CLIV.—*Photochemical Equilibrium in Nitrogen Peroxide. Part II. The Dependence of Quantum Efficiency on Wave-length.*

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IT has been shown (J., 1927, 761) that nitrogen peroxide exposed to the light of the mercury-vapour lamp undergoes a perfectly reversible decomposition and reaches a state of photochemical equilibrium represented by the equation

$$2NO_2 \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftarrows}} 2NO + O_2.$$

This involves an increase of pressure in the system while under illumination, and the magnitude of this increase was found to be in agreement with the hypothesis that the reaction occurs as the result of a collision between a photoactive and an inactive molecule of peroxide, whilst the reverse " dark " reaction takes place according to a termolecular law, as shown by Bodenstein and Lindner (*Z. physikal. Chem.*, 1922, **100**, 87). These general conclusions have been confirmed by Dickinson and Baxter (*J. Amer. Chem. Soc.*, 1928, **50**, 774), who, by a different method, have studied the reaction at a lower pressure range, where the reverse dark reaction is insignificant. By freezing out the residual nitrogen peroxide and the nitric oxide produced, these authors were able to measure the extent of the light reaction from the oxygen formed, and to determine its quantum efficiency for the series of wave-lengths 436, 405, and 365 $\mu\mu$. Their results demonstrated the existence of a sharp photochemical threshold in the blue part of the spectrum, as will be seen from their mean figures for the quantum efficiency referred to nitrogen peroxide decomposed :

λ	436	405	365
γ	0·0092	0·72	1·54

Part of the work now described was in hand at the time of Dickinson and Baxter's publication, but in view of the importance of their results it has been delayed for a more extensive study of the relationship between quantum efficiency and wave-length. This has been carried out by a static method differing in principle from that employed by those authors, whose observation of a photochemical threshold existing well within the region of high absorption has been confirmed. The present indications are, indeed, that this photochemical threshold is sharper than originally supposed by Dickinson and Baxter, for, contrary to their result, it has been established that blue light of wave-length 436 $\mu\mu$ is without perceptible photochemical effect, the quantum efficiency being certainly less than 0·001.

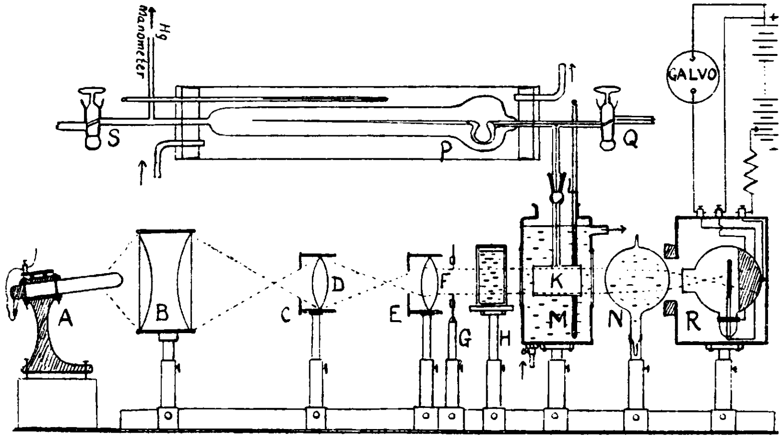
The principle of the method of measurement was to determine the pressure increase in the system when a photochemical stationary state had become established under the influence of monochromatic light of known intensity, and thence, from a knowledge of the velocity coefficient of the reverse dark reaction, to compare the number of quanta absorbed with the number of molecules of nitrogen peroxide decomposing in unit time. The results obtained indicate this as the first known case of a photochemical reaction showing a sharply developed threshold in the middle of a region of strong absorption, and yield data of considerable importance for the comparison of thermal and photochemical reactions (see Part III).

EXPERIMENTAL.

The apparatus[*] designed for this work (see Fig. 1) aimed at rapid and accurate measurements of light intensity and pressure change, and at the production of monochromatic light of various wavelengths of sufficiently high intensity to bring about easily measurable photochemical change.

