Recommended Procedure.—Accurate results were obtained from the following procedure: the solution was made alkaline with ammonium hydroxide and 5-cc. excess of concentrated ammonium hydroxide added. An excess of ammonium oxalate was then added at room temperature, stirred and the precipitate allowed to stand for at least one hour. The precipitate was filtered off, washed with water containing a small amount of ammonium hydroxide, transferred on the paper to the precipitation beaker, dissolved in dilute sulfuric acid and titrated with a 0.1 *N* potassium permanganate solution. Considerable variation from this scheme may be made with the results obtained within the normal range of error, but the above outline was found by a large number of analyses to be the most dependable.

Summary

1. Calcium oxalate may be precipitated quantitatively in the presence of phosphate ions.
2. The solutions should be made alkaline before the addition of ammonium oxalate, and a small excess of ammonium hydroxide added.
3. The best temperature for precipitation is 20–25°.
4. Reprecipitation of calcium oxalate is not always necessary.

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THE DECOMPOSITION OF NITROGEN PENTOXIDE IN INERT SOLVENTS

BY HENRY EYRING AND FARRINGTON DANIELS

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The nitrogen pentoxide decomposition has been used to test theories of reaction rates—the radiation hypothesis, the collision theory and the chain mechanism. The theory of activation through collision is promising but more experimental facts are needed. It is necessary to distinguish between activation caused by ordinary collisions and activation caused by collisions with the decomposition products.

The mechanism of activation does not affect the decomposition rate provided that the rate of activation is high enough to maintain the equilibrium number of activated molecules. A decision may be made between the collision theory and the chain theory by providing conditions which will deactivate the products of decomposition before they collide with unactivated nitrogen pentoxide molecules. Several investigators have sought to make collisions of the decomposition products with the walls relatively numerous as compared with collisions with nitrogen pentoxide. Sprenger[1]

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[1] Sprenger, *Z. physik. Chem.*, **136**, 49 (1928).

reported that the decomposition rate fell off markedly at low pressures, but Tolman[2] found the decomposition rate down to 0.2 mm. to be the same as the normal rate at high pressures.[3,3a]

The present investigation is concerned with the rate of decomposition of nitrogen pentoxide in various inert solvents. The decomposition in chemically active solvents is reported in the following communication. In solution the decomposition products must collide many times with solvent molecules before encountering a nitrogen pentoxide molecule and it is possible that a chain mechanism, if it exists, might be hindered under these conditions.

In this Laboratory it was found by Lueck[4] that the decomposition rate of nitrogen pentoxide is only slightly affected by inert solvents but new developments in the field of kinetics have made it necessary to extend the work to more solvents with the greatest possible precision. The slight deviation from the normal decomposition rate caused by solvents becomes a matter of considerable interest.

The study of nitrogen pentoxide decomposition in solutions makes it possible to bridge the gap between unimolecular reactions in the gas phase and in the liquid phase. The choice of inert solvents is restricted but some exhibit catalytic effects sufficient to double the decomposition rate. In solution it was possible to study solutions up to a calculated osmotic pressure of seventy-five atmospheres—a concentration which cannot be reached in the gas phase. The results are of value in the study of concentrated solutions, and measurements on saturated solutions are of interest in connection with the concept of activities as applied to reaction rates.

Preliminary Experiments

Mr. Roger H. Lueck[4] reported the decompostion rate of nitrogen pentoxide in carbon tetrachloride and chloroform, and then extended the measurements to other solvents. His later measurements also gave excellent unimolecular constants and the decomposition rates at 35° in the different solvents were as follows: CS_2 (fastest), $CH_3(C_2H_5)CHBr$, $CHCl_3$, $CCl_4 \cdot C_2H_2Cl_4$, vacuum (*i. e.*, gas phase), CH_3NO_2 (slowest). These results[5] were not published because a satisfactory interpretation was not available and because it was feared that some secondary phenomenon might be involved. The more extensive measurements of the present investigation have con-

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[2] Ramsperger, Nordberg and Tolman, *Proc. Nat. Acad. Sci.*, **15**, 450 (1929).

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

[3a] Recent investigations indicate that the specific decomposition rate falls off at pressures below 0.05 mm., Ramsperger and Tolman, *Proc. Nat. Acad.*, **16**, 6 (1930); Schumacher and Sprenger, *ibid.*, **16**, 129 (1930).

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

[5] Quoted in *Trans. Faraday Soc.*, **24**, 732 (1928); and "L'Activation et la Structure des Molécules," Paris, **1928**.

firmed the general order of solvents observed before and show that the earlier results were subject to small fluctuations caused by an unpredictable concentration effect which affected the calculation of the activation energy. Carbon disulfide and isopropyl bromide were found to undergo chemical reaction.

