TABLE III

TEST ANALYSES FOR FINAL PROCEDURE

No.	1	2	3	4
Iodine added, ml.	35	35	35	35
Iodate used, ml.	22.25	22.27	38.47	38.50
Vanadium found, mg.	79.40	79.29	79.34	79.19

The calculated weight of vanadium present was 79.41 milligrams.

In No. 1 half of the hydrochloric acid was added before adding the potassium iodide and the remainder during the titration. In No. 2 all of the acid was added before the iodide, while in Nos. 3 and 4 half of the acid was added before the iodide and half just before beginning the titration.

Summary

A method for the volumetric determination of vanadium by means of standard solutions of potassium iodide and potassium iodate has been developed. The method depends upon the reduction of vanadate by a known amount of iodide in hydrochloric acid solution and conversion of the iodine formed and of the excess of iodide into iodine monochloride by titration with iodate.

It is shown that when the concentration of the hydrochloric acid is 6 molal or more, quadrivalent vanadium is not oxidized by the iodine monochloride and the reactions are quantitative.

Tests analyses proved that vanadate can be determined by this method in the presence of phosphate, arsenate or ferric iron, and also in the presence of tungstic acid, which may be held in solution by adding phosphoric acid.

PASADENA, CALIFORNIA

THE ABSORPTION SPECTRUM AND DECOMPOSITION OF HYDROGEN PEROXIDE BY LIGHT

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Very extensive studies have been made on hydrogen peroxide in dilute and concentrated solutions and recently in the pure liquid state.[1] These studies have dealt particularly with its thermal, photochemical and catalytic decomposition in solution.[2] No work has been done on its decomposition in the gaseous state other than that of Elder and Rideal,[3] showing that the thermal decomposition is predominantly a surface reaction.

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[1] (a) Maass and Hatcher, THIS JOURNAL, **42**, 2548 (1920); (b) Maass and Hiebert, *ibid.*, **46**, 2693 (1924).

[2] For a complete review of this work, see Kistiakowsky, "Photochemical Processes," McGraw-Hill Book Co., Inc., New York, **1928**, pp. 173–177.

[3] Elder and Rideal, *Trans. Faraday Soc.*, **23**, 545 (1927).

The thermal, photochemical and catalytic decomposition is undoubtedly a very complicated one and in view of the work of Rice and Reiff[4] and of Rice and Kilpatrick[5] on the effect of ultramicroscopic particles on the thermal and photochemical decomposition it seems that much of the previous work cannot be regarded as conclusive.

The absorption spectrum of hydrogen peroxide solutions has been photographed by Henri and Wurmser,[6] who found that it was continuous, but no studies have been made on its absorption spectrum in the gaseous state and no determinations of the coefficient of absorption at different wave lengths, either in solution or as a gas. It was the purpose of this research to investigate these two subjects to see what light they might throw on the photochemical decomposition.

Preparation of the Hydrogen Peroxide.—We have used the methods of Maass and Hatcher[1] and of Rice, Reiff and Kilpatrick[7] in the preparation of the hydrogen peroxide. For the study of the dilute solutions, a 30% solution of the trade substance, Superoxol, was diluted down to the required concentration and in order to get more concentrated solution the water was evaporated off in a vacuum desiccator over sulfuric acid to a concentration of 88 to 90%. From this point pure hydrogen peroxide was made by repeated crystallizations. The strength of the hydrogen peroxide was determined by titration with potassium permanganate. The concentration of the liquid used in the study of light absorption of the vapor was always greater than 95%.

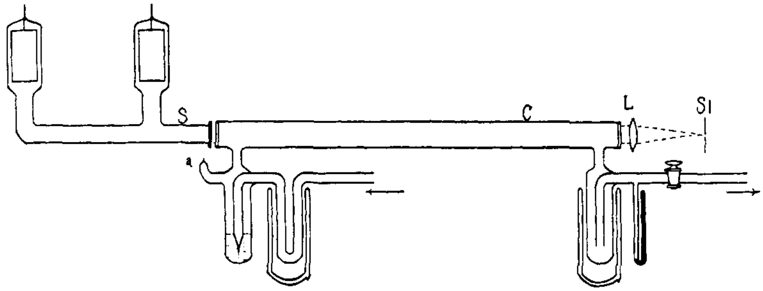

Fig. 1.

