

combine to form molecules, though they may also then react with other substances if these are present.

It may be pointed out that, since from Richardson's equation the heat of dissociation of the gas inside the metal can be calculated, one could obtain the heat of dissociation of the gas outside the metal if the heat of absorption of the gas were known.

Grateful acknowledgment is hereby made of a studentship granted to one of the authors by the Research Council of Canada, during the tenure of which part of this work was carried out.

Summary

1. An apparatus has been devised in which two or more gases can be continuously and automatically mixed in any proportions and a constant flow of any definite mixture can be maintained.

2. The rate of diffusion of oxygen through silver has been measured with welded plates of 0.135, 0.205 and 0.30 mm. thickness, and the results have been shown to agree with those previously obtained.

3. Results obtained previously by one of the authors under experimental conditions different from those described in the first paper showed an agreement with the square-root relation between rate of diffusion and pressure.

4. It has been shown (as far as the data allowed) that Richardson's equation represents, within the experimental error, the diffusion of gases through metals.

5. A possible explanation of how diffusion takes place has been given and it has been shown to be compatible with the results obtained.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE PHOTOLYSIS OF POTASSIUM NITRATE

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Introduction

When potassium nitrate in aqueous solution is exposed to ultraviolet light it decomposes into potassium nitrite and oxygen. Many investigators have studied this reaction.² Warburg³ has found that the photolysis in polychromatic light proceeds much more rapidly in alkaline than in neutral or acid solutions. He has also determined in alkaline solutions the moles transformed per calorie absorbed for the wave lengths 207,

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² Thiele, *Ber.*, **40**, 4914 (1907). Lombard, *Compt. rend.*, **150**, 228 (1910). Berthelot and Gaudechon, *ibid.*, **152**, 522 (1911). Baudisch, *Ber.*, **44**, 1009 (1911).

³ Warburg, *Sitzb. kgl. preuss. Akad. Wiss.*, **1918**, 1228; *Z. Elektrochem.*, **25**, 334 (1919).

253 and $282\mu\mu$. In this work have been determined the quantum efficiencies (molecules transformed per quantum absorbed) at seven wave lengths between 254 and $366\mu\mu$, inclusive, and at values of PH between 6 and 13. Anderson⁴ and Suryanarayana⁵ have found evidence of a photochemical equilibrium between potassium nitrate and the nitrite formed. Anderson's conclusions could be ascribed to a faulty analytical method as is shown below. Suryanarayana does not describe the analytical method which he used. Employing a nitrite titration similar to that used by Warburg but with minor improvements, I have found no evidence of equilibrium.

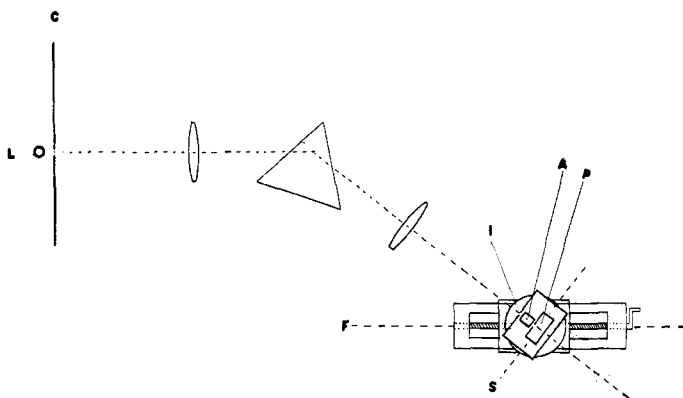


Fig. 1.—Schematic diagram of monochromator. *A*, absorption cell; *C*, collimator slit; *F*, focal plane; *I*, image slit; *L*, light source; *P*, thermopile; *S*, direction thermopile is moved when used to integrate total light transmitted by absorption cell.