Experimental Procedure

Apparatus.—The apparatus was similar to that described before by Lueck[4] but it was decided to eliminate any chance of water leakage or of chemical contamination by using an all-glass apparatus.

The apparatus is shown in Fig. 1. A small flask of 5-cc. capacity containing the nitrogen pentoxide in solution was connected to the gas buret through a coil of thin-walled glass tubing 1 mm. in diameter and about 1 meter long. The glass tube had sufficient flexibility to permit rapid shaking of the solution in a pendulum cradle. The flask contained two or three glass pearls to assist in agitating the liquid. The solution was introduced through the side arm, which was then sealed off. The flask was then placed in the thermostat and strapped to the shaker.

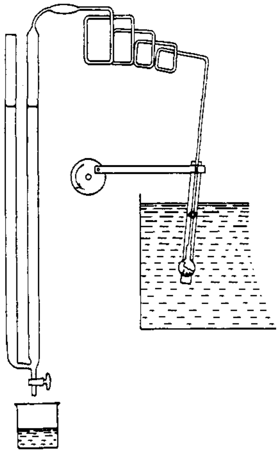

Fig. 1.—Apparatus for measuring the decomposition rate of nitrogen pentoxide in solution by the evolution of oxygen.

The buret was filled with nitrobenzene, which was drained out as needed to maintain the level in the two arms. Before reaching the buret the oxygen passed through glass wool saturated with concentrated sulfuric acid to remove any nitrogen dioxide. The flask was made small to economize nitrogen pentoxide and to minimize any error due to the partial pressure of nitrogen dioxide produced by the decomposition.

Temperature.—A thermoregulator with oscillating contact kept the temperature of the thermostat within 0.01°. The temperature was determined by reference to a thermometer from the U. S. Bureau of Standards.

The shaker operated through an arc of 10 cm. 360 times per minute and it was shown by experiments that this agitation was ample to prevent supersaturation of the solution with oxygen.

A thermocouple inserted in the solution showed that at 600 oscillations the temperature of carbon tetrachloride in the flask at 45° was raised 0.0277° by the mechanical shaking but at 360 oscillations it was raised less than 0.02°. The thermocouple gave a zero reading when the shaker was stopped. This temperature rise makes a difference of less than 1% in the reaction rate and is within the limit of experimental error.

The heating was slightly less when the nitrogen pentoxide was decomposing, due probably to the evaporation of the solvent by the escaping oxygen gas. The experiment shows that the shaking is not a source of error and is particularly gratifying in proving also that the reaction is carried out under isothermal conditions in spite of any heat changes from the reaction.

Materials.—The nitrogen pentoxide was prepared by the method of Daniels and Bright.[6]

Solvents of different purity were used but no difference in the results could be detected. For most of the experiment very pure liquids were used—prepared by Pro-

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[6] Daniels and Bright, This Journal, **43**, 53 (1921).

fessor Timmermans in Brussels under the authority of the Bureau International d'Étalons Physico-Chimiques and distributed by the United States Bureau of Standards. The constants of these very pure compounds have been published by Professor Timmermans.[7]

The liquid nitrogen tetroxide was made by heating lead nitrate. It was then stored in a sealed tube with phosphorus pentoxide and distilled into the flask as needed.

The flask was filled in different ways. Sometimes the crystals were sublimed into the flask and the solvent was added later and sealed off. Sometimes the nitrogen pentoxide was dissolved in a large reservoir, kept cold and pipetted into the flask. No systematic difference could be detected in the results. The solutions were usually of a light straw color at 0°, indicating a trace of nitrogen dioxide from the decomposition. When placed in the thermostat at 45° the solution turned brown very quickly on account of the decomposition.

Dry Solutions.—In several experiments special precautions were taken to exclude moisture. The nitrogen pentoxide and solvent were distilled into U-tubes containing phosphorus pentoxide, the arms were then sealed off and the tubes stored overnight in contact with the phosphorus pentoxide at 0°. The materials were then distilled into the reaction flask, which was sealed off while immersed in liquid air. A vacuum was applied through the tube and gas buret to facilitate the distillation. The apparatus was thoroughly heated and evacuated before each experiment.

Saturated Solutions.—The decomposition rate in saturated solutions is a matter of particular interest. The thermostat was set at 15° in these experiments because the solubility is too great at higher temperatures, and inconveniently large quantities of oxygen are evolved.

An excess of nitrogen pentoxide was sublimed into the flask, a weighed quantity of the solvent was introduced at 0° and the arm was sealed off. As soon as some nitrogen pentoxide in solution decomposed, its place was immediately taken by more nitrogen pentoxide from the crystals and in this way the concentration in solution was maintained constant. An excess of crystals was present at all times. The solubility was determined by heating the solution (freed from crystals) and measuring the total evolution of oxygen.