Apparatus for Determining the Absorption Spectrum.—In Fig. 1 is given a sketch of the apparatus, which remained essentially the same throughout the various experiments on absorption, though different types of absorption cells were used at different times. A hydrogen vacuum discharge tube, similar to that used by Tingey and Gerke[8] in their study of the absorption spectra of the hydrogen halides, was used as a source of continuous light and is shown in the figure at S. Electrolytic hydrogen was sealed off into the pyrex tube after degassing by passing a strong discharge through the tube, which raised it to a temperature of about 300°. A quartz window was sealed to the end with de Khotinsky cement to allow the passage of the ultraviolet light. We found

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[4] Rice and Reiff, *J. Phys. Chem.*, **31**, 1352 (1927).

[5] Rice and Kilpatrick, *ibid.*, **31**, 1507 (1927).

[6] Henri and Wurmser, *Compt. rend.*, **156**, 1012 (1913); *ibid.*, **157**, 126, 284 (1913).

[7] Rice, Reiff and M. L. Kilpatrick, THIS JOURNAL, **48**, 3019 (1926).

[8] Tingey and Gerke, *ibid.*, **48**, 1838 (1926).

that at the high pressures of hydrogen within the tube necessary for the production of the hydrogen continuous (about 3 mm. of mercury) it was not satisfactory to cool the tube, with water directly, due to puncture of the glass by the high potential required to produce the discharge but we had to immerse it in transformer oil through which water circulated in a copper coil. The tube gave a dense continuous emission extending from the sensitivity of our plates in the green down into the Schumann region. The maximum of the intensity of the continuous emission appeared to be about 3500 Å., though due to the greater dispersion in the ultraviolet is undoubtedly further to the violet. The first three lines of the Balmer series appeared; the green line was intense, and the blue line weak, being lost in the continuous. The color of the discharge was light blue with a tinge of pink. The current was supplied to the tube from a separate 110-volt, 60-cycle generator and stepped up to about 5000 volts across the tube. The current in the primary of the transformer was kept at 25 amperes and thus the emission intensity of the discharge tube remained quite constant. This tube has been used through the course of a year without renewing the hydrogen. The light from this source was passed through the absorption cell, C, of which several kinds were used. The light passing through the cell is approximately parallel due to the fact that the light from the luminous portion of the discharge tube passed through about 10 cm. of tubing before passing the quartz window. A lense at L focused the light on the slit of the spectrograph at S1.

Two Hilger quartz spectrographs were used in our measurements, the larger, E-3, being used for the absorption curve, and the small one, E-37, to investigate the region 1850 to 2350 Å. and the fluorescence. A Hilger rotating sector photometer was used to vary the times of exposure in the comparison photometry to estimate the coefficient of absorption.

In the first experiment a quartz cell was constructed of 67.5 cm. length and 3 cm. diameter, and it was so arranged that the temperature of the cell and containing bulb could be raised to any desired temperature between 25 and 100° by means of an electrical heating coil surrounding both cell and containing bulb. The absorption spectrum of the vapor photographed through this cell held at different temperatures showed that the spectrum is continuous throughout the range from 2000 to 3100 Å. No absorption could be detected on our plates for wave lengths longer than about 3000 or 3100 Å., but the absorption extends further to the violet with no indication of a maximum in this region. It was impossible to duplicate the intensities of blackening for the same wave length in different experiments at temperatures above 25°, probably due to poor temperature control and thermal decomposition of the vapor. For this reason experiments at higher than room temperature were discontinued.

By using a cell 183.5 cm. in length and 3 cm. in diameter, it was possible to get the product of concentration and the length sufficiently great to determine the coefficient of absorption at 2750 Å. and shorter wave lengths with a vapor pressure of about 1.5 mm., corresponding to 20°. This long cell was constructed of a pyrex tube with quartz windows sealed on with de Khotinsky cement. The hydrogen peroxide vapor at room temperatures did not attack the de Khotinsky cement appreciably, though such action is to be expected. No difference in the absorption could be detected when this cell was used and when other shorter cells not having the de Khotinsky cement were used.

Method for Determining the Coefficient of Absorption.—The coefficient of absorption per molecule is defined by the formula

$$I = I_0 e^{-acd} \text{ or } a = 1/cd \ln I/I_0 \tag{1}$$

where c is the concentration in molecules per cc., d the length of the column of gas and I and I_0 are the intensities after passing through the filled and empty cells, respectively. Assuming[9] that

$$I/I_0 = t_0/t \tag{2}$$

where t_0 and t are the times required for the plate to be blackened to the same extent at a particular wave length by the light passing through the empty cell and the filled cell, respectively, we have