Apparatus

Monochromator (See Fig. 1).—An unusually large, 60° , fused quartz prism ($105 \times 105 \times 105 \times 80$ mm.) and two fused quartz lenses (80 mm. in diameter, $f = 2.2$ for $\lambda 254\mu\mu$) were furnished by the General Electric Company. The adjustable collimator slit was usually 27×1.5 mm. and the adjustable image slit usually 32×1.0 mm. The latter could be moved by a screw along the focal plane. Behind the image slit could be interchangeably mounted either the absorption cell or the thermopile. Behind the absorption cell was a support on which the thermopile could be moved in a horizontal direction at right angles to the emergent light beam.

The prism showed few patterns in polarized light, the lenses more. The degree of purity of several "monochromatic" radiations given by the monochromator was investigated qualitatively. Fig. 2 shows a series of spectrograms obtained by focusing successive monochromator lines of

⁴ Anderson, *THIS JOURNAL*, **46**, 797 (1924).

⁵ Suryanarayana, *J. Sci. Assoc. Maharajah's College, Vizianagaram*, **2**, 12 (1924).

the wave lengths designated on the slit of a small quartz spectrograph.⁶ The time of exposure was identical in each spectrogram. It may be seen that the error from scattered light is quite considerable for the weak lines, a fact generally overlooked by photochemists.

Absorption Cells.—Three types were used. (1) A clear Vitreosil test-tube of 10 ml. capacity, used only with polychromatic light. (2) A glass cell with crystal quartz plates cemented on by de Khotinsky cement. This cell could not be used in alkaline solutions as the cement became peptized. (3) A cell made of a horizontal quartz cylinder 30 mm. in diameter with a neck and a ground-in quartz stopper at the top. The ends were plane and were fused to the cylinder.

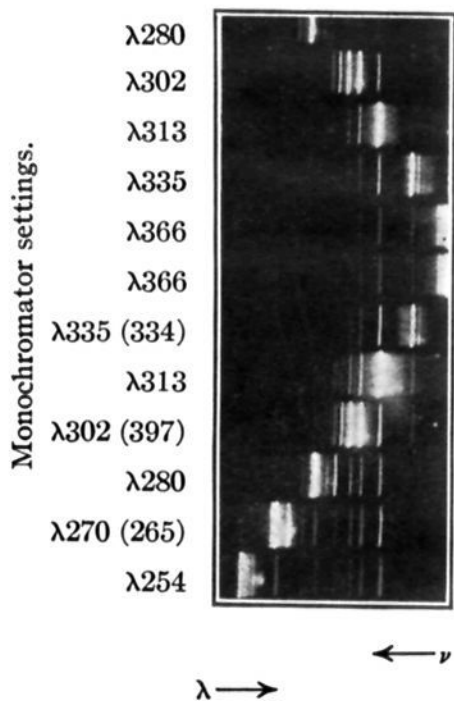


Fig. 2.—Spectrograms of monochromatic light.

Thermopile.—This was made according to the directions of Coblenz⁷ with minor modifications suggested by Professor G. R. Harrison. It consisted of a line of 20 bismuth-silver couples 25.15 mm. in length; the slit was 1.10 mm. wide. Its resistance was 23 ohms and when combined with a Leeds and Northrup D'Arsonval galvanometer of internal resistance 17.81 ohms and sensitivity 15 mm./ μ v, it gave a deflection of 0.109 cm. on a scale at a distance of 5.6 meters for 1.00 erg per second falling on the total thermopile surface. It was calibrated in accordance with the directions of the

Bureau of Standards against their lamps C39 and C40. The throw was found to be proportional within 0.5% to the energy flux up to 11 ergs per sq. mm. per second or 34 cm. deflection. A linear relation was assumed to hold up to 850 ergs per sq. mm. per second and up to galvanometer deflections of 90 cm.

Light Source.—Three kinds of quartz mercury arc were used. The first two lamps described were used for polychromatic work; the third for monochromatic work.

1. A horizontal Uviarc.
2. A vertical lamp run under atmospheric pressure, which gave an almost constant light intensity. This was designed by Mr. P. A. Leighton and I wish to thank him for the use of it.