Experimental Results

Calculations.—The specific reaction rate k is given by the equation used before[4]

$$k = \frac{2.303}{t_2 - t_1} \log \frac{V_\infty - V_1}{V_\infty - V_2}$$

in which V_1 is the volume of oxygen liberated at time t_1, V_2 is the volume at time t_2, and V_∞ is the final or total volume.

The critical increment E is calculated with the help of the familiar equation

$$\log \frac{k_2}{k_1} = \frac{E\,(T_2 - T_1)}{2.303\,RT_2T_1}$$

in which R is the gas constant and T is the absolute temperature.

Usually six to ten constants were calculated at intervals over the course of the reaction. The average was checked with logarithmic graphs. The constants were uniform and the average deviation was usually less than 3%. The data showed no trend except that over the range of the last cc. there was

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[7] Timmermans and Martin, *J. chim. phys.*, **23**, 733 (1926); **25**, 251 (1928).

a tendency for the constant to increase slightly, due in many cases to the magnification of errors in this region. In the most concentrated solutions the constant was higher by about 8% at the beginning of the reaction and a calculation indicated that the volatilization of nitrogen pentoxide during the first part of the experiment could cause the constant to be greater by about 8% at the beginning.

Solvent Effect.—The data for different solvents are given in Table I. In these experiments the concentration was kept nearly the same, approximately one-thousandth of a mole in 5 cc. of solution, corresponding to a calculated osmotic pressure of about 5 atmospheres.

TABLE I

SPECIFIC DECOMPOSITION RATE OF NITROGEN PENTOXIDE IN DIFFERENT SOLVENTS

Values of $k \times 10^4$

Solvent	15°	20°	25°	35°	40°	45°	E
Nitrogen tetroxide	0.159	0.344	...	...	..	..	25,000
Ethylidene chloride	...	.322	...	2.54	(4.22)	(7.26)	24,900
Chloroform	...	.274	0.554	...	(3.78)	(7.05)	24,600
Ethylene chloride	...	.238	.479	...	(3.70)	(6.21)	24,400
Carbon tetrachloride	...	.235	.469	...	(3.62)	(6.29)	24,200
Pentachloro-ethane	...	.220	.430	...	(3.26)	(6.02)	25,000
Bromine	.114	.215	...	...	..	..	24,000
Gas phase[a]	.079	.165	...	...	2.52	4.73	24,700
Nitromethane	.0747	...	...	...	(2.14)	4.33	24,500

[a] Calculated from data of Daniels and Johnston, THIS JOURNAL, **43**, 53 (1921).

Over a hundred and fifty determinations were made and practically all of them gave satisfactory unimolecular constants. It was not realized for a long time, however, that the magnitude of the constants depended on the concentration of nitrogen oxides, and although this concentration effect was small, it was sufficient to lead to considerable errors in the calculation of the critical increment, E. Although several experiments were averaged, the value of E varied by two or three thousand calories.

It was necessary to adopt a new technique in which the value of k was determined at two temperatures using the same solution. Better results were obtained at lower temperatures with lower reaction rates. The solution was put into the thermostat at 20° and the rate of gas evolution determined. Before the decomposition was half finished, the apparatus was removed to a thermostat at 25° (or other temperature) where the rate of gas evolution was determined, and the final volume, V_∞, measured. The final volume was then calculated for the lower temperature, and values of k were calculated at both temperatures.

These last results are all recorded in the columns of Table I under 15, 20 and 25° (and 45° for nitromethane). They are used in calculating the critical increments, E, given in the last column. All the values of E are probably the same within the limit of experimental error.

The values of k at 40 and 45°, given in parentheses, represent the averages of several experiments obtained with the first technique in which different solutions were used at the two temperatures. It is to be noticed that the order of solvents is practically the same in all cases. The solvent effect is very real and reproducible. The values in parentheses cannot be used, however, for calculating the critical increment because the concentration at the two temperatures was not always the same. In some cases the concentrations happened to be the same and then the value of E is the same as the more reliable value calculated from data obtained with the new method and recorded in the last column.

Concentration Effect.—It was noticed that the specific decomposition rate k was faster at the higher concentrations. Accordingly, a stock solution of nitrogen pentoxide in carbon tetrachloride was kept at a low temperature and a series of experiments was carried out after diluting with definite quantities of carbon tetrachloride. The results are recorded in Table II.

