centration is somewhat uncertain. It is quite exact if the surface tension is a linear function of the molality in this region, as seems to be indicated by the adjacent portion of the curve and almost all other measurements on salt solutions. However, this may not be the case, since if it is assumed that the activities of the dilute solutions are the same as those given by Lewis and Randall for solutions of barium chloride, this linear interpolation gives a thickness of 4.05 Å. at 0.0001 *M*, and of 4.26 Å. at 0.001 *M* which is thinner than that indicated at 0.1 *M* (4.5 Å.). The thickness for these dilute solutions should be obtained from measurements of the highest exactness possible with the capillary-height method. This work is now in progress in the Kent Chemical Laboratory and it is hoped that sufficient accuracy will be attained to warrant a comparison with the predictions of the Debye-Hückel theory which concern the variation of the surface tension of such dilute salt solutions.

Summary

Careful measurements of the surface tension of water and of aqueous solutions of calcium chloride at 25° have been made at concentrations up to 7 moles of salt per 1000 g. of water. From the surface tensions and the values of the activity coefficients for calcium chloride calculated from data found in the papers of various investigators, the mean thickness of the water film on the calcium chloride solutions is calculated.

The thickness of the film at 1.25 *M* is 3.1 Å., which is the cube root of the volume of a water molecule. At lower concentrations the film is thicker and at higher concentrations *thinner*, but up to 3 or 4 *M* (at least) it is essentially a monomolecular water film.

CHICAGO, ILLINOIS

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

THE PHOTO-CHEMICAL INACTIVITY OF INFRA-RED RADIATION WITH SPECIAL REFERENCE TO THE DECOMPOSITION OF NITROGEN PENTOXIDE

BY FARRINGTON DANIELS

RECEIVED SEPTEMBER 9, 1925 PUBLISHED MARCH 5, 1926

The decomposition of nitrogen pentoxide is a valuable reaction for testing theories of the mechanism of chemical reaction. Not only is it a homogeneous gas reaction but, according to three different researches, it now appears to be truly unimolecular.[1,2,3] As such, it has been supposed to be uninfluenced by collision, and experiments have shown that its

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[1] Tolman and White, THIS JOURNAL, **47**, 1240 (1925).

[2] Hirst, *J. Chem. Soc.*, **127**, 657 (1925).

[3] Hunt and Daniels, THIS JOURNAL, **47**, 1602 (1925).

decomposition rate is independent of the frequency of collision over a wide range of concentrations.[3] It has been calculated that sufficient energy cannot be obtained from collisions to account for the observed reaction rate.[4,5] Perrin[6] has concluded that if the decomposition rate does not depend on collisions, the energy necessary for bringing about the reaction can come only from radiation, probably infra-red radiation, emitted by the walls of the containing vessel.

The energy required to bring about a unimolecular reaction (its critical increment) may be calculated from the temperature coefficient of the reaction rate. In the case of reactions proceeding with measurable velocity, this critical increment is of such a magnitude as to suggest, on the basis of the quantum hypothesis, that radiation in the short infra-red region should bring about the chemical change. In the original communications on nitrogen pentoxide,[7] it was calculated that, according to the radiation hypothesis, the activating radiation should fall at 1.16μ, and this calculation has been checked in other laboratories.[2] It was found that light of this frequency did not accelerate the reaction, but it was pointed out that there were well-defined absorption bands at multiples of this wave length, namely, at 3.4 and 5.8 μ and it was suggested that light of these frequencies *might* be active.[7,8]

Since the publication of the first investigation an intensive study of nitrogen pentoxide has been made in this Laboratory and it is the object of the present communication to describe experiments designed to determine whether these radiations are photochemically active. One is forced to the conclusion that nitrogen pentoxide is not decomposed by the infra-red radiation which it absorbs.

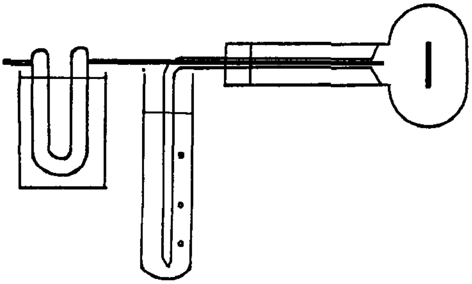

Fig. 1.—Apparatus for measuring the decomposition of nitrogen pentoxide by chemical analysis. A thin quartz bulb in front of a Nernst filament.

Experimental Part

In the apparatus shown in Fig. 1 nitrogen containing nitrogen pentoxide at a partial pressure of 51 mm. (crystals at 0°) was passed through a very thin quartz bulb which was placed 3 cm. in front of a Nernst glower, operated at one ampere.