⁶ This was kindly loaned by Professor F. A. Saunders of the Jefferson Physical Laboratory.

⁷ Coblenz, *Bur. Standards Sci. Papers*, 11, 131 (1914).

3. Two constricted arcs similar to that developed by Forbes and Harrison.⁸ The difficulties⁹ arising in the use of this lamp at amperages between 4 and 5 may be overcome by observing the following precautions in addition to those mentioned by Forbes and Harrison. (a) In case distilled water cannot be used on the constriction, cool the upper electrode of the lamp by a strong air blast free from oil and the lower electrode by a stream of tap water. The blower should have a capacity of several cu. meters per minute. (b) The diameter of the constriction should be the greatest for which the upper mercury meniscus is stable. Four mm. seems to fit this requirement more satisfactorily than 2 mm. as recommended by Forbes and Harrison.

If these precautions are observed, the lamp may be run three or four days at a current of 4 amp. without deteriorating greatly in light intensity. After a run, the mercury is removed, the lamp is washed with hydrofluoric acid and the constriction is worked over in an oxygen-gas flame. As the hydrofluoric acid attacks the capillaries very rapidly, it is necessary from time to time to melt them down to their original size (0.5 mm.). After refilling the lamp with mercury, the air is boiled out and it is then ready for another run. The lamp was started by boiling the mercury in the constriction through which passed a current of about 2 amp. The blower was started after the arc had struck, and resistance was cut out of the lamp circuit gradually until it operated at approximately 4 amp. and 80 v.

Procedure

In the monochromatic work not more than 0.05% and in the polychromatic work not more than 1.7% of the nitrate was photolyzed. Therefore, it was unnecessary to stir the solutions.

In polychromatic work the absorption cell was simply placed at a definite fixed distance about 10 cm. from the lamp.

To determine the quantum efficiency Φ in a photolysis the following operations were necessary.

A shield (") was placed over the image slit to reduce its length to 13.7 mm. This was to make sure that the thermopile during its motion from one side to the other behind the cell would completely cover the beam transmitted.

While regulating the amperage and voltage of the lamp the image slit was placed at the focus of the line desired with the help of a fluorescent screen of anthracene. The thermopile was then mounted in the position ordinarily assumed by the absorption cell, and the deflection f and time of observation were noted. The cell full of liquid was next substituted for the thermopile which, in turn, was mounted behind the former. Gal-

⁸ Forbes and Harrison, (a) *J. Optical Soc. Am.*, 11, 99 (1925); (b) *THIS JOURNAL*, 47, 2449 (1925).

⁹ Ref. 8 b, p. 2452.

vanometer deflections a and the times of observation were noted as the pile was moved at right angles to the emergent beam at successive space intervals (δx) of 2 mm. After such a series of readings the galvanometer deflection at the f position was again noted. If the lamp intensity had varied over 5% (as shown by the f readings) the f value corresponding to the time of each reading was interpolated linearly. The sum of the quotients of the single a readings, each divided by the proper interpolated f reading, $\sum (a_x/f)$, gives a quantity proportional to the total light transmitted by the cell. If f_i is the thermopile reading at a given moment, the total energy transmitted by the cell at that moment is then $(2/1.1)f_i \sum (a_x/f) \equiv Bf_i$. Data for the value of B were obtained for water (B_0), water + buffer (B_b), and water + buffer + nitrate ($B_b + n$) before starting each photolysis.

A different shield ('), used during the photolysis, allowed to fall upon the cell a beam having the same height (23.0 mm.) as the cell. An approximate correction factor for the fact that the beam now more than covered the sensitive thermopile surface was $(23.0/13.7)(f''/f') = 1.117$. The possible inaccuracy of the assumption that the total energy was proportional to the slit length is recognized.

