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Kinetics of OH Radicals as Determined by Their Absorption Spectrum

I. The Electric Discharge Through Water Vapor

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(1) The order of the reaction causing the rapid disappearance of OH radicals after interrupting an electric discharge through H_2O vapor is measured by photometry of absorption spectra taken in snapshots. (2) These spectra are taken in time intervals of a few tenths of a second with a 21-foot grating and rotating interrupter and sector. (3) Relative concentrations of OH radicals are derived by comparing intensities of rotational lines within one branch of the $0\rightarrow0$ band of OH, the relative intensities being given by the theory of Hill and Van Vleck. (4) The decay of OH with time for various H_2O pressures and addition of He is given in diagrams and a table of rate constants. (5) A discussion of the kinetics leads to triple collisions consuming OH. (6) KCl covering the surface of the absorption tube materially increases the rate of the reaction. (7) The absorption spectrum of H_2O_2 investigated simultaneously showed that no appreciable H_2O_2 is formed in the reaction. (8) In the processes consuming OH radicals after interrupting the discharge through H_2O vapor in clean glass tubes, the triple collision $H+OH+M\rightarrow H_2O+M$ plays a predominant part.

I. PROBLEM AND PREVIOUS WORK

IN preceding papers[1] observations have been reported of the absorption spectrum of free OH radicals in a reacting gas at room temperature. In particular it was shown that OH as produced by the electric discharge through H_2O vapor could be observed to last for at least $\frac{1}{8}$ second after interrupting the discharge. It was concluded that the recombination process determining the disappearance of OH is not so fast that a bimolecular association has to be assumed, as had been suggested by other observations.[2]

The work here reported was carried out in order to obtain further information regarding this process, and consists in determining quantitatively relative values of the OH concentration and so obtaining the rate of disappearance of OH as a function of the composition of the reacting gas mixture.

II. EXPERIMENTAL

The apparatus was essentially that described previously, but improved in several respects in order to allow for more quantitative results. It consisted of:

(a) Source of continuous radiation
(b) Absorption tube
(c) Rotating sector and switch
(d) Spectrograph

The OH λ3064 band was to be observed in absorption. The carbon arc in nitrogen as used previously did not provide a sufficiently continuous radiation to be used as a source in quantitative work. However, the carbon arc burning in flowing helium was found to be satisfactory in this respect and was used in a number of experiments. This source was discarded later in favor of a particularly intense hydrogen discharge tube.[3] The latter carried a current of one to two amperes through a 1×5 mm capillary and was less intense by a factor of two to four, but was much easier to operate, and provided a radiation which was constant over long periods of time.

The absorption tube was 150 cm long and 4.7 cm in diameter and closed at each end with quartz windows. Large aluminum electrodes were placed in side tubes at a distance of about 20 cm from the absorption tube proper.

A synchronous motor operated a revolving sector which allowed light to pass to the spectrograph during the desired interval of time. On the same shaft with the sector was a sliding contactor which served to control the discharge through the gas in the absorption tube. At first this contactor was placed in series with the discharge and the secondary of a transformer, an arrangement which proved unsatisfactory because of the high potential involved. This

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[1] O. Oldenberg, J. Chem. Phys. **2**, 713 (1934) and **3**, 266 (1935).

[2] W. H. Rodebush and M. H. Wahl, J. Chem. Phys. **1**, 696 (1933).

[3] Constructed by N. D. Smith, Thesis, Harvard University. To be published.

TABLE I.

Rotational Quantum Number	Relative Absorption Coefficient
$1\frac{1}{2}$	0.571
$2\frac{1}{2}$	0.725
$3\frac{1}{2}$	0.605
$4\frac{1}{2}$	0.390
$5\frac{1}{2}$	0.195
$6\frac{1}{2}$	0.081

problem was solved by putting the contactor in the grid circuit of a thyratron (FG–29) which regulated the current through the transformer primary.[4] 60-cycle a.c. 110 and 220 volts was used in the primary, the power varying from 2 to 4 kilowatts. One or four half-cycles were passed through the primary depending upon the gear system used with the synchronous motor. The shaft was rotated at 6 revolutions per second, or at $1\frac{7}{8}$ revolutions per second, different speeds being necessary in order to follow the reaction under widely differing conditions.