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

[5] Tolman, THIS JOURNAL, **47**, 1524 (1925).

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

[7] Daniels and Johnston, THIS JOURNAL, **43**, 55, 72 (1921).

[8] Lewis, *Trans. Faraday Soc.*, **17**, 585 (1922).

The large area and close proximity to the Nernst glower assured extreme conditions of energy input, while the walls were thin enough to be practically transparent out to about 8 μ. Radiations of all wave lengths were passed into the bulb and decomposition by the blue light was prevented by keeping down the concentration of the brown nitrogen dioxide which is a necessary photocatalyst for this light.[7] The bulb was too fragile for convenient thermostating and a correction was made for the thermal decomposition at room temperature, by duplicate experiments in which the filament was not heated. The decomposition was determined by titration methods, already described,[3] which are capable of detecting with certainty the decomposition of one millionth of a mole of nitrogen pentoxide. The quartz bulb used for most of the experiments was somewhat elliptical. Its volume was 20 cc. and its walls ranged from 0.012 to 0.017 mm. in thickness. It was found possible to make these thin bulbs by blowing out, simultaneously with the removal of the heated quartz from the oxygen flame.

The radiant energy absorbed was determined in a rather simple manner by calorimetric measurements of the total energy input, determination of the distribution of energy from the Nernst glower, and determination of the absorption spectrum of nitrogen pentoxide. In getting the total energy input the bulb was placed in a vertical position and filled with 20 cc. of 0.4 N cupric chloride solution, which absorbs all the radiation down to 0.6 μ. In a typical experiment the temperature rose from 25° to 37° in two minutes, giving for ten minutes an input of 1200 calories. Another experiment showed 1100 calories, giving an average of 1150. A small correction was made for the heat capacity of the thermometer bulb. The radiation was so intense that a bare thermometer, placed behind the empty bulb, was maintained 22° above room temperature.

The curve for the distribution of energy is shown in Fig. 2. It was determined with an infra-red spectrometer at intervals of 0.05 μ, proper correction being made for the effective slit width at different wave lengths. The total area under the curve is 11,450 units. One large square contains 100 units, and each unit has for its abscissa 0.05 μ, and for its ordinate 5 mm. galvanometer deflection. The graph is used in determining the actual absorption of radiant energy by the nitrogen pentoxide as shown in Table I, which is given later.

The gases were passed through for ten-minute intervals, at a rate of about 35 cc. per minute. Between 600 and 750 micromoles (millionths of a mole) of nitrogen pentoxide was absorbed by the sodium hydroxide, depending on the surface of the crystals exposed to the nitrogen stream. In the control experiments in the dark the decomposition was 9, 10 and 10 micromoles. With the filament passing 1150 calories of radiation through the bulb in ten minutes the decomposition was 22 and 21 micromoles. The decomposition was increased by 12 micromoles when the filament was glowing. A glass screen reduced it to 14, 15 and 14, while immersion in cold water reduced it to 8, 9 and 7. In other experiments, various factors were changed but the extent of decomposition was not increased. It is shown in Table I that if all the energy absorbed is photochemically active, the decomposition should have been increased by 2200 micromoles, requiring an increase of 440 cc. of 0.01 *N* potassium permanganate solution instead of the 2.5 cc. actually used.

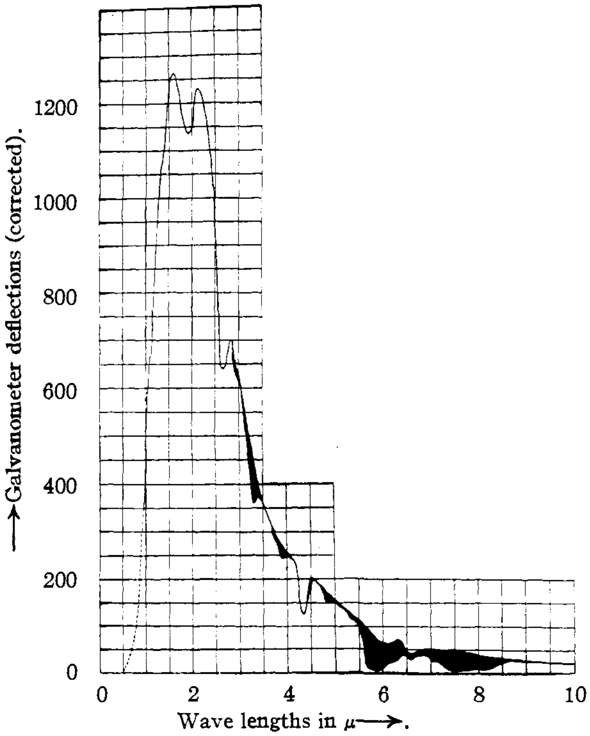

Fig. 2.—Distribution of energy in the Nernst filament at 1 ampere. Shaded areas represent absorption by 8 cm. of nitrogen pentoxide at 51 mm. pressure.