The next step, therefore, after replacing shield (") by shield (') and taking a galvanometer reading f' was to substitute the cell for the thermopile and start the photolysis. From time to time throughout the run the cell was removed and further thermopile readings were obtained. The total energy p , which would have fallen on the thermopile had it been in place throughout the run, is $\sum [(f_i + f_{i+1})/2] \Delta t \times b = p$, where b is the proper factor to convert deflections into ergs. The different conversion factors used corresponded to different series-shunt resistances which were inserted in the circuit to reduce the throw of the galvanometer at the high intensities.

In addition to the factors B and 1.117, a third factor, E , was calculated which allowed for the reflection of the light at the quartz-liquid and quartz-air interfaces of the rear wall of the absorption cell. The fractions of the incident light reflected at these two interfaces, respectively, and re-reflected at the former are D_{qw} , $D_{aq}(1 - D_{qw})$, and $D_{aq}(1 - D_{qw})D_{qw}$, where $D = \{(1 - r)/(1 + r)\}^2$ and r is the index of refraction. The amount of light present in the liquid just before the beam entered the rear quartz wall was then the amount of transmitted light times the factor $E = 1/[1 - D_{qw} - D_{aq}(1 - D_{qw}) + D_{aq}(1 - D_{qw})D_{qw}]$.

To account for the greater chemical action caused by the light reflected back through the liquid the above must be multiplied by the factor $1 + D_{aq}(B_b + n/B_0)$.

The amount of energy falling upon the solution was multiplied by the

factor $1 - (B_b + n/B_0)$ to obtain the total absorbed energy. To find the energy absorbed by the nitrate alone, this had to be multiplied by still another factor, $E = \epsilon_n C_n / (\epsilon_n C_n + \epsilon_b C_b)$, where ϵ and C are the extinction coefficient and concentrations, respectively, of the nitrate and buffer. They were calculated from data on the B factor taken before starting the photolysis. $\epsilon_b C_b = (1/3.15)\log(B_0/B_b)$; $\epsilon_n C_n = (1/3.15)\log(B_b/B_b + n)$, where 3.15 is the distance between the front and rear walls of the absorption cell. The use of this formula in diverging light is justified by the writer elsewhere.¹⁰

The total amount of light energy absorbed during a photolysis was then the product of all of the above factors, $A = pEB_0(1 + D_{aq}B_n + b/B_0) \cdot F(1 - B_n/B_0) \times 1.117$ ergs. It is necessary to average the values of B_0 taken before and after each run, as a small change in position of the lamp will change B quite considerably.

After a photolysis the amount of chemical change was determined analytically and the quantum efficiency was calculated.

Analytical Part

Nitrite formed in the photolysis of potassium nitrate solutions was at first titrated with permanganate.¹¹ To the solution acidified at 0° was added a considerable excess of 0.01 *N* potassium permanganate solution and, after standing five minutes, an excess of 0.004 *N* ferrous sulfate solution, which could be titrated back to a distinct end-point. The apparent content of the solution in nitrite increased with the time of standing and never attained its full value (checked against silver nitrite). This was because of the very slow reaction between permanganate and nitrite. The procedure followed by Anderson, in which permanganate in excess was not allowed to react with nitrite, would therefore give even lower results than the above method. A very indistinct end-point was a further disadvantage.

The permanganate titration was, therefore, discarded in favor of an iodimetric titration described by Warburg.¹² This gave very good results if modified by making the solution quite alkaline before the aeration by carbon dioxide. Warburg, observing that iodine was liberated during the aeration and before the final acidification, concluded that in the photolysis of the nitrate "in strongly alkaline solutions another substance of unknown chemical nature besides nitrite is formed which oxidizes potassium iodide."¹³ I have found that if extra alkali is added before aeration, no iodine is liberated before the final acidification of even the most alkaline solution used. It seems unnecessary, therefore, to conclude with Warburg that a

¹⁰ Villars, *J. Optical Soc. Am.*, **14**, 30 (1927).

¹¹ Rose, "Handbuch der analytischen Chemie," Barth, Leipzig, 1871, vol. 2, p. 833.