TABLE II

INFLUENCE OF CONCENTRATION ON DECOMPOSITION RATE OF NITROGEN PENTOXIDE IN CARBON TETRACHLORIDE AT 45°

1. 5.33 moles N_2O_5/liter			2. 2.33 moles/liter			3. 1.40 moles/liter		
Time	Cc. of O_2 remaining	$k \times 10^4$	Time	Cc. of O_2 remaining	$k \times 10^4$	Time	Cc. of O_2 remaining	$k \times 10^4$
0	32.60	..	0	9.58	..	0	5.93	..
82	30.79	6.97	184	8.53	6.32	423	4.61	5.95
162	29.19	6.67	319	7.84	6.23	753	3.75	6.26
409	24.82	6.57	526	6.89	6.22	1116	3.04	5.78
604	20.57	6.37	867	5.57	6.23	1582	2.30	5.98
1129	14.49	6.67	1198	4.56	6.03	1986	1.83	5.66
1721	9.60	6.95	1877	2.98	6.27	2343	1.47	6.13
1929	8.30	6.99	2315	2.25	6.42	..	..	..
3399	3.27	6.69	3144	1.38	5.88	..	..	..

It is obvious that the decomposition in the concentrated solution (1) is fastest and that it decreases in speed as the solution is diluted. The effect is rather unexpected in view of the unimolecular character of the decomposition. For example, in the latter part of Expt. 1 the concentration of nitrogen pentoxide is the same as at the beginning in Expt. 3, but the rate is faster in No. 1 and still there is no deviation from the unimolecular law. Apparently there is a concentration effect in which the decomposition products N_2O_4 and NO_2 are just as effective as the original nitrogen pentoxide molecules. In a single experiment the nitrogen pentoxide in solution (0.1 mole fraction) becomes less and approaches zero while the nitrogen tetroxide starts at nearly zero and increases until it has nearly the same concentration as the original nitrogen pentoxide. Further experiments at 45° on the concentration effect are shown in Fig. 2. The unimolecular constant k is plotted against the concentration of nitrogen pentoxide expressed in moles per liter. In the most concentrated solutions the loss of nitrogen pentoxide through volatilization with the oxygen could cause the constant *k* to increase by as much as 8% at the beginning of the reaction, and the averaged value over the whole course of the reaction would be somewhat too high. The observed concentration effects are much greater than this.

In this connection it is interesting to note that in the earlier work it was observed that determinations in nitromethane checked better than those in carbon tetrachloride. This fact may be explained by the smaller concentration effect in nitromethane.

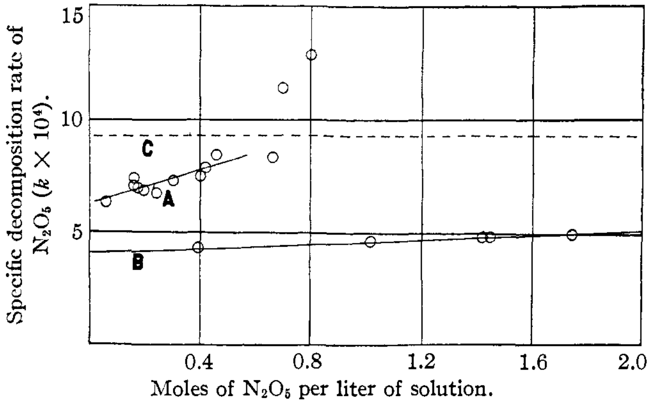

Fig. 2.—Influence of concentration on the specific decomposition rate of nitrogen pentoxide in solution at 45°: A, carbon tetrachloride; B, nitromethane; C, nitrogen tetroxide.

Moisture.—The experiments using special precautions to make the solutions as dry as possible may be summarized as follows. In one case *k* was found to be 5.83×10^{-4} and in another it was 5.68, giving an average of 5.75×10^{-4}. The average of several experiments without special drying precautions was 6.29. The difference between 5.75 and 6.29 might be attributable to the concentration effect. In another experiment 0.04 g. of water was added directly to the solution but the value of *k* was not affected. No change was observed in the decomposition rate in nitromethane when the solution was dried in the manner described for carbon tetrachloride. If moisture has any effect at all on the decomposition rate, it is a very small effect.

Saturated Solutions.—The specific decomposition rates, *k*, in saturated solutions are given in Table III. The values of *k* are calculated from the formula

$$k = -1/c \, \mathrm{d}c/\mathrm{d}t$$

where *c* is the solubility (in volume of oxygen) and $\mathrm{d}c/\mathrm{d}t$ is the constant rate of evolution of oxygen.

TABLE III

DECOMPOSITION RATE IN SATURATED SOLUTIONS AT 15°

Solvent	CCl_4	CH_3NO_2
O_2 per 2 cc. solvent (per sec.), cc.	0.0022	0.00148
Soly. of N_2O_5 per 2 cc. solv., as cc. of O_2	120	110
$k \times 10^4$	0.183	0.135

The value of k in each case is much higher than in dilute solutions, a fact which is in accord with the concentration effect noted before. The value of k for N_2O_5 almost saturating N_2O_4 is 0.159×10^{-4}.

Mixed Solvents.—In order to test the influence of polar molecules *o*-dinitrobenzene and *m*-dinitrobenzene were dissolved in carbon tetrachloride and the solution was used as the solvent for nitrogen pentoxide.