$$a = 1/cd \ln t_0/t \tag{3}$$

In our experiments it was necessary to use rather wide absorption cells because of the great length of absorbing vapor at low pressures required to secure absorption and this made it impossible to use two parallel identical cells, one empty and the other filled, as is usually done. We therefore adopted the following procedure. Exposures of the continuous spectrum through the empty cell for different values of ln t_0 were taken, leaving alternate spaces on the photographic plate unexposed; then with the cell filled with the absorbing vapor exposures were made at these intermediate positions, using different values of ln t. In this way we cannot compare the intensities of two spectra lying right side by side. We therefore matched the limit of the observable blackening of the plate. Taking two spectra, one through the empty cell and one through the filled cell having the same limit of blackening, the coefficient of absorption for this wave length is secured by substituting the values of ln t and ln t_0 for these two spectra in (3) and it was found by trial that this limit was very reproducible. This method differs from the more usual one only in that we match the blackening on the plate for the point of zero blackening instead of at a finite intensity of blackening. We believe the errors of observation by this method are at least not much greater than in the more usual method.[10] Variation in the intensity of illumination was avoided by maintaining the current in the primary of the transformer constant during the experiments. We believe that this variation is small even over several hours, since the tube has been in use for months and therefore should not change with time, and, since it is well cooled, there should be no variation due to temperature. In practice we found it best to plot curves of ln t and ln t_0 against wave length for the limits of blackening for the light passing through the filled cell and empty cell, respectively, and take the difference in ln t and ln t_0 for a particular wave length from these curves.

Method of Experimental Procedure.—Into the bulb, a, a quantity of 97–100% hydrogen peroxide was introduced and air was bubbled through the liquid after first passing through the U-tube cooled in liquid air to remove all moisture. The dry air was admitted through a capillary tube and bubbled slowly through the liquid hydrogen peroxide to insure saturation with the vapor at the temperature of the bulb. Thus a constant current of vapor at a constant partial pressure streamed through the absorption cell while the absorption was being measured. This method of distilling the vapor partly eliminated the decomposition effect of the hydrogen peroxide due to the ultraviolet light. The total pressure maintained during a measurement was about 300 mm. of air and hydrogen peroxide. The hydrogen peroxide and any water produced were caught at the right end of the absorption cell in another liquid-air trap, beyond which were the mercury manometer and the oil pump.

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[9] Schwarzschild first wrote this equation in the form $I/I_0 = (t_0/t)^n$ where n is slightly less than unity. Recent work by Gibson, McNicolas, Tyndall and Frehafer (Scientific Papers of the Bureau of Standards, No. 440, June, 1922) and by Baly, Morton and Riding, *Proc. Roy. Soc. London*, **113A**, 709 (1927), shows, however, that the exponent may be taken as unity with an error of not over a few per cent.

[10] Henri, "Études de Photochimie," Gauthier-Villars et Cie, Paris, **1919.**

The bulb was held at a temperature of about 20° so that the vapor pressure according to Maass and Hatcher[1a] is 1.5 mm. The value of *cd* is therefore $cd = 2.702 \times 10^{19} \times 273/293 \times 1.5/760 \times 183.5 = 0.88 \times 10^{20}$. We believe that this value is correct within about 10 to 20%. The possible sources of error are the rapid change of the vapor pressure with temperature, the incomplete saturation of the air passing through the liquid and any decomposition of the hydrogen peroxide due to the light and heat.

The coefficients of absorption of the aqueous solutions were determined by using a cell 5 cm. in length and varying the concentration in order to get suitable blackening at different wave lengths. Absorption begins between 3700 and 3800 Å.; the absorption coefficient increases slightly to 3000 Å., after which it increases rapidly with decreasing wave length. These *cd* values were correct to within 1 or 2% because of the more precise method for determining the concentration.

Table I is a summary of our measurements and Fig. 2 shows them in graphical form. The circles represent values of a calculated from two plates for the solution and show the magnitude of deviation from the mean value. The crosses represent the absorption coefficients for the vapor. These cannot be regarded as very precise because of the uncertainty of the *cd*, but within this estimated uncertainty the curves for the vapor and solution coincide.

TABLE I

SUMMARY OF MEASUREMENTS

Wave length	Mean a	Number of plates	Wave length	Mean a	Number of plates
3800	0	2	2700	4.1	6
3700	0.1	2	2650	5.4	7
3600	0.2	2	2600	6.9	7
3500	0.2	2	2550	8.3	4
3400	0.3	2	2500	10.2	4
3300	0.4	2	2450	12.2	3
3200	0.5	3	2400	14.7	3
3100	0.7	3	2350	17.9	3
3000	1.0	4	2300	22.0	3
2900	1.5	5	2250	25.6	3
2800	2.4	5	2200	28.9	3
2750	3.1	5	2150	31.5	3

Value of *cd* for the vapor $= 0.882 \times 10^{20}$; values for the liquid $cd = 1.148, 0.579, 0.289, 0.114, 0.0723, 0.0362 \times 10^{20}$.