¹² Ref. 3, p. 1233.

¹³ Ref. 3, p. 1238.

new unknown photochemical compound is formed. A more likely explanation seems to be that when this high concentration of alkali is not present, the carbon dioxide lowers the P_H of the solution to such a point that hydrolysis of the nitrite occurs. If nitric oxide is thus formed before complete expulsion of oxygen, an unduly great liberation of iodine results.

The following procedure was therefore used. To the solution (about 30 cc.) was first added 5 cc. of 0.2 N sodium hydroxide solution and then 5 cc. of 10% potassium iodide and starch indicator solutions. A rapid stream of carbon dioxide was bubbled through the mixture. After about three minutes, when all of the oxygen had been expelled, the solution was

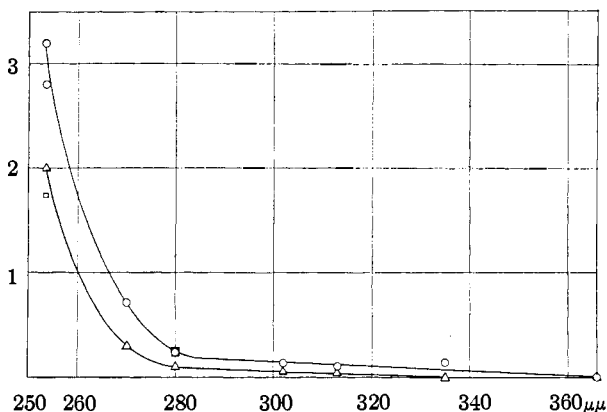


Fig. 3.—Quantum efficiency of monochromatic light absorbed by M KNO_3 . $\circ = \Phi \times 10$ (buffered, P_H 9.9). $\triangle = \Phi \times 10^2$ (unbuffered, P_H 5.8). $\square = \Phi \times 10$ (Warburg, KNO_3 0.33 M , $NaOH$ 0.0003 M) where Φ = moles transformed per quantum absorbed.

acidified with oxygen-free sulfuric acid (5 cc., 5 M) and was titrated with 0.01 N thiosulfate solution from a weight buret. This method was checked against P. W. R. (Analytical) silver nitrite.

$AgNO_2$, g.: 0.00390, 0.0083; 0.0104 N thiosulfate, g.: 2.461, 5.217; blank: 0.036, 0.036; purity, %: 99.2, 100.2.

The thiosulfate had been standardized against P. W. R. Analytical iodine which had been resublimed from potassium iodide.

Results

Effect of Wave Length on Quantum Efficiency.—Warburg has found that the quantum efficiencies, Φ (molecules transformed per quantum absorbed), for the wave lengths 207, 253 and 282 $\mu\mu$ are, respectively, 0.25, 0.17 and 0.024. These values were for 0.33 M potassium nitrate solutions, 0.00033 M with respect to sodium hydroxide. The wave-length

region between 254 and 366 $\mu\mu$ has been investigated. Fig. 3 gives the values found for *M* potassium nitrate solutions unbuffered (initial *P_H* 5.8) and buffered (*P_H* 9.9, borate buffer).

Warburg has calculated from thermochemical data that the energy required for the change of nitrate to nitrite corresponds to a quantum of wave length between 280 and 315 $\mu\mu$. If the photo-equivalence law held, one might expect that for increasing wave lengths, Φ would be unity until the critical wave length was reached, when it would suddenly drop to zero. It is seen (Fig. 3) that it is about 0.25 for the shorter wave lengths and starts to decrease in value at 254 $\mu\mu$, a wave length some 30 $\mu\mu$ shorter than the shortest calculated critical limit. Warburg has explained that Φ is small because part of the quantum energy is lost by collision before the molecule has had a chance to decompose.

This may explain the low efficiencies of quanta just possessing the critical energy of decomposition. It seems reasonable to suppose that the energy of a molecule which has undergone collision during the interval between excitation and decomposition would be more likely to exceed its critical decomposition value if it had absorbed a quantum of greater energy. This may explain qualitatively the greater efficiencies of the shorter wave lengths.