Although the dielectric constants are different, the decomposition rates in these solutions are practically the same as in pure carbon tetrachloride, as shown in Table IV. Nitrogen pentoxide does not react with dinitrobenzene.

TABLE IV

DECOMPOSITION OF NITROGEN PENTOXIDE IN CARBON TETRACHLORIDE SOLUTIONS OF DINITROBENZENE AT 45°

1.	Carbon tetrachloride	0.000619
2.	0.2 *M* *o*-dinitrobenzene in carbon tetrachloride	.000582
3.	0.2 *M* *m*-dinitrobenzene in carbon tetrachloride	.000586

A determination was made in a mixture of nitromethane and carbon tetrachloride. In a mixture of 0.1 mole fraction of nitromethane and 0.9 mole fraction of carbon tetrachloride, the value of k was found to be 5.51×10^{-4}. The effect of these solvents appears to be proportional to their mole fraction and independent of catalytic effects produced by small quantities of the solvent.

Theoretical Discussion

All the experiments give confidence that the decomposition of nitrogen pentoxide in these solutions is a simple unimolecular reaction which is significant for theoretical study. The reproducibility of results, the unfailing unimolecularity of the calculated rates, the small differences in velocity caused by a change in concentration (from 0.1 to 1.8 molar) or in solvent preclude the possibility that the reaction is complicated by traces of catalysts. Some bimolecular reactions follow the unimolecular equation simply because the solvent is in large excess, but these experiments were extended to include concentrated solutions up to 1.8 molar or approximately $^1/_3$ mole fraction.

In a second communication which follows this one it will be shown that an intermediate reaction may occur without destroying the unimolecularity of the constant, but gas analysis of the products and refractive index measurements failed to show any reaction with the solvents described here.

The relative influence of the different solvents on the decomposition rate has been checked so many times and under so many different conditions that the solvent effect must be a significant thing, depending on the nature of the solvent rather than on secondary phenomena such as dissolving of water from the air or the presence of catalysts.

The Arrhenius Equation.—The mechanism of the reaction can be studied best after expressing the facts mathematically and for this purpose the Arrhenius equation is very satisfactory, as given in the following forms

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E}{RT^2} \tag{1}$$

$$\log k = \frac{-E}{2.303\ R} \times \frac{1}{T} + \log s \tag{2}$$

$$k = s\,e^{-E/RT} \tag{3}$$

$$\log k_2/k_1 = \frac{E\ (T_2 - T_1)}{2.303\ RT_2T_1} \tag{4}$$

in which k is specific reaction rate, *i. e.*, fraction of molecules decomposing per second; E is critical energy of activation, or the excess which one mole must have in order to decompose; R is gas constant; T is absolute temperature; s is constant. For the decomposition of nitrogen pentoxide in the gas phase[3] the equation becomes

$$k = 5.08 \times 10^{13}\ e^{-24{,}700/1.98\ T} \tag{5}$$

and at 298°K.

$$k = 0.0000338 = 5.08 \times 10^{13}\ e^{-24{,}700/1.98 \times 298} \tag{6}$$

$$\log k_{308}/k_{298} = \log\frac{0.000131}{0.0000338} = \log 3.88 = 0.5888 = \frac{24{,}700\ (308 - 298)}{2.303 \times 1.98 \times 298 \times 308} \tag{7}$$

The constant s has the dimensions of a number divided by time, and Dushman[8] and others have pointed out that it may have the physical significance of a frequency of light. Polanyi and Wigner[9] have given a derivation recently showing that it is a frequency and that the time depends on the surging of energy among the atoms in a molecule after activation.

As a first approximation, the present authors will take the simple view that s is a frequency and that $1/s$ or, better, $^1/_2\ s$ represents the time taken for the two atoms or groups of atoms at a valence bond to fly apart, after activation—*i. e.*, the natural vibration period in the valence bond which is to break. Certainly it is dimensionally correct and of the right magnitude to correspond to atom vibrations in the molecule—*i. e.*, in the short infrared. Fortunately, in the infra-red region of the spectrum the frequency of light absorbed by the molecule is nearly the same as the frequency of oscillation of its parts. It is possible then to estimate the order of magnitude of s from known infra-red absorption spectra. The significance of s will be discussed more fully in a later communication.

[8] Dushman, THIS JOURNAL, **43**, 431 (1921).

[9] Polanyi and Wigner, *Z. physik. Chem.*, **139A**, 439 (1929).