Discussion of the Absorption Experiments.—Since the spectrum is continuous, with no structure of any kind, we must conclude that the elementary process of the absorption of light is to dissociate the molecule into two or more fragments in accordance with Franck's[11] interpretation of continuous absorption spectra of the hydrogen halides and halogens. The conservation of energy requires that the energy of the quantum absorbed shall be

$$h\nu = E_1' + E_2' + \ldots\ldots + D + {}^1/_2 M_1 v_1^2 + {}^1/_2 M_2 v_2^2 \ldots\ldots \qquad (4_2)$$

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[11] For the theory of the dissociation process see Franck, *Trans. Faraday Soc.*, **21,** 536 (1925); Condon, *Phys. Rev.*, **28,** 1182 (1926).

where E'_1, E'_2...... are the energies of excitation of the resulting molecules, D is the energy of dissociation and $^1/_2M_1v_1^2$, $^1/_2M_2v_2^2$.... are the kinetic energies of the resulting molecules relative to the center of mass of the system. Since these resulting molecules can have unquantized kinetic energy of translation, the continuous absorption spectrum will lie on the violet side of the wave length for which

$$h\nu = E'_1 + E'_2 + \ldots\ldots + D \tag{5_2}$$

and any discontinuous spectrum on the long wave length side. It may happen that the main intensity of absorption may occur considerably toward the violet side of this limit and thus only a continuous spectrum will be observed. This appears to be true of hydrogen peroxide. In the case of the alkali halides and hydrogen halides[12] only such continuous absorption spectra are observed, while in the case of the halogens the discontinuous and continuous absorption spectra are both known and meet at the frequency defined by (5). These considerations are repeated here because they have a direct bearing on the interpretation of this continuous spectrum.

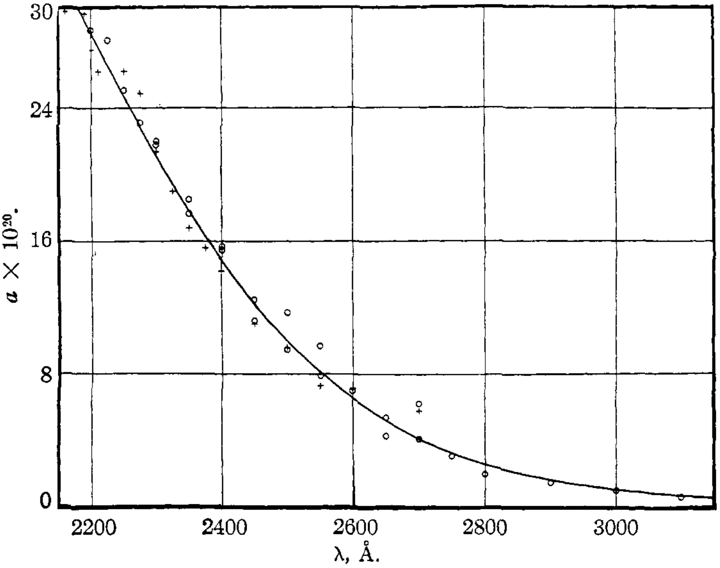

Fig. 2.

Henri has found that such continuous spectra are observed for associated vapors and there is a possibility that the absorption in the vapor state is due to the presence of a small percentage of $(H_2O_2)_n$. The absorption of light by such a molecule might result in its dissociation into

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[12] Franck, Kuhn and Rollefson, *Z. Physik*, **43**, 155 (1927); Franck and Kuhn, *ibid.*, **43**, 164 (1927); **44**, 607 (1927); Franck and Hogness, *ibid.*, **44**, 26 (1927).

one excited and one unexcited molecule and thus even if the molecule is not dissociated into atoms or unstable molecules such as OH, the spectrum might be continuous. Most of our work has been done at very low pressures, however, and under these conditions we expect that any such association would be very small. Elder and Rideal[3] find no evidence of association of hydrogen peroxide at 85 mm. and 85°. Kendall[13] has considered the question of association of water vapor and concludes that over a considerable range of pressures and temperatures there is no evidence for association. Because of the great similarity of physical properties of hydrogen peroxide and water, this makes it probable that such association of hydrogen peroxide must be small. Even if a continuous absorption of a very small fraction of polymerized molecules were present, one would expect a band spectrum of greater intensity superimposed on it. The absence of such a band spectrum indicates that the normal unassociated molecule must also have a continuous absorption spectrum. The question could be definitely decided by studying the absorption of the vapor at high and low pressures with the same value of *cd*, for the absorption should be greater at the higher pressures if polymerized molecules are responsible for the absorption and it should be the same if the unpolymerized molecules are responsible for the absorption. This would be very difficult with hydrogen peroxide because of its low vapor pressure at temperatures where thermal dissociation is slow. Thus to compare the absorption by two columns of vapor, one at 1.5 mm. pressure and say 183 cm. long, and another at 0.15 mm. pressure and some 18 meters long, would be impossible.