The quantum efficiency observed for the wave length 335 $\mu\mu$ cannot be explained by the above hypothesis. Neither can it be explained by the addition of collision energy to that of the quantum, for only 0.003% of the collisions can furnish a deficit of 20 $\mu\mu$. This particular value of the quantum efficiency may, however, be ascribed to the light of shorter wave length passing the image slit when this is set for the line 335. The percentage of scattered light was estimated from densitometer measurements on the spectrograms of the separate monochromator lines (Fig. 2). This was negligible for wave lengths shorter than 335 but not for 335 itself. This serves to illustrate the point mentioned above that in monochromatic reactions of low efficiency, the scattered light may cause a considerable error and must be accounted for.

Effect of *P_H* on Decomposition Velocity.—By using a quinhydrone electrode it was found that the original "neutral" solution of *M* potassium nitrate had a *P_H* of 5.8. A solution only 0.025% saturated with carbon dioxide would have this *P_H*. A 0.00033 *N* sodium hydroxide solution made up without guarding it against atmospheric carbon dioxide was found to have a *P_H* of 6.06. According to Warburg, the rate of photolysis of potassium nitrate was some three times as great in solutions 0.00033 *N* with respect to sodium hydroxide as in solutions 0.00033 *N* with respect to sulfuric acid. In view of the fact that the *P_H* of Warburg's solutions may have been indefinite it appeared necessary to determine how the rate of photolysis and quantum efficiency varied with *P_H*. For this purpose the

following buffer solutions¹⁴ were used: potassium dihydrogen phosphate–disodium phosphate; sodium tetraborate–boric acid; sodium borate–sodium hydroxide. These did not interfere with the analysis for nitrite. A correction was made as indicated above for the amount of light absorbed thermally by them.

The results are given in Fig. 4. The solid curve gives the quantum efficiencies of the wave length $254\mu\mu$ when different buffers were used (temp., 25°). The dotted curve gives relative velocities of decomposition in polychromatic light (temp., $60\text{--}70^\circ$). It is possible that the difference between the Warburg value of Φ , 0.17, and mine, 0.30, for $254\mu\mu$ is due more to a difference in P_H than to a difference in nitrate concentration (Warburg's, 0.33 M ; mine, 1 M).

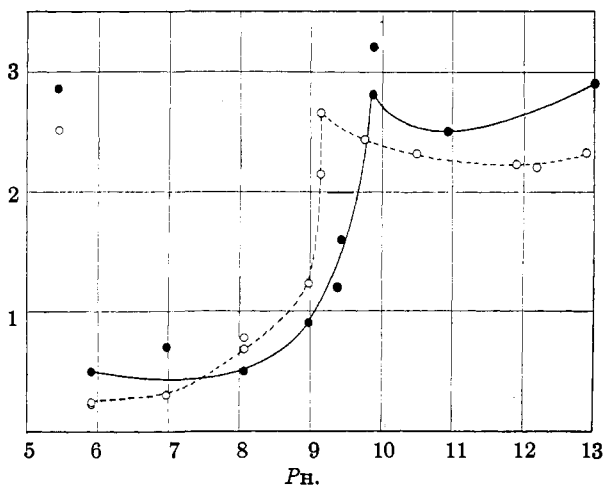


Fig. 4.—Effect of P_H on quantum efficiency. $M \text{KNO}_3$. Φ = moles transformed per quantum absorbed. ● = $\Phi \times 10$ (λ $254 \mu\mu$). ○ = relative decomposition velocity (polychromatic).

No attempt is made at the present writing to explain the effect of P_H on the quantum efficiency. It brings to mind the greater ease with which the reduction of nitro to nitroso compounds proceeds in alkaline solutions.