In the study of unimolecular reactions ten years ago it was thought that a molecule decomposed instantly as soon as it was activated, and it was difficult to explain the reaction on the basis of collisions. This difficulty led to the invention of the ill-fated radiation hypothesis. It is evident now that decomposition is not synonymous with activation and that the atoms held together at a valence bond cannot fly apart in less time than the natural period of vibration of those atoms. Molecules receive energy of activation, E, from collisions but it is distributed in a random manner among the atoms and time is necessary before this energy is localized in the particular valence bond. During the rearrangement period many of the activated molecules are deactivated by collisions, and since the number decomposing depends on the equilibrium number in this specially activated condition rather than on the total number activated, the reaction appears to be independent of the number of collisions; *i. e.*, the reaction follows the unimolecular equation.

If the Arrhenius equation is correct (and it is in excellent agreement with the facts), and if the constant s corresponds to the frequency of atom vibrations in the molecule, several relations may be deduced which were formerly regarded as empirical facts. In this discussion the following numerical relations will be helpful.

According to Equation 7 an error of 2% in k_1 makes an error of 1.4% in E or 350 calories, whereas in Equation 6 it makes an error of only 0.05% or 12 calories. k is increased a thousand times by decreasing E 16% or 4000 calories according to Equation 6 but a 16% decrease in E produces only a 16% decrease in log k_2/k_1 according to Equation 7 and k_{308}/k_{298} is changed only from 3.88 to 3.12. From Equation 6 it is seen that the value of k can be doubled by decreasing E only 425 calories, or 1.7%.

Most reaction rates which are measurable at room temperature double or treble for a ten degree rise. Experimental measurement of reaction velocities has been ordinarily limited to a thousand or ten thousand-fold range because it is difficult to measure very rapid reactions on account of the uncertain time of mixing or of bringing the system to temperature equilibrium and because it is troublesome to measure slow reactions lasting over a month. The equations just given show that a thousand-fold variation in k changes the temperature effect (k_{308}/k_{298}) by only about 20%. As long as k varies only from 10^{-2} to 10^{-6} and s varies only from 10^{13} to 10^{14}, k_{308}/k_{298} must fall in the neighborhood of 3 or 4.

Although the velocities of related reactions may vary a hundred-fold or more, as in the case of the hydrolysis of different esters, the temperature effects are very closely the same.[10] All these esters react at the same bond and infra-red absorption spectra show that the oscillation frequencies

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[10] Rice, Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, **1924**, p. 927.

(corresponding to s) at a bond are only slightly changed by introducing more atoms into the molecule. It has been shown that if s remains constant, the value of E and hence k_2/k_1 cannot change materially as long as k varies only a thousand-fold or less.

The constant s appears to be a universal constant within certain limits for unimolecular reactions, Christiansen and Kramers[11] and Polanyi[2] have collected data from a large number of reaction rate experiments and they have shown that E/T and k have such values that s varies only from about 10^{12} to 10^{14}. The results of the present investigation are interesting in this connection. In the earlier work in this Laboratory by Lueck and by the present authors, variations of 1000 to 2000 calories were found in the critical energy, E, for nitrogen pentoxide decomposition in different solvents. The experimental work had been done so carefully and the constants were so reproducible and so satisfactorily unimolecular that these variations were accepted without question. Only after discovering the concentration effect described elsewhere in this communication and after taking special precautions was it established that although the constants varied as much as 100% in the different solvents, the values of k_2/k_1 and hence the critical increments were constant within the limit of experimental accuracy. In the earlier work E varied 10% on account of experimental error in the value of k in Equation 4, and since k was closely fixed by experiment, s varied over seventy-fold. Experimental improvement reduced this variation from 70 to 2 or 3.

Extraordinary care is necessary in determining k if its temperature coefficient is to be used in calculating E or s. It seems probable that in more complicated reactions or in velocity experiments where the rate is less accurately known, some of the deviations in E and s recorded in the literature may be attributed to experimental error. In fact, the form of the Arrhenius equation is such that in many cases where the data are not very accurate and the "constants" are not constant, the value of E can be calculated more accurately with Equation 2 from k at one temperature on the assumption that s is about 5×10^{13}, than it can be calculated in the usual way from the k's at two temperatures in Equation 4.

The constancy of s in all reactions is in accord with the idea that it represents an oscillation frequency between atoms and is related to absorption bands in the near infra-red. A frequency of 5×10^{13} corresponds to 6μ and almost all organic and inorganic compounds have absorption in this region corresponding to valence bonds which are broken when the molecule decomposes.

One more relation has been noted,[12] namely, that E/RT is approximately constant for many reactions if T is taken so that the different reactions have

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

[12] Hinshelwood, *Chem. Rev.*, **3**, 247 (1926).

the same value of k. For example, the specific decomposition rate for nitrogen pentoxide is 0.00158 at 328° absolute and for nitrous oxide it is 0.00150 at 562° absolute. For the former reaction E is 24,700 and $E/RT = 38.0$, while for the latter $E = 68{,}500$ and $E/RT = 41.4$. If k is the same by selection and s is an approximate constant (about 5×10^{13}) representing the natural oscillation frequency of atoms or groups of atoms, then by Equation 3, E/RT must be a constant. Slight variations in s and hence in k are to be expected because the oscillations will vary somewhat for different atomic groups.