The mercury-vapour lamp A, lens system, and reaction vessel were fixed permanently on an accurate optical bench. The maximum quantity of light from the lamp was collected by the large condensing lens B, and concentrated to a parallel beam by the lenses D and F, the field being limited by the variable iris-diaphragm stops C and E, before entering the reaction chamber K. A shutter G, worked from a distance by a pneumatic control, permitted illumination of the reaction vessel at will. The lenses were arranged for parallel light as intense as possible to pass through the reaction chamber. When it was later desired to use light of wave-length shorter than 365 $\mu\mu$, which is absorbed by glass, this lens system was replaced by quartz flasks containing a solution of the colour filter. By using a large flask as the condenser, in conjunction with a smaller flask, a convergent, sharply defined beam was obtained, which proved as satisfactory in all respects as the beams of longer wave-length obtained with the glass lenses.

FIG. 1.



The mercury lamp was of the horizontal U-type made by the

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[*] The grateful acknowledgment of the author is due to Mr. H. M. Roberts, in collaboration with whom this apparatus was originally set up for another purpose.

Hewittic Company, and was worked from a 220-volt supply furnished by storage batteries. The burner voltage was 150 volts and the current 2·25 amps., and under these conditions a light emission of very constant intensity was obtained.

The reaction chamber itself consisted of a cylindrical quartz vessel, of length 4 cm. and diameter 3 cm., with parallel, plane, quartz end-plates fused on. It was mounted axially with the lens system, and was connected by a capillary tube and a ground-glass joint L to the Bourdon gauge P (see Part I, *loc. cit.*) and to the nitrogen peroxide supply and pumps *via* tap Q. The temperatures of the reaction vessel and gauge were controlled to 25° ± 0·01° by pumping water from an electrically controlled thermostat to a cistern with a constant-level regulator, fixed above the apparatus, and allowing the water to run back to the thermostat through (1) an external jacket surrounding the gauge, and (2) a rectangular tank, M, with plane plate quartz faces, mounted axially on the optical bench as a thermostat for the reaction vessel. By this means it was possible to control the temperature of both gauge and reaction vessel to ± 0·01° for as long as desired, only occasional slight adjustment of the speed of water flow being necessary.

The pressure changes in the system could be measured very accurately by following the movement of the gauge pointer with a travelling microscope mounted in front of the apparatus. The microscope could be set accurately to 0·005 mm., and it was found that the deflexion of the gauge varied in a linear manner with pressure for small deflexions. The gauge was calibrated by measuring small pressure differences between its inside and outside directly on vertical mercury manometers, using a travelling telescope; and it was found that a deflexion of the gauge pointer by 1 mm. corresponded to a pressure change of 7·00 mm., the probable error in the determination of a pressure change of the order of 2 mm. being not greater than 2%.

The arrangements for evacuating the apparatus and filling it with nitrogen peroxide or other desired gas were exactly as stated in Part I (*loc. cit.*). The nitrogen peroxide was prepared and purified as there described.

Colour Filters.—In order to obtain monochromatic light beams of sufficient strength and purity the following colour filters were mounted on the stage H in the path of the light, immediately in front of the reaction vessel tank.

(1) Yellow at 575 $\mu\mu$: Wratten mercury monochromat filter.

(2) Green at 546 $\mu\mu$: Wratten mercury monochromat filter.

(3) Blue at 436 $\mu\mu$: 3 Cm. layer of 1% solution of aqueous tetramminocopper sulphate (Vanino, " Präparative Chemie," 1921,

I, p. 500), combined with ½ cm. layer of 6% aqueous quinine hydrochloride solution.

(4) Violet at 405 μμ : 3 Cm. layer of 0·02*N*-iodine in carbon tetrachloride solution, combined with ½ cm. layer of 0·1% aqueous quinine hydrochloride solution.

(5) Ultra-violet at 365 μμ : Wratten mercury monochromat filter.

(6) Ultra-violet at 316—270 μμ : 7% Nickel chloride hexahydrate in aqueous solution contained in quartz flasks used as lenses of total thickness about 20 cm. This filter also transmits green light, but as this affects neither the nitrogen peroxide decomposition nor the sodium photoelectric cell used to measure the intensity of the ultra-violet light, it can be neglected.

Measurement of Light Intensity.—Measurements of light intensity and light absorption were made by a gas-filled sodium photoelectric cell with a quartz window, which was satisfactorily sensitive over the spectrum range λλ 450—250 μμ. The cell, fixed in a light-proof box with a shutter, was mounted on the optical bench at R, the light emerging from the reaction vessel being brought to a sharp focus in the cell by means of a spherical quartz globe, N, filled with water and mounted axially in the system. The photoelectric current generated was measured by a sensitive moving-coil mirror galvanometer.