Hydrogen peroxide may be considered to be a pseudo-halogen. The normal states of the halogen atoms are inverted ^2P states with inner quantum numbers 3/2 and 1/2, the 3/2 state being the one with lower energy. Similarly, the OH molecule has the same number of electrons as the fluorine atom and also its normal state is an inverted ^2P state according to Mulliken.[14] We may make the postulate that the hydrogen peroxide molecule is formed of two OH molecules in a way similar to the formation of the halogen molecules from the individual atoms. Our experiments on the absorption of light described above support such an assumption. It is true, of course, that in chemical and physical properties there is very little similarity between hydrogen peroxide and the halogens, but the curves for the coefficients of absorption for I_2, Br_2 and Cl_2 show a progressive change which would lead us to expect that this curve for hydrogen peroxide would lie as it does. According to Ribaud and Kuhn,[15] the maxima for the absorption by I_2, Br_2 and Cl_2 lie 400,

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[13] Kendall, THIS JOURNAL, **42**, 2477 (1920).

[14] Mulliken, *Phys. Rev.*, N. S., **32**, 388 (1928).

[15] Ribaud, *Ann. Physik*, **12**, 107 (1919); Kuhn, *Z. Physik*, **39**, 77 (1926).

900 and 1400 Å., respectively, to the violet side of the critical wave lengths required for dissociation into a normal and excited atom, respectively. These critical wave lengths are 4995, 5107 and 4785 Å. and thus the three maxima lie at 4595, 4207 and 3385 Å., respectively. The absorption spectrum of fluorine is unknown, but it would probably have a maximum absorption at a considerably shorter wave length than that of chlorine, and if the action of light on the hydrogen peroxide molecule is similar, the maximum should also lie to the violet side of that for chlorine, as it does. The continuous absorption by I_2, Br_2 and Cl_2 is due to molecules in the lowest vibrational state; in the case of Cl_2 absorption by molecules in the lowest vibrational state occurs only in the continuous region, and its band spectrum is due to absorption by molecules in the first or second vibrational state. In the case of hydrogen peroxide it appears that molecules in all the vibrational states present in appreciable number at 20° absorb only in the continuous region, and that this continuous region is far to the violet side of the critical wave length for dissociation. We shall now consider in detail the known energy relations for the various conceivable ways that the molecule could dissociate.

Assuming hydrogen peroxide to have the structural formula H–O–O–H, it appears that primary dissociation might occur in three ways, namely, to produce two OH molecules in their normal states, or to break off one H atom leaving the HOO molecule; the removal of an oxygen atom from the middle of the molecule, thus leaving a water molecule, appears less probable. We wish to calculate the energy change for these three reactions from known data. In the thermochemical equations which follow, we employ the usual convention in regard to sign of the energy change, namely, the energy of the products minus that of the reactants. The energy of dissociation into H_2O and O can be exactly calculated as follows

$$\begin{array}{llll}
\text{(a)} & \text{HOOH} = \text{HOH} + {}^1/_2\text{O}_2 & -25.2\ \text{cal.[16]} \\
\text{(b)} & {}^1/_2\text{O}_2 = \text{O} & 81.0\ \text{cal.[17]} \\
\hline
\text{(c)} & \text{HOOH} = \text{HOH} + \text{O} & 55.8\ \text{cal.}
\end{array}$$

The energy change for dissociation into two OH molecules cannot be exactly calculated, but can be approximated from the following equations

$$\begin{array}{lll}
\text{(a)} & \text{HOOH} = \text{HOH} + {}^1/_2\text{O}_2 & -25.2\ \text{cal.} \\
\text{(d)} & 2\text{HOH} = 2\text{H} + 2\text{OH} & 224.0\ \text{cal.[18]} \\
\text{(e)} & 2\text{H} = \text{H}_2 & -102\ \ \text{cal.[19]} \\
\text{(f)} & \text{H}_2\text{O} + {}^1/_2\text{O}_2 = \text{HOH} & -57.8\ \text{cal.[16]} \\
\hline
\text{(g)} & \text{HOOH} = 2\text{OH} & 39\ \text{cal.}
\end{array}$$

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[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, pp. 477 and 495.