Solvent Effect.—As recorded above, the decomposition rate of nitrogen pentoxide is changed by filling up the empty space between the nitrogen pentoxide molecules in the gas phase with molecules of an inert solvent. Thus far no *inert* solvent has been found which increases the velocity by more than 100% and none has been found which appreciably decreases the decomposition rate. Large differences in the specific decomposition rate have been found in some cases but these are due to definite chemical reactions with the solvent and they are described in the next communication.

The concentration effect is to be regarded as a special case of a solvent effect in which liquid nitrogen pentoxide is the solvent. Nothing is known of the properties of liquid nitrogen pentoxide[13] and it will be very difficult ever to get direct information because at temperatures above its sublimation point (35°)[14] where it might exist in the liquid phase, it decomposes rapidly and the liquid N_2O_4 formed in the decomposition would dissolve the nitrogen pentoxide and contaminate it. It may be concluded, however, that liquid nitrogen pentoxide would be very much like nitrogen tetroxide because the latter has been shown in this communication to be just as effective as the former in increasing the decomposition rate and maintaining the unimolecularity of the constant over the whole range of decomposition.

Extrapolation to the zero concentration axis should give the maximum solvent effects under conditions where each nitrogen pentoxide molecule is isolated from other nitrogen pentoxide molecules but each is surrounded completely by the solvent molecules. The solutions are sufficiently nearly ideal so that the values at infinite dilution will not be expected to differ much from those for the dilute solutions used here.

Extrapolation to 100% nitrogen pentoxide is not significant on account of the limited solubility, but if the concentrated solutions could exist, the solvent effects would be minimized and all solutions would behave alike, probably much like the solution in liquid nitrogen tetroxide. The concentration curves for all solvents in concentrated solutions would then coincide with the curve for N_2O_4 (Fig. 2).

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[13] The liquid nitrogen pentoxide described in the early literature was probably a solution in N_2O_4 or water.

[14] Daniels and Bright, THIS JOURNAL, **42**, 1139 (1920).

The manner in which the solvent atmosphere affects the decomposition rate is important. According to the Arrhenius equation it can affect k either by changing s, the frequency of atom oscillation, or by changing E, the energy of activation. The authors take the view that E is changed rather than s, because a 100% change in s is required to double k and only a change of 425 calories in E is required. The former is quite unlikely. Infra-red absorption bands may shift slightly when new atoms are introduced into the molecule and they may shift slightly in different solvents, but they do not give anything like a 100% shift. Nitrogen pentoxide absorption bands in the infra-red do not show any shift as great as 0.05μ when dissolved in these solvents.[15]

A change of 425 calories per mole in the heat of activation on the other hand is easily possible. For example, if a compound is formed between nitrogen pentoxide and the solvent with the absorption of heat, the average heat content of the molecules will be increased, the difference (the critical increment, E) between this and the heat content of the activated molecules will be decreased and k will be increased. It is possible that heat effects in other parts of the molecule away from the bond which breaks to give decomposition may obscure the heat effect which is concerned with the reaction. It is possible also that the solvent may quench activated molecules and involve reactions with activated molecules rather than with average molecules. In these cases the heat of solution may not be significant. The thermochemistry of nitrogen pentoxide and its solutions is being investigated in this Laboratory.

Activities.—The experimental data in saturated solutions offer an unusually favorable means of distinguishing between the use of total concentrations and activities in reaction rate measurements. Neither is completely satisfactory. Crystalline nitrogen pentoxide, gaseous nitrogen pentoxide and saturated solutions in the various solvents are all in equilibrium and the escaping tendency of simple N_2O_5 molecules or vapor pressure is the same in every case, but the total concentrations in moles per liter are widely different.

The gas phase may be considered as a special case of solution in which the vacuum acts as solvent. At saturation the increased solubility in solvents over that in vacuum may be attributed for the sake of concreteness to a complex between the nitrogen pentoxide and the solvent, as follows

$$\text{Crystalline } N_2O_5 \rightleftarrows \text{gaseous } N_2O_5 \rightleftarrows \text{simple } N_2O_5 \text{ molecules in solution} \rightleftarrows \text{solvated molecules } (N_2O_5\text{-solvent})$$

The present discussion is not concerned with the type of complex or whether it is chemical or physical in nature.

The experimental facts connected with the decomposition in saturated solutions are summarized in Table V, where k, the specific decomposition

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[15] Daniels, THIS JOURNAL, **47**, 2856 (1925).

rate, in the saturated solution is given by the expression $(1/c)$ $(-\mathrm{d}c/\mathrm{d}t)$, C_s is the solubility in mols per liter, and r is the rate of decomposition per liter $-\mathrm{d}c/\mathrm{d}t$.