The photoelectric cell can only be used to measure the absolute intensity of light of a given wave-length after calibration by a thermopile for that particular wave-length. These calibrations were made for the separate wave-length regions of the mercury-vapour lamp at 436, 405, 365, and 316—270 μμ by the help of a Moll thermopile which had been previously calibrated for energy radiation by means of a Leslie cube. The procedure adopted is described below :

(1) *Calibration of thermopile.* The thermopile was used in conjunction with a Broca galvanometer of about 100 ohms resistance, deflexions being measured with a lamp and scale at 1 metre distance. The Leslie cube contained water maintained at 100° by means of an internal electric heater. The dimensions of the black face of the cube were 10 × 10 cm., and the diameter of the face of the thermopile which was used without its funnel was 1·36 cm.

The thermopile was mounted in front of the Leslie cube at distances of 1 and 1½ metres, and screened from its rays by a photographic shutter which could be actuated from a distance. With the temperature of the air at 19°, the following mean galvanometer deflexions were obtained with the thermopile :

(*a*) Cube at 1 metre : mean deflexion 3·16 cm.

(*b*) Cube at 1½ metres : mean deflexion 1·44 cm.

The readings did not vary by more than 1 mm. amongst themselves. Since $150^2/100^2 = 2{\cdot}25$ and $3{\cdot}16/1{\cdot}44 = 2{\cdot}20$, it will be seen that the law of inverse squares is approximately obeyed.* From these figures, allowing for the fact that the total radiation from the cube is only 90% of the theoretical (Poynting and Thomson, " Heat," 5th edtn., 1919, p. 321), we calculate that 1 cm. galvanometer deflexion corresponds to a total flux of 460 ergs per second on to the thermopile.

(2) *Calibration of photoelectric cell.* The following procedure relates to the calibration for the lines 436, 405, and 365 $\mu\mu$. First the thermopile and secondly the photoelectric cell were mounted at R (Fig. 1) and arranged so that their sensitive surfaces received the whole of the light field, concentrated by the quartz–water lens N. The appropriate colour filters were mounted at A, in combination with a filter of 6% aqueous solution of copper sulphate 3 cm. thick to remove infra-red radiation. The deflexions of the galvanometers attached to the thermopile and cell were compared, the mean values calculated from 20 observations in each case being recorded in Table I (*a*). The calibrations for the various wave-lengths were then calculated for the photoelectric cell, and are shown in the last two columns in ergs and quanta per second.

TABLE I.

(*a*) (Calibration for thermopile : 1 cm. galvo. deflexion $\equiv$ 460 ergs/sec.).

Wave-length ($\mu\mu$) or spectral region.	Mean thermopile reading (Broca galvo.).	Mean photoelectric reading (moving-coil galvo.).	1 Cm. deflexion of second galvanometer corresponds to	
			ergs/sec.	quanta/sec.
436	5·80 cm.	9·10 cm.	293	$6{\cdot}5 \times 10^{13}$
405	3·32	9·02	170	$3{\cdot}51 \times 10^{13}$
365	3·60	21·08	78·9	$1{\cdot}46 \times 10^{13}$
(*b*) (Calibration for thermopile : 1 cm. galvo. deflexion $\equiv$ 1360 ergs/sec.).				
Passed by $NiCl_2$ filter alone	8·4	40·2	—	—
Passed by $NiCl_2$ + glass plate	4·3 + 9%	2·9 + 9%	—	—
316—270 $\mu\mu$ *	3·7	37	136	$2{\cdot}0 \times 10^{13}$

* Mean value of $h\nu = 6{\cdot}8 \times 10^{-12}$ erg.

A separate calibration for the spectral region 316—270 $\mu\mu$ was made in the following way : A different setting of the Broca galvanometer gave a sensitivity corresponding to 1360 ergs per sec. per cm. deflexion for the thermopile. The light passing the nickel chloride filter consisted almost entirely of the mercury green light, and the

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* The geometrical deviation from the simple inverse-square law due to the extended surface of the source is easily shown to be not greater than 0·3% at a distance of 1 metre.

ultra-violet light of wave-length region 316—270 μμ, the latter being almost completely absorbable by a glass plate. Two sets of readings of the thermopile and photoelectric cell were therefore taken, (1) through glass, and (2) with the light falling direct. The difference of these two sets of readings, allowance being made for a 9% reflexion by the glass plate, gives the effect corresponding to the ultra-violet light alone.