[17] Birge and Sponer, *Phys. Rev.*, N. S., **28**, 259 (1926).

[18] Taylor and Bates, *Proc. Nat. Acad. Sci.*, **12**, 714 (1926); THIS JOURNAL, **49**, 2438 (1927).

[19] Witmer, *Phys. Rev.*, **28**, 1223 (1926); Dieke and Hopfield, *Z. Physik*, **40**, 299 (1926).

The uncertainty in this figure is in the energy required to remove one hydrogen atom from water and this is less than 112 cal., since Taylor and Bates were able to dissociate water vapor with mercury atoms excited to the $^3P_1$ state. The energy change for dissociation into HOO and H cannot be calculated. The energy change for the reaction HOOH = $2H + O_2$ can be calculated from the following equations

(h) $HOOH = H_2 + O_2$ 32.6 cal.[16]
(e) $H_2 = 2H$ 102.0 cal.[19]
(i) $HOOH = 2H + O_2$ 134.6 cal.

and assuming that the change for the removal of the two hydrogen atoms, successively, is the same, we have

(j) $HOOH = HOO + H$ 67.3 cal.
(k) $HOO = H + O_2$ 67.3 cal.

In the case of water the removal of the first hydrogen requires less energy than the second, for from the equations given for the dissociation of O_2 and H_2 and the energy of formation of water, (b), (e) and (f), we have

(m) $HOH = 2H + O$ 240.8 cal.

and thus using (d)

(n) $OH = O + H$ 128.8 cal.

From analogy, the energy change for (j) may be less than 67.3 cal. and that for (k) greater than 67.3 cal., though this is not necessarily true.

The longer wave-length limit of absorption of the liquid is about 3750 Å., which is equivalent to 76.2 cal., and the longest wave length for the observed absorption of the vapor is about 3000 Å., corresponding to 95 cal. Over the range from 2250 to 2750 Å., where we found it possible to determine the coefficients of absorption for the solution and the gas, these coefficients agree within the limits of our measurements. It was impossible to determine the absorption coefficient for the gas at longer wave lengths because of the impossibility of getting a larger value of *cd* without increasing the temperature. It may be that the vapor would also absorb out to 3750 Å., if a sufficiently thick layer could be secured. It is evident in any case that there is sufficient energy even at 3750 Å. to cause any of the three reactions postulated to take place, and give considerable kinetic energy of translation or internal vibrational or rotational energy to the products. We cannot on this basis alone exclude any of them.

Effect of an Electric Discharge on Hydrogen Peroxide.—It is well known that the so-called water bands due to the OH molecule and the atomic spectrum of hydrogen appear with great intensity when water vapor is excited by an electric discharge at low pressures. The atomic oxygen spectrum appears only with comparatively low intensity. With a condensed discharge, or, if the discharge tube is allowed to become hot, the oxygen spectrum appears. We interpret this to mean that the comparatively low velocity electrons of the uncondensed discharge cause a disruption of water molecules into excited or unexcited OH molecules and H-atoms. The faintness of the O and H_2 spectra indicates that these are not primary products of bombardment of water in the uncondensed discharge.

An uncondensed electric discharge in hydrogen peroxide gives quite a different spectrum from that of water, if the hydrogen peroxide is streamed rapidly through the discharge tube, and the tube is kept well cooled. In these experiments hydrogen peroxide of nearly 100% purity was passed through a quartz tube 1 cm. in diameter by evaporating liquid hydrogen peroxide from a side arm of the tube and condensing it and any water formed in a liquid-air trap and pumping off the gases. Under these conditions the hydrogen peroxide must have been in this discharge only 0.1 to 0.01 second. As long as the tube was cool and the evaporation of hydrogen peroxide was rapid, the tube had a dull blue color in contrast to the characteristic red color of the discharge in water. By using a spectroscope we found that both atomic and molecular spectra of hydrogen were almost entirely absent. The faint blue color of the tube is due to a faint continuous spectrum. A photograph of the spectrum with the quartz spectrograph shows that the water bands are very intense and also that the continuous in the ultraviolet is faint. We are unable as yet to decide whether the continuous spectrum is identical with that of hydrogen or not.