TABLE V

DECOMPOSITION IN SOLUTION OF NITROGEN PENTOXIDE WHICH IS IN EQUILIBRIUM WITH CRYSTALLINE NITROGEN PENTOXIDE AT 15°

		N_2O_5 saturating	C_s =	r =	k =
Crystalline N_2O_5	$\leftrightarrows$	Vacuum (gas phase)	0.0102	0.0080×10^{-5}	0.79×10^{-5}
	$\leftrightarrows$	Liquid CH_3NO_2	4.38	5.92×10^{-5}	1.35×10^{-5}
	$\leftrightarrows$	Liquid CCl_4	4.78	8.75×10^{-5}	1.83×10^{-5}
	$\leftrightarrows$	Liquid N_2O_4	..	....	1.59×10^{-5}

If the activity determines the reaction rate, the evolution of oxygen $(-\mathrm{d}c/\mathrm{d}t$ per liter) should be the same in all cases because the escaping tendency is the same in all. A glance at the table shows that this situation is far from the truth. Such a result would be obtained if the solvated molecules did not decompose at all.

If the total concentrations determine the decomposition rate, then the *specific* reaction rates, k, should be the same in all solvents. Again, the tables show that this cannot be the case. Such a result would be obtained if all the molecules, solvated and unsolvated, decomposed at the same rate.

Obviously both these views are incomplete. Solvated molecules apparently do decompose but they do not decompose at the same rate as the unsolvated molecules. If they decompose faster, k will be larger and if they decompose more slowly, k will be smaller. The experimental facts show that k is increased by the addition of these solvents and the solvated molecules must be decomposing faster, but apparently not more than twice as fast as the simple molecules. Nitromethane gives a very slight lowering of k and this fact suggests that the solvated molecules may be decomposing very slightly more slowly than the simple molecules.

The case of the solid crystalline nitrogen pentoxide is interesting. It does not decompose at all. Its heat of sublimation—14,600 calories[15]—is added to the critical increment, E.

In other words, a molecule must acquire $24{,}700/(6 \times 10^{23})$ calories of energy more than an average gas molecule before it can become activated; but it must acquire $(24{,}700 + 14{,}600)/(6 \times 10^{23})$ calories of energy more than an average molecule in the crystal lattice. This value of E is so large that the crystal would have to be heated up to 194° on the basis of Equation 3 before the specific decomposition rate would be equal to that in the gas phase at room temperature.

Summary

1. Using an all-glass apparatus the decomposition of nitrogen pentoxide has been measured at various temperatures in the following inert solvents, nitrogen tetroxide, ethylidene chloride, chloroform, ethylene chloride, carbon tetrachloride, pentachloro-ethane, bromine, "vacuum" and nitromethane.

2. The decomposition is strictly unimolecular in all cases. The specific decomposition rate decreases in the order given above. In nitrogen tetroxide it is about twice as large as in the gas phase.

3. The critical increment, E, calculated from the temperature coefficient of reaction rate is 24,700 calories within the limit of experimental error in every case.

4. The specific decomposition rate is somewhat greater in concentrated than in dilute solutions and yet the unimolecularity is maintained throughout the whole course of the reaction. Apparently N_2O_4 and N_2O_5 are equally effective in accelerating the decomposition.

5. Moisture does not affect the decomposition rate.

6. In a mixed solvent the effects of the solvents are proportional to their mole fractions.

7. The decomposition rate was determined in saturated solutions. The results are of interest in the study of activities.

8. The stability of crystalline nitrogen pentoxide is discussed.

9. The constancy of E in different solvents and the universal constancy of the temperature effect are interpreted on the basis of the Arrhenius equation, $k = se^{-E/RT}$ using the experimental data for nitrogen pentoxide.

10. The factor, s, in the Arrhenius equation was found to be constant when the temperature coefficient of reaction rate was determined with great accuracy. It is predicted that s will approach an approximate constant in nearly all unimolecular reactions as experimental measurements become more accurate. The quantity, s, may be identified with the infra-red oscillation frequency at the valence bond which is about to break.

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

THE DECOMPOSITION OF NITROGEN PENTOXIDE IN CHEMICALLY ACTIVE SOLVENTS

BY HENRY EYRING AND FARRINGTON DANIELS

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In the preceding communication[1] it was shown that the normal decomposition rate of nitrogen pentoxide is not appreciably affected by inert solvents. It was found that the specific decomposition rate might vary from the normal rate in the gas phase to twice the normal rate but that the temperature effect and the critical energy of activation, E, remained the same within the limits of experimental error.

Another group of solvents is described here in which the decomposition rates and their temperature coefficients are quite abnormal. The distinction between "inert" and "chemically active" solvents is a matter only of

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[1] Eyring and Daniels, THIS JOURNAL, **52**, 1472 (1930).