No copper sulphate filter for infra-red was needed in this case, since the nickel chloride itself acts effectively in this respect, and in any case the differential method of calibration used would automatically correct for any infra-red effect if it existed. From the results of this calibration (Table I *b*) it will be seen that over 92% of the ultra-violet radiation transmitted by this filter is absorbable by glass, a result which conclusively demonstrates the absence of any appreciable quantity of the longer wave-length ultra-violet light at 365 μμ. The total absence of all light between the green at 546 μμ and the ultra-violet at 336 μμ has been further proved by a series of absorption photographs of the nickel chloride filter, and there is every reason to believe that the residual photoelectric effect through glass is due to the slight transmission of the shorter ultra-violet light between 316 and 270 μμ. This being so, and since green light has no effect on the photoelectric cell, we may take the photoelectric galvanometer deflexion as a measure solely of the ultra-violet light in the beam.

The Measurement of Quantum Efficiency.—The measurement of quantum efficiency was made for wave-lengths ranging from the yellow to the ultra-violet by filling the reaction vessel with nitrogen peroxide at any desired pressure, and exposing it to the monochromatic radiation until the system had come to a photochemical stationary state, the oxygen produced in the reaction being calculated from the increase in pressure. The amount of light absorbed by the system was determined simultaneously in terms of quanta by the photoelectric cell, by observing its deflexions with the reaction vessel (1) filled with the nitrogen peroxide and (2) evacuated. From the pressure of oxygen produced, we may calculate the speed of its recombination with the nitric oxide at equilibrium (Bodenstein and Lindner, *Z. physikal. Chem.*, 1922, **100**, 87) and hence the equal rate of decomposition of nitrogen peroxide. From this, a knowledge of the dimensions of the apparatus gives the number of molecules breaking up photochemically per second, and the quantum sensitivity.

Special attention was paid to the following precautions and corrections :

(*a*) Removal of all excess oxygen from the system before filling with nitrogen peroxide in order to obviate suppression of the photochemical equilibrium: this was done by continued pumping out and washing with pure nitrogen.

(*b*) The heating effect of the recombination of the nitric oxide and oxygen, which, as shown in Part I, may cause a pressure increase: in the present case, however, this was negligible, for with the comparatively low intensities of light used, and the correspondingly smaller degree of photodecomposition, no measurable residual heating effect was observable on adding excess of nitric oxide.

(*c*) The loss of light by reflexion after leaving the reaction vessel, and before reaching the radiometer: the light, after entering the reaction cell, has to pass four quartz faces, *viz.*, the back faces of the cell and thermostat and the two faces of the water lens, before it is measured by the radiometer. The measured intensity must therefore be corrected for light lost by reflexion at these faces. Taking the refractive index of the quartz as 1·47 (value for fused silica), we may calculate that each water–quartz surface reflects 0·2% of the incident light, and each gas–quartz surface 3·6%. Since there are four surfaces of each type, the measured intensity must be multiplied by the factor 1·17 to obtain the true intensity of the light leaving the reaction vessel.

(*d*) The accurate determination of the volume of the reaction cell and gauge: this was effected by filling the reaction system with air at atmospheric pressure and a known temperature, evacuating it completely by means of a Toepler pump, and measuring the volume of the air pumped out. In this way the volume of the reaction system, cell and gauge was found to be 30·3 c.c.

(*e*) The calculation of the pressures of oxygen and nitric oxide produced at equilibrium: the increase of pressure at photochemical equilibrium must be corrected for the change in dissociation of the N_2O_4 in order to obtain the true pressure of oxygen produced in the reaction $2NO_2 \rightleftarrows 2NO + O_2$. This was done as follows: If P and P_0 represent respectively the initial total pressure of nitrogen peroxide (*i.e.*, N_2O_4 and NO_2) and partial pressure of NO_2, and P' and P'_0 have the same significance when photochemical equilibrium has been reached, we have at 25°, by the relationship of Wourtzel (*Compt. rend.*, 1919, **169**, 1397),

$$P_0^2/(P - P_0) = P'^2_0/(P' - P'_0) = 108 \quad . \quad . \quad (1)$$

Further, if x represents the true pressure of oxygen produced, and $2x$ that of the nitric oxide, the observed pressure increase p is given by

$$p = (P' + 3x) - P \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Finally, representing all the nitrogen peroxide in terms of NO_2, we have for the initial quantity $(2P - P_0)$, and for the quantity present at photochemical equilibrium ($2P' - P'_0$). These amounts differ by $2x$ the pressure of NO_2 decomposed; hence

$$2P' - P'_0 = 2P - P_0 - 2x \quad . \quad . \quad . \quad . \quad (3)$$

Eliminating P_0, P', and P'_0 from equations (1), (2), and (3), we obtain

$$x^2 - (p + \sqrt{27P + 730} - 20{\cdot}25)x + p\left(\frac{p}{4} + \tfrac{1}{2}\sqrt{27P + 730} - 6{\cdot}75\right) = 0 \quad . \quad . \quad (4)$$

and since P and p are known, this may be solved for x, the equilibrium pressure of oxygen.

