitrogen pentoxide, Daniels and Johnston have shown that light of this wavelength is not effective in bringing about decomposition, and further that nitrogen pentoxide possesses no absorption bands in this region. From similar considerations Langmuir[13] has suggested that the whole radiation theory for chemical action be abandoned.

The present writer feels that there lies considerable promise in the suggestion of Tolman[14] who holds that E is in general not a constant nor does it correspond to a single frequency except in the limiting case, adopted by Perrin, where only a spectrum "line" is active. He replaces the constant, ν or E/Nh, of the Dushman equation with a variable, $e^{S\frac{de}{RT}}$, thus taking into account the fact that photochemical reactions are often brought about by radiant energy having a wide range of frequencies and also the probability that the molecules, having themselves different internal states, may require different quantities of energy for activation. This range of activating frequencies must be specific for any one substance but the particular frequency within the band which is most active can readily be thought of as varying with different reaction mediums. The introduction of a variable into the Dushman equation should account for the variable differences obtained in the calculation of the velocity constants for the decomposition of nitrogen pentoxide, using the expression as it stands at present.

The catalytic effect of nitrogen pentoxide.—It was found in the photochemical work of Daniels and Johnston that blue light of wavelength between 400 and 460 $\mu\mu$ was effective in decomposing the pentoxide but *only* in the presence of brown nitrogen dioxide which shows almost complete absorption of light in this region. Their other work carried out in

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[13] Langmuir, THIS JOURNAL, **42,** 2190 (1920).

[14] Tolman, *ibid.*, **42,** 2506 (1920).

the absence of light indicated that the nitrogen dioxide was not an auto-catalyst to the dark reaction.

In this connection the two points, A and B of Fig. 3, obtained at 50° in carbon tetrachloride solution are important. Point A was obtained using a solution of the nitrogen pentoxide where special precautions were observed to keep the initial concentration of nitrogen dioxide as low as possible, whereas Point B represents the velocity constant in a solution previously saturated with the dioxide. It should be stated that, despite the precautions observed in the former case, the initial concentration of nitrogen dioxide was considerably greater than that which existed initially in any of the experiments carried out in the gas phase.

Comparing this odd value, A, with those obtained in the gas phase and with the others obtained in carbon tetrachloride solution, one is led to believe that nitrogen dioxide is an auto-catalyst to the dark reaction and that the catalytic effect is proportional to the amount present up to a "limiting concentration" which is rather low. At this point further increase in the nitrogen dioxide present has little effect on the velocity constant.

The fact that the values obtained for the velocity constant in carbon tetrachloride lie so well on the straight line, Fig. 3, despite the fact that no attempt was made to maintain a constant initial value for the nitrogen dioxide concentration, receives a ready explanation from the above considerations, for, in all cases except that represented by Point A, the initial concentration was considerable and above that designated as the "limiting concentration." Similarly, in the gas phase, where this initial concentration of nitrogen dioxide was always very low and in the region where slight variation in its content has an appreciable effect on the rate of reaction, one would naturally expect to find lower values for the velocity constants in general and greater variations from the straight line when plotted as in Fig. 3. Results, indicative of this same phenomenon, were obtained by Daniels and Johnston in their study of the photochemical decomposition of nitrogen pentoxide.

Further experiments will be carried out to determine what effect the nitrogen dioxide and the nitrogen tetra-oxide, with which it must exist in equilibrium, have on the absorption spectra of the solutions in which the velocity of this reaction is measured.

The writer wishes to express his sincerest thanks to Dr. Farrington Daniels at whose suggestion and under whose direction this work was done.

Summary

1. The velocity of the decomposition of nitrogen pentoxide in carbon tetrachloride and in chloroform solutions has been determined gasometrically between 25° and 55°. Such systems are of special value in study-

ing the new theories concerning the relation of radiant energy to chemical action.

2. The fact that the velocity constants obtained in solution so closely approximate those obtained in the gas phase by Daniels and Johnston is of peculiar significance since, as far as the writer is aware, this is the first time that the velocity of a monomolecular reaction has been measured under so wide a variation of conditions.

3. The experimental facts show the energy of activation or the critical increment to be practically independent of the temperature.

4. It has been shown that, in accordance with a necessary deduction from the Perrin-Lewis radiation theory, a change in reaction velocity brought about by temperature effects or the influence of solvent diminishes as the magnitude of the velocity constant increases.

5. A comparison has been made between the values of the velocity constant experimentally obtained and those calculated from the critical increment, *E*, by means of the equation recently proposed by Dushman. Although the agreement is not exact, it is far better than can be obtained using the older equations developed by Trautz and Lewis.

6. The nitrogen peroxide formed in the reaction has been shown to exert an auto-catalytic effect on the thermal decomposition of the nitrogen pentoxide.

7. This work is at present being extended in this laboratory to other solvents and to a study of the absorption spectrum of nitrogen peroxide in the various solvents.

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

THE SIZES OF ATOMS IN CRYSTALS

BY ROBERT N. PEASE[1]

Received February 1, 1922

The author has recently shown[2] that molecular volumes, as revealed by the constant *b* of van der Waals' equation, are consistent with the view that the volumes of atoms and groups of atoms depend upon the number and arrangements of electrons about the positive nuclei of the atoms rather than on the particular kinds of atoms involved. It was shown, for example, that the volumes of the nuclear carbon, nitrogen and oxygen atoms in methane, ammonia and water respectively, are nearly the same and equal to that of the rare gas, neon. The number and arrangements of electrons about the positive nuclei of these nuclear atoms and of neon are the same for all. Similarly, the volumes of the

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[1] National Research Fellow in Chemistry.

[2] Pease, THIS JOURNAL, 43, 991 (1921).