The experiments with screens indicate that neither blue light nor light of 1.16 μ could cause the slight decomposition observed. The latter wave length has been further ruled out by failure to detect any absorption in this region. The cell was next fitted with an oil manometer and arranged to function as an air thermometer. When it was filled with dry air free from carbon dioxide the radiation caused an increase in the temperature of the gas of 2°. When it was filled with air and nitrogen pentoxide at 51 mm. the temperature rose 4° when radiated. This increase in temperature is sufficient to account for the slight increase in decomposition resulting from the radiation, when the nitrogen pentoxide is already decomposing at room temperature. Apparently the small rise in temperature is due partly to absorption of heat by the thin quartz bulb and partly to absorption by the nitrogen pentoxide gas itself.

It was evident that decisive tests to determine if radiation is photochemically active must be carried out at a temperature below that at which appreciable thermal decomposition can occur, and accordingly the apparatus shown in Fig. 3 was designed to permit experiments in an ice-bath. A tube 20 cm. long and 2.2 cm. in diameter was provided with a fluorite window and with inlet and outlet tubes for introducing nitrogen pentoxide. A glass diaphragm of improved design permitted accurate measurements. The fluorite window which was ground from a large crystal passed 80% of all the radiation out as far as 8 μ.

It was cemented to the glass chamber with paraffin which had stood in contact with nitrogen pentoxide for several weeks to remove any ingredients that might be attacked by the nitrogen pentoxide. The ground glass edge of the chamber was covered with this paraffin, the window was laid on it, and radiation from the Nernst filament was passed through the cold fluorite, sufficient to melt the paraffin and fasten the window in place. It was then strengthened with beeswax and paraffin. The whole apparatus was sealed off, immersed in an ice-bath, and a stream of dried air was swept across the window to prevent the condensation of moisture on its surface.

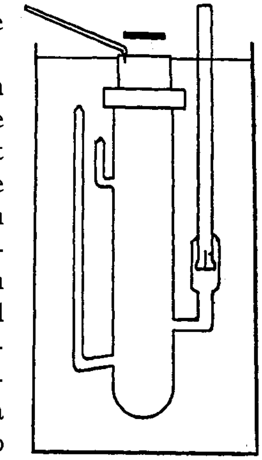
Fig. 3.—Apparatus for measuring the decomposition of nitrogen pentoxide manometrically. A Nernst glower above a fluorite window.

A Nernst filament at 1 ampere was mounted 3 cm. above the window, and about 1 cm. above the top of the collar. The heat radiation was sufficient to melt tin foil which had been placed over the ice-bath. The brown nitrogen dioxide was pumped out, before the tubes were sealed off. Calorimetric experiments showed that 300 calories or more entered the chamber, as radiation, in ten minutes.

Several experiments were carried out with solid crystals of nitrogen pentoxide exerting their pressure of 51 mm., sometimes in the presence of air at about 700 mm. pressure and sometimes in the evacuated cell. The paraffined joint gave considerable trouble with leakage, especially when evacuated, and additional experiments included some with a quartz bulb, sufficiently thin to pass all but the longest radiations, but thick enough to withstand a vacuum.

In no case except one was there a detectable increase of pressure in ten minutes, or even in half an hour. An increase of 1 mm. would have been detected with certainty and such an increase would have occurred if 2 micromoles had decomposed; $(80/22{,}400) \times (1 \times {}^2/_5 \div 760) = 2 \times 10^{-6}$. In this calculation 80 gives the volume of the reaction cell and the factor ${}^2/_5$ is included because two molecules of nitrogen pentoxide at low pressures give five molecules of decomposition products, and the solid crystals in the tube maintain the original concentration of nitrogen pentoxide. It is shown in Table I, that if all the radiant energy absorbed is photochemically active, 572 moles of nitrogen pentoxide should have decomposed in ten minutes, giving a pressure rise of over 200 mm. In the one exception referred to above, the crystals were at the bottom of the chamber, directly in the path of the intense radiation, where they were raised to a high temperature.

Experiments using monochromatic illumination were carried out with an infra-red spectrometer by Mr. M. W. Jones. No increase in decomposition of the nitrogen pentoxide could be detected, but calibration with a standard lamp from the Bureau of Standards showed that it was barely possible to introduce sufficient energy to make the experiments conclusive.