Calculation of the Quantum Efficiency.—At photochemical equilibrium the number of molecules of nitric oxide and oxygen recombining per second is known from the value of x (as obtained above), the volume of the vessel, and the velocity coefficient of the reaction, determined by Bodenstein and Lindner (*loc. cit.*). Thus, at 25°

$$d[2NO_2]/dt = 1{\cdot}66 \times 10^6 \times [2NO]^2[O_2]$$

the concentrations being measured in mols. per litre and the time in minutes. The equilibrium pressure of oxygen is x; hence, in the present instance

$$[2NO] = \tfrac{1}{2}[NO] = [O_2] = x\left(\frac{1}{760} \cdot \frac{273}{298} \cdot \frac{1}{22{\cdot}4}\right)$$

The number of mols. of NO_2 decomposed per litre per second is therefore

$$-\frac{d[NO_2]}{dt} = -2\frac{d[2NO_2]}{dt} = 2\left(\frac{x}{760} \cdot \frac{273}{298} \cdot \frac{1}{22{\cdot}4}\right)^3 \times \frac{1{\cdot}66}{60} \times 10^6.$$

Taking the volume of the cell as 30·3 c.c. and the Avogadro number as $6{\cdot}06 \times 10^{23}$, we find for the number of molecules decomposed per second

$$n = 2\left(\frac{x}{760} \cdot \frac{273}{298} \cdot \frac{1}{22{\cdot}4}\right)^3 \times \frac{1{\cdot}66 \cdot 10^6}{60} \times \frac{6{\cdot}06 \cdot 10^{23} \cdot 30{\cdot}3}{1000}$$
$$= 1{\cdot}587 \times 10^{14} \times x^3.$$

If A represents the light absorbed by the NO_2, measured in terms of galvanometer deflexion, the number of quanta absorbed per second is $m = 1{\cdot}17Af$, where f represents the appropriate factor (see Table I) for converting the galvanometer deflexion into quanta per second, and the factor 1·17 corrects for loss of light by reflexion (see above). The quantum efficiency is then given by

$$\gamma = n/m = 1{\cdot}587 \times 10^{14}x^3/1{\cdot}17Af = 1{\cdot}36 \times 10^{14}x^3/Af.$$

The experimental results and the values of the quantum efficiency calculated from them are shown for various wave-lengths in Tables II and III. The light intensities for Table II were measured by the thermopile, and those for Table III by the photoelectric cell, the appropriate values of the factor f (from Table I) being shown in the latter case.

TABLE II.

Wave-lengths 575 and 540 $\mu\mu$.

Wave-length, $\mu\mu$.	Pressure of NO_2.	Energy of beam (cals./sec.).	Energy absorbed, %.	Pressure increase in NO_2 (mm.).	γ.
575	223	$1{\cdot}0 \times 10^{-4}$	Slight	0·00	0·000
546	32	$1{\cdot}2 \times 10^{-4}$	39	0·13	0·000
546	150	$1{\cdot}2 \times 10^{-4}$	70	0·07	0·000
546	190	$1{\cdot}2 \times 10^{-4}$	80	0·15	0·000

TABLE III.