Nitrate—Nitrite Equilibrium.—Anderson has found evidence that potassium nitrate in neutral solution (0.1 to 2.0 M) ceases to decompose in ultraviolet light after the nitrite concentration has reached $2.65 \times 10^{-4} M$. He also found that the rate of decomposition of 0.1 M potassium nitrate, $2.9 \times 10^{-4} M$ with respect to potassium nitrite, is only 10% of the original rate. If an equilibrium is obtained in this reaction it seems

¹⁴ Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1923, pp. 112–115.

that in this latter experiment the nitrite concentration used should stop the photolysis entirely. As these results are mutually inconsistent, I have repeated the experiments of Anderson, using the reliable modified Warburg nitrite analysis.

Fig. 5 shows that in polychromatic light acting upon a solution at 60° to 70° the decomposition proceeds for the first 480 minutes without showing signs of an equilibrium. A 1 *M* potassium nitrate solution buffered at *PH* 9.4 decomposes almost linearly with time. An unbuffered (initial *PH*, 5.8) potassium nitrate solution decomposes at a much slower rate but forms in the same time much more nitrite (17.7×10^{-4} *M* potassium nitrite) than that found by Anderson.

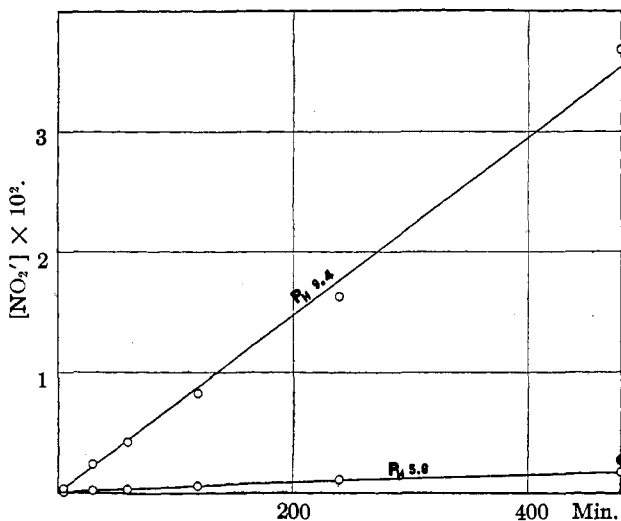


Fig. 5.—Photolysis of *M* KNO₃.

Thinking that organic impurities in the nitrate which I used might destroy an equilibrium by reducing the oxygen formed by the photolysis, I boiled P. W. R. potassium nitrate with redistilled, fuming nitric acid and recrystallized it six times, using water of conductivity 0.8×10^{-6} mhos. The purified nitrate was kept from fumes of organic matter.¹⁵

The black dot in Fig. 5 gives the concentration of nitrite obtained in the photolysis of one of these purified samples. This seems to establish the fact that the highly purified potassium nitrate behaves in the same manner as the ordinary sample and that there is no indication of an approach to equilibrium even at nitrite concentrations 20×10^{-4} *M*.

Fig. 6 shows that a 0.001 *M* potassium nitrate solution buffered at *PH*

¹⁵ I wish to thank Professor G. P. Baxter and Dr. H. W. Starkweather of the T. Jefferson Coolidge Laboratory, both of whom gave me helpful suggestions concerning this purification process.

9.4 decomposes completely in polychromatic, ultraviolet light. The nitrite concentration in an unbuffered solution reaches a maximum concentration and then diminishes in value. This is probably due to the loss, in spite of the stopper, of nitrogen oxides formed in the decomposition of nitrite at the high temperature (70°) and high acidity (P_H , 5.8).¹⁶ A solution of the highly purified potassium nitrate, $1.6 \times 10^{-4} M$, behaves in a similar manner but loss of the nitrogen oxides was less in this case, perhaps because the absorption cell was stoppered more efficiently.