Experiments were carried out with other reactions, using the thin quartz bulb and the general procedure first described. The infra-red absorption spectrum was determined for each of the gases.

A stream of oxygen and alcohol vapor was tested for aldehyde with Tollen's solution, which registered a distinct color change for one micromole of aldehyde. While 100 calories of radiant energy were actually absorbed by the alcohol vapor during an hour, the increase of aldehyde in the radiated bulb over that in a simultaneous blank was less than 5 micromoles. This slight reaction might have been due to ultraviolet light. Assuming that even as much as 100,000 calories is necessary to cause the reaction of a gram molecule, 1000 micromoles should have been formed if the radiation absorbed is effective. Heating the quartz bulb with a low Bunsen flame for three minutes gave a strong test for aldehyde.

Seven thousand calories of radiation was passed through a stream of hydrogen chloride gas and about 70 calories of this was absorbed. No trace of decomposition into chlorine could be detected with the starch-iodide test, which was sensitive to less than 0.1 micromole. If all the radiation absorbed was chemically active and the recombination of traces of hydrogen and chlorine was negligible, there should have been over a thousand micromoles decomposed, assuming an energy of activation as great as 100,000 calories.

When 720 calories of radiant energy was absorbed by carbon dioxide over a period of several hours, 0.5 micromole of monoxide (or aldehyde) was formed as determined by the iodine pentoxide test. Since practically the same amount was obtained through a 2cm. water screen, the *slight* decomposition was possibly due to ultraviolet light.

Conclusions

The experiments at 25° showed that radiation increased the decomposition of nitrogen pentoxide 12 micromoles, by raising the temperature of the gas. At 0° the decomposition was less than 2 micromoles, the limit of sensitivity of the apparatus. These observations are to be compared with the calculations of Table I.

Table I

Calculations of Input of Radiant Energy, and Possible Decomposition of Nitrogen Pentoxide in Micromoles, Assuming Photochemical Activity

1.	Absorption band, μ	2.9	3.3	3.9	4.4	4.9	5.8	7.5	Sum	Total
2.	Absorption (51 mm.)	4%	18	8	7	11	92	98	..	..
3.	Absorption (279 mm.)	14%	52	29	14	25	92	98	..	..
4.	Width taken, μ	0.10	0.20	0.20	0.10	0.20	0.40	0.40	..	..
5.	Shaded area (Fig. 2)	12	57	13	6	11	113	65	277	540
6.	Fraction total radiation absorbed	0.10%	0.50	0.11	0.05	0.10	0.99	0.57	2.42	4.71
7.	Calories absorbed (25°)	1.1	5.7	1.3	0.6	1.1	11.4	6.5	27.7	54.2
8.	Micromoles decomposed (critical increment) (25°)	45	230	53	24	45	462	263	1120	2200
9.	Micromoles decomposed assuming 1 molecule per quantum (25°)	110	650	180	100	190	2300	1700	5230	..
10.	Micromoles decomposed (critical increment) (0°)	12	60	13	6	12	121	69	294	572
11.	Micromoles decomposed assuming 1 molecule per quantum (0°)	30	170	50	20	50	600	460	1380	..

The figures of the first three rows are taken from a graph given in another communication from this Laboratory.[9] The figures of the fourth row give the width of the band near its bottom, or at an ordinate corresponding to at least two-thirds absorption. The fifth row gives the shaded area of Fig. 2 between the limits set by (4). When these areas are divided by the total area (11,450) the values of (6) are obtained. They give the fraction of the total radiation from the Nernst filament which is absorbed by a layer of nitrogen pentoxide 8 cm. thick at a partial pressure of 51 mm. The values of (7) give the energy absorbed at each of the bands in the experiments at 25° with the thin quartz bulb. They are obtained by multiplying the values of (6) by the total radiation (1150) determined calorimetrically. The possible decomposition is calculated by dividing the energy actually absorbed, by the energy necessary to decompose one gram molecule of nitrogen pentoxide, that is, the critical increment of 24,700 calories.[7] The values of (8) then give the number of micromoles which would be decomposed if the infra-red radiation which is absorbed is effective in bringing about chemical decomposition. Similar calculations for the experiments at 0° are included in (10).

In order that a comparison of observed and calculated decomposition may not have to depend entirely on the calculation of the critical increment, the number of micromoles that should have decomposed, if one

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[9] Daniels, This Journal, **47**, 2856 (1925).

molecule is decomposed by the absorption of one quantum, are given in (9) and (11). It is apparent that if one or even five or seven quanta are required for the decomposition of one molecule, nevertheless the decomposition should have been very much greater than that actually observed.