Initial press. of NO_2, mm.	Intensities (galvo. deflexion). Incident.	Intensities (galvo. deflexion). Transmitted.	Intensities (galvo. deflexion). Absorbed.	Press. increase, mm.	x.	γ.
(a) Wave-length 436 $\mu\mu$; $f = 6{\cdot}5 \times 10^{13}$.						
10	7·1	3·0	4·1	0·00	0·00	0·000
56	11·7	1·0	10·7	0·00	0·00	0·000
100	12·9	0·3	12·6	0·00	0·00	0·000
150	11·9	0·0	11·9	0·08	0·05	0·000
(b) Wave-length 405 $\mu\mu$; $f = 3{\cdot}51 \times 10^{13}$.						
22	15·6	3·7	11·9	1·79	1·28	0·68
25	10·2	2·4	7·8	1·71	1·20	0·85
56	10·0	0·8	9·2	1·92	1·20	0·72
100	10·2	0·3	9·9	2·06	1·22	0·72
265	11·3	0·0	11·3	2·35	1·29	0·74
					Mean	0·74
(c) Wave-length 365 $\mu\mu$; $f = 1{\cdot}46 \times 10^{13}$.						
22	54·0	17·0	37·0	2·87	2·06	2·18
25	22·6	7·3	15·3	2·17	1·52	2·13
56	19·0	1·2	17·8	2·56	1·60	2·14
100	21·8	0·3	21·5	2·85	1·69	2·07
268	27·0	0·0	27·0	3·26	1·79	1·98
					Mean	2·10
(d) Wave-length 316—270 $\mu\mu$; $f = 2{\cdot}0 \times 10^{13}$.						
22	35·8	23·0	12·8	2·23	1·59	2·13
30	16·1	7·5	8·6	2·03	1·38	2·07
48	30·5	15·7	24·8	3·05	1·95	2·03
105	33·5	1·5	32·0	3·50	2·06	1·87
213	31·3	0·0	31·3	4·05	2·26	2·45
					Mean	2·07

The data of Table III (a) indicate no detectable photochemical effect for blue light of 436 $\mu\mu$. This is contrary to the observation of Dickinson and Baxter, who reported a quantum efficiency of 0·0092, a magnitude well within the scope of the present apparatus. For example, light absorption corresponding to 11 galvanometer scale divisions would involve a value of x of about 0·4 mm. and a total pressure change of the order 0·5—0·7 mm., whilst, as stated above, pressure changes of the order 0·05 mm. could be easily detected. It would therefore appear that the blue colour filter employed by Dickinson and Baxter was somewhat inefficient and slightly transparent to ultra-violet or violet radiation.

The results given in Tables II and III raise certain issues of importance to the theory of photochemical change. The existence of a sharp photochemical threshold between wave-lengths 436 and 405 $\mu\mu$ in a region of high absorption suggests the inquiry as to what happens to the absorbed energy of the former wave-length. The quantum involved, 64,000 cals. per g.-mol., is at least double the magnitude of energy required in the corresponding homogeneous bimolecular thermal reaction, where the energy of activation is about 33,000 cals. per [$2NO_2$] and the heat of reaction 26,000 cals. (Bodenstein and Lindner, *loc. cit.*; Norrish, *Nature*, 1928, **122**, 923); and yet this quantity of energy is absorbed without chemical effect. Again, to what cause must one attribute the partial efficiency of violet light which introduces ample energy into the molecule for bimolecular decomposition? It is clear that only a part of the absorbed energy is available for chemical change, and that certain probability considerations affect its utilisation.

The fact that with further increase of wave-length the quantum efficiency reaches a maximum constant value of 2 indicates that the probability factor soon reaches unity, and demonstrates the absence of any chain reaction. In this respect the present finding confirms the collision hypothesis advanced in Part I (*loc. cit.*), and makes possible a comparison on equal terms of the homogeneous photochemical and thermal decompositions of nitrogen peroxide.

The points raised above will be considered at greater length in Part III.

Summary.

The quantum efficiency (γ) of the photochemical reaction $2NO_2 \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftarrows}} 2NO + O_2$ has been investigated for six wave-lengths of the mercury-vapour lamp in the visible and ultra-violet, a photoelectric cell being used to measure light intensity. The following values were obtained: for 575, 546, 436 $\mu\mu$, $\gamma = 0{\cdot}000$; for 405 $\mu\mu$, $\gamma = 0{\cdot}74$; for 365 $\mu\mu$, $\gamma = 2{\cdot}10$; and for 316—265 $\mu\mu$, $\gamma = 2{\cdot}07$. The photochemical threshold in the middle of the nitrogen peroxide absorption region noticed by Dickinson and Baxter has been found to be sharper than was originally supposed, their observation of slight photochemical activity of light of λ 436 $\mu\mu$ being definitely unconfirmed. No difference could be observed between the quantum efficiency of light of λ 365 and λ 316 μμ; the values obtained indicated complete efficiency. The existence of fine structure in the NO_2 absorption spectrum is in agreement with the mechanism $NO_2 + h\nu = NO_2'$; $NO_2 + NO_2' = 2NO + O_2$, which is also confirmed by the kinetic observations in Part I.

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