The absence of the molecular and atomic spectra of hydrogen under these conditions leads us to believe that the comparatively slow electron bombardment causes the dissociation of hydrogen peroxide into two normal OH molecules and their subsequent excitation, or into one excited and one unexcited OH molecule, or into two excited OH molecules, so that the predominant spectrum is that of the water bands. The dissociation in such a way that oxygen or hydrogen atoms appear is at least much less probable. Since inelastic collisions of electrons with atoms and molecules are more probable, if the transition is one permitted by the selection rules for the emission and absorption of light, this experiment favors the postulate that light also dissociates hydrogen peroxide into normal or excited OH molecules.[20]

Experiments on the Fluorescence of Hydrogen Peroxide.—Our calculations on the energy changes thus far have considered only the dissociation into molecules in their lowest energy states. If the dissociation of hydrogen peroxide by light is similar to that of the halogens, the one OH molecule should be left in a $^2P_{1/2}$ state and the other in a $^2P_{3/2}$ state. However, since the energy difference of these two states is only 140.25 wave numbers according to Kemble,[21] which is equivalent to only 0.4 cal., and of the

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[20] See Franck and Jordan, "Handbuch der Physik," Julius Springer, **1926**, Vol. 23, p. 721.

[21] Kemble, *Phys. Rev.*, N. S. **30**, 387 (1927).

order of the rotation energy of the molecule, it is too small to be of importance in our thermochemical calculations. The next higher state is probably the ^2S state, which is the excited state for the emission of the water bands. Five of these bands are well known; their wave lengths and the initial and final values of the vibration quantums, n', and n'', are: 3064 (0,0); 2811, (1,0); 2875 (2,1); 2608 (2,0); and 3428 (0,1).[22] The wave numbers of the 3064, 2811 and 2608 bands give directly the energies required to excite the OH molecule to the ^2S state with vibrational quantum numbers 0, 1 and 2, respectively. These wave numbers are 32,637, 35,575 and 38,343, respectively. If then hydrogen peroxide is illuminated with light of sufficiently high wave number to dissociate the molecule into a normal OH molecule and an excited OH molecule in a ^2S state and one of these vibrational states, and if the dissociation in this way is a possible one, it should be possible to observe the OH bands in fluorescence under proper conditions. The essential experimental requirements are *intense illumination of the vapor at low pressure* so that the fluorescence is not quenched by collisions with other hydrogen peroxide molecules or water molecules. Since the vapor pressure of water at 20° is 17.4 mm. of mercury, while that of hydrogen peroxide is only 1.5 mm., it is necessary to use very pure hydrogen peroxide.

The energy required to dissociate hydrogen peroxide into two normal OH molecules is less than 39 cal. (Eq. g), which is equivalent to 13,660 wave numbers. The wave number, $\tilde{\nu}$, and wave lengths of the light required to dissociate the molecule and excite the one OH molecule to the ^2S state with different amounts of vibrational energy are

		$\tilde{\nu}$	λ
(g)	$HOOH = OH(^2P) + OH(^2P)$	13660 cm.$^{-1}$	7320 Å.
(o)	$HOOH = OH(^2P) + OH(^2S, n' = 0)$	46350 cm.$^{-1}$	2160 Å.
(p)	$HOOH = OH(^2P) + OH(^2S, n' = 1)$	49020 cm.$^{-1}$	2040 Å.
(q)	$HOOH = OH(^2P) + OH(^2S, n' = 2)$	52050 cm.$^{-1}$	1920 Å.

Hydrogen peroxide vapor at a pressure of about 1 mm. of mercury was illuminated with the 2025, 2060, 2087, 2100 and 2138 Å. lines of the zinc spark, and the presence of the 3064 Å. water band was detected in fluorescence. The light from a zinc spark was passed through an acetone filter, which absorbed all the light from 2138 to 3075 Å., and transmitted longer wave lengths and shorter wave lengths to about 2025 Å., so that this zinc line is faint. The longer wave lengths are only slightly absorbed by hydrogen peroxide and are therefore of no importance. The zinc

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[22] For references see Mulliken, *Phys. Rev.*, **32**, 403 (1928); L. Grebe and O. Holtz, *Ann. Physik*, **39**, 1243 (1912); T. Heurlinger, "Dissertation," Lund, **1918**; R. Fortrat *J. Phys.*, **5**, 20 (1924); W. W. Watson, *Astrophys. J.*, **60**, 145 (1924); G. H. Dieke, *Proc. Acad. Sci. Amsterdam*, **28**, 174 (1925); R. T. Birge, Chapter LV, Part 5, National Research Council Report on Molecular Spectra in Gases; D. Jack, *Proc. Roy. Soc. London*, **115A**, 373 (1927); **118A**, 647 (1928); E. C. Kemble, *Phys. Rev.*, **30**, 337 (1927).

spark has only the five strong lines between 2138 Å. and 2025 Å. Thus these five intense lines and less intense ones are the only ones effective in producing fluorescence. After passing the acetone filter the light passed through a long cell of hydrogen peroxide vapor. The spectrograph was placed in the direct line of this incident light. The photographic plate showed these incident wave lengths strongly so that the entire tube must have been excited to fluorescence. The fluorescent water bands fall in the region of absorption of acetone so that the presence of the incident light on the plate did not prevent the detection of the fluorescent light. The head of the 3064 Å. water band falls about 11 Å. to the short wave-length side of the 3075 Å. line of the zinc spark and appears as a faint sharp edge just in this position. No other water bands were detected, probably because of their lower intensities or because the light used may not be of sufficiently short wave length to excite the higher vibration levels.