In the next to the last column are added up all the energies absorbed at the separate bands. In addition to this energy, the last column includes also the general absorption existing between the bands.

These calculations all refer to an absorption cell 8 cm. in depth, whereas the depth of the cell in the experiments at 25° was 2 cm. and in those at 0° it was 20 cm. Corrections based on Beer's law and the data of (2) and (3) range from practically nothing to 25% for the thin cell. For the sake of simplicity, these corrections are not included here, as they do not affect the conclusions. In the experiments at 0° the effective length may have been very much greater than 20 cm. on account of reflection. In addition to the experimental results recorded here a search of the literature has failed to reveal a single case[10] where chemical reaction has been caused by the absorption of radiation at a band in the infra-red, beyond 1 μ. If infra-red radiation is chemically active, it is strange that the fact should not have been recorded by physicists in extended exposures during which infra-red absorption spectra have been mapped.

It is possible, of course, that only a small section of the absorption bands may be photochemically active. Greater spectroscopic resolution would show fine structure for the bands and only the central lines may be active. Such an explanation is difficult to disprove experimentally, but it may be emphasized that in the calculations of energy input, the absorption bands have been restricted in width to a considerable extent, and that the calculated decomposition exceeds the observed, by a considerable margin of safety. It is true also that the present investigation does not include infra-red radiation beyond 10 μ, nor absorption due to molecular rotation.

The failure of near infra-red radiation to cause chemical action is significant. The "radiation hypothesis" of chemical reaction is rendered improbable, for it is difficult to see how ordinary thermal reactions can be caused by radiation emitted by the walls of a containing vessel, if the radiation is inactive.

According to present theories, absorption in the near infra-red is due to the displacement of atoms within the molecule, while visible and ultraviolet absorption is due to the displacement of electrons. The latter process results, frequently, in chemical decomposition, but there is no evidence that the former process does. The experiments of this investigation suggest that the two processes are fundamentally different in mechanism, and

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[10] See Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1924, p. 1273, for criticism of a case in aqueous solution reported by Rideal and Hawkins, *J. Chem. Soc.*, **117**, 1288 (1920).

that atoms may be loosened in a molecule by displacement of the electrons which hold them together, but not by direct displacement of the atoms.

Summary

1. Infra-red radiation did not cause the photochemical decomposition of nitrogen pentoxide.

2. The sensitivity of the tests and the possible decomposition, calculated from the energy input, have been critically discussed. At least 99.5% of the radiation, actually absorbed, was proved to be chemically inactive.

3. A *slightly* increased decomposition at room temperature was traced to thermal decomposition. The effect disappeared at 0°, at which temperature thermal decomposition is negligible.

4. Infra-red radiation was shown to be inactive also in the decomposition of carbon dioxide, the decomposition of hydrogen chloride gas and the oxidation of alcohol vapor.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 83]

THE INTER-IONIC ATTRACTION THEORY OF IONIZED SOLUTES. V. TESTING OF THE THEORY BY SOLUBILITY EXPERIMENTS AT HIGHER TEMPERATURES

BY WARREN P. BAXTER[1]

RECEIVED OCTOBER 13, 1925 PUBLISHED MARCH 5, 1926

Introduction

The functional relation between the activation α_A of an ion of sort A, its valence z_A, and the ionic strength $\frac{1}{2}\Sigma(cz^2)$ prevailing in a solution of dielectric constant κ is given by the inter-ionic attraction theory[2,3] for sufficiently small concentrations by the following expressions, in which A is the product of certain universal constants,

$$-ln\ \alpha_A = \frac{A\ z^2{}_A\sqrt{\Sigma cz^2}}{(\kappa T)^{3/2}};\quad \text{or} -\log \alpha_A = 1.07 \times 10^{14}\,\frac{z^2{}_A\sqrt{\Sigma (cz)^2}}{(\kappa T)^{1.5}} \qquad (1)$$

when the concentrations are in moles per liter. Even at such fairly small concentrations as 0.02–0.10 M experimental observations[2,3] show considerable deviations from the requirements of this equation. The work of Brönsted and La Mer,[4] however, on the solubility of slightly soluble cobalt ammines in very dilute aqueous solutions of other salts seems to have veri-

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[1] Du Pont Fellow in Chemistry, 1925–1926.

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). Debye, *ibid.*, **24**, 334 (1923); **25**, 97 (1924).

[3] Noyes, THIS JOURNAL, **46**, 1080, 1098 (1924).

[4] Brönsted and La Mer, *ibid.*, **46**, 555 (1924).