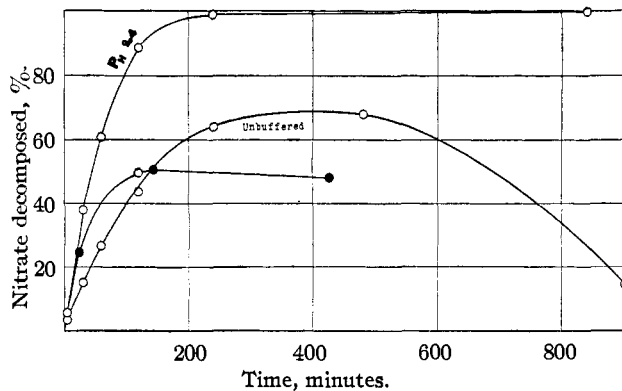


Fig. 6.—Nitrate-nitrite equilibria. \circ = $0.001 M KNO_3$. \bullet = $0.00016 M KNO_3$ recrystallized six times ($\text{min.} \times 10^{-1}$).

As these experiments on the kinetics of the photolysis contradict the hypothesis of a steady state, it seemed necessary to repeat Anderson's work on the inhibition of the photolysis by adding nitrite to nitrate. Results are given in Table I. The final column gives the relative decomposition rates for different initial concentrations of nitrite. It is seen

TABLE I		
PHOTOLYSIS IN THE PRESENCE OF NITRITE		
$M KNO_3$ buffered at P_H 9.4; 15 min. exposure to Uviarc		
Initial $[NO_2']$ $\times 10^3$	Final $[NO_2']$ $\times 10^3$	$\Delta[NO_2']$ $\times 10^3$
0.00	1.73	1.73
.00	1.78	1.78
1.06	2.82	1.76
5.42	7.23	1.81
11.00	12.73	1.73
$M KNO_3$ unbuffered (P_H 5.8); 1 hr. exposure to Leighton lamp		
Initial $[NO_2']$ $\times 10^3$	Final $[NO_2']$ $\times 10^3$	$\Delta[NO_2']$ $\times 10^3$
0.00	0.33	0.33
1.01	1.34	.33
2.02	2.36	.34

¹⁶ See Reinders and Vles, *Rec. trav. chim.*, **44**, 1 (1925).

that in an unbuffered solution an initial concentration of nitrite seven times that used by Anderson causes no inhibition.

The failure to check Anderson's experiments may be easily explained. The method of nitrite analysis used by him was a permanganate titration. Permanganate and nitrite react so slowly when the reaction is nearing completion that no definite end-point is discernible, especially when no large excess of permanganate has been added. The conclusion that there is an equilibrium between nitrate and nitrite in ultraviolet light is, therefore, untenable in the light of these data, and Warburg's¹⁷ calculations of specific photochemical action are completely vindicated.

Before concluding, I wish to express my grateful appreciation to Professor George Shannon Forbes who extended to me the facilities of his private laboratory and who was ever ready with helpful suggestions.

I wish also to thank the General Electric Company for the loan of a motor-generator which furnished the direct current used in all of this work.

Summary

Precautions are given to be observed in the use of the constricted mercury arc of Forbes and Harrison.

The monochromatic experimental technique followed in this research is given in detail.

The Warburg iodimetric method for nitrite titrations is modified.

The quantum efficiency (molecules transformed per quantum absorbed) of the reaction $\text{KNO}_3 = \text{KNO}_2 + \text{O}$ is very small for wave lengths longer than $280\mu\mu$.

The quantum efficiency (λ $254\mu\mu$) increases regularly with increasing P_H to 0.25 at P_H 9.9 and remains constant as the P_H is further increased.

Molar potassium nitrate decomposes in polychromatic light at a rate gradually diminishing with time, but shows no evidence of reaching an equilibrium. An initial concentration of nitrite of 0.01 M does not lower the rate of decomposition more than 2%. Eight hours' direct exposure to a Uviarc of 0.001 M potassium nitrate solution buffered at P_H 9.4 brings about 100% decomposition.

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¹⁷ Warburg, *Z. Physik*, 29, 1344 (1924).