This experiment shows definitely that the reaction (o) is one possible way in which light dissociates the molecule.[23]

One of us (L. H. D.) is continuing this phase of the work with better methods for exciting this fluorescence expecting to secure the other water bands and determine, if possible, the energy change of (g) more accurately by this method. Furthermore, the recent work of Kondratjew and Leipunsky[24] on the recombination spectra of the halogens and that of Bates and Urey[25] on the continuous spectra emitted by flames containing hydrogen and the halogens and interpreted by them as the recombination spectra of halogen atoms, suggest that further study of the continuous emission spectrum of hydrogen peroxide may give more information

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[23] Since the writing of this paper an article has appeared [Bonhoeffer and Haber, *Z. physik. Chem.*, **137**, 263 (1928)] in which the heat of dissociation of the OH molecule has been taken as 123 cal. and the energy of dissociation of the first H atom from the water molecule as 115 cal. The energy of dissociation of hydrogen peroxide into gaseous hydrogen and oxygen is taken as 38 cal. by a different method of calculation. However, the value of 32.8 cal. for the energy of formation of hydrogen peroxide as calculated by Lewis and Randall[16] seems to us a better value than that calculated by Wartenberg and Sieg [*Ber.*, **53**, 2192 (1920)] and the energy of formation of water from the atoms is 240.8 according to our calculations. These values have not been calculated to absolute zero and are therefore not very accurate. If the value of 54 Cal. for Equation (g) is correct, we should not have been able to secure the 3064 Å. water band in fluorescence and in fact the energy change in this reaction cannot be much greater than 39 cal. if the 3064 Å. band is to be excited by the wave lengths we have used. The photochemical experiments of Bates and Taylor[18] and Senftleben and Rehren [*Z. Physik*, **37**, 529 (1926)] and also Bonhoeffer and Reichardt [*Z. Elektrochem.*, **34**, 652 (1928)] on the equilibrium $2H_2O = H_2 + 2OH$ at high temperatures indicate that 115 cal. is too large. If we use 115 cal. instead of 112 cal. and leave the remaining values in our calculations the same, the water band should not appear in our experiments.

[24] Kondratjew and Leipunsky, *Z. Physik*, **50**, 366 (1928).

[25] Bates and Urey, *Phys. Rev.*, N. S., article to appear soon.

in regard to the processes taking place in the discharge; this will be studied further.

Summary

1. The absorption spectrum of hydrogen peroxide vapor in the ultra-violet has been found to be continuous with no indication of any structure beginning at about 3000–3100 Å. and extended toward the ultra-violet.

2. The coefficients of absorption of hydrogen peroxide in solution have been determined for wave lengths from 3750 to 2150 Å. and those of its vapor for wave lengths 2150 to 2750 Å. Over this latter range and within the limits of experimental error the two absorption curves are the same.

3. The possible photochemical processes are discussed and it is found that the quantum of energy of the longest wave lengths absorbed would be more than sufficient to cause any of the following three reactions to take place

$$H_2O_2 + h\nu \longrightarrow 2OH \qquad H_2O_2 + h\nu \longrightarrow HO_2 \qquad H_2O_2 + h\nu \longrightarrow H_2O + O$$

4. The emission spectrum of hydrogen peroxide when streamed rapidly through a cool discharge tube is predominantly that of the water bands (due to OH). This favors the first of these three reactions as the one occurring in the photochemical process.

5. Illumination with the zinc spark lines from 2025 to 2138 Å. caused the water bands to appear in fluorescence. This shows that the following reaction takes place under these conditions

$$H_2O_2 + h\nu = OH(^2P) + OH(^2S)$$

6. The analogy of hydrogen peroxide to the halogens with respect to structure is pointed out and the evidence, though not conclusive, favors the following reaction as the one occurring when it is illuminated with wave lengths from about 2200 to 3000 Å.

$$H_2O_2 + h\nu = OH(^2P_{1/2}) + OH(^2P_{3/2})$$

This would be similar to the primary process occurring when the halogens absorb light in the continuous region of their spectra.

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