A high frequency discharge was used in several runs and was produced with the aid of a 250-watt power oscillator, the high frequency potential being applied between external electrodes running the full length of the absorption tube. The advantage of this arrangement was that a discharge could easily be obtained with much higher pressures of water vapor, up to 5 mm Hg.

For obtaining the weak band absorption, the second order of a 21-foot concave grating spectrograph was used. The high resolving power was necessary in order to observe the very narrow absorption lines of the band. To decrease the exposure time as much as possible a cylindrical lens was placed in front of the photographic plate.[5] This increased the intensity over the small spectral range to be observed by a factor of about 20 without affecting the resolving power. Eastman IV–O plates were used.

III. EVALUATION OF RELATIVE OH CONCENTRATIONS

The individual OH absorption lines being so very narrow (cf. the spectrum reproduced, reference 1, Fig. 2) it was not found possible to measure the intensity of absorption with the available microphotometer. However, the following method involving only visual comparison of absorption lines was found to be reasonably satisfactory. It so happens that instead of the conventional intensity marks, the individual lines of one branch of a band represent concentration marks since the relative concentrations of the rotational quanta for a given temperature and their absorption coefficients are theoretically predictable on the basis of the theory of Hill and Van Vleck.[6] Lines of the Q_1 branch were used because of their intensity and freedom from overlapping with lines of other branches. Assuming that the rotation of OH is in equilibrium at slightly above room temperature (300°K) the relative values of the absorption coefficients (Boltzmann factor × statistical weight × probability of transition) are given in Table I.

In order to obtain relative OH concentrations corresponding to two different exposures, the exposures were placed side by side in the field of view of a microscope and the absorption lines compared until one or more pairs of lines were found, the lines of each pair having nearly the same intensity of absorption.[7] In this comparison care must be taken to have equal intensity of the continuous background in the two exposures and to use the photographic plate in the linear portion of its characteristic. One exposure is taken as a standard furnishing an arbitrary unit pressure of OH. All measurements discussed in the following sections are expressed in the same standard units of OH pressure. Suppose the mth line of the unknown is paired with the nth line of the standard and let k_m and k_n be the respective values of the relative absorption coefficients found in Table I. Then the OH concentration for the unknown is k_n/k_m units. Several such concentration values may be obtained for a single exposure if interpolation of intensities between lines is made use of. Only the third, fourth, fifth and sixth lines and two or three gradations between each neighboring pair were used in the comparison. The available concentration range was about 1 : 100. A typical set of values of OH

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[4] Following a suggestion by Dr. F. V. Hunt.

[5] O. Oldenberg, J. Opt. Soc. Am. **22**, 441 (1932).

[6] E. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928). Calculations for the special case under discussion were carried out by L. T. Earls, Phys. Rev. **48**, 423 (1935). We appreciate the advice of Professor Van Vleck in the problem of intensities.

[7] An instrument was devised which enabled this comparison to be made without the need of cutting the plates up into their separate exposures.

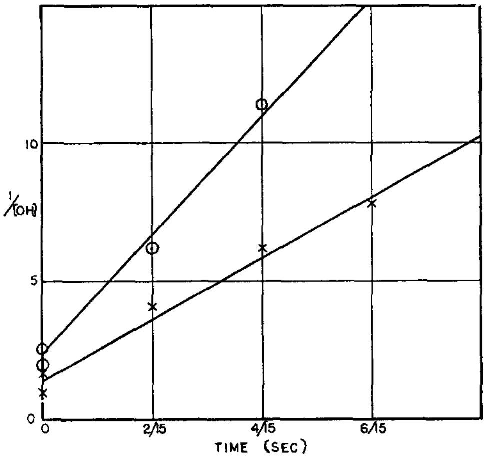

FIG. 1. Dependence of 1/[OH] upon time; ×, H_2O 1.1 mm; ○, H_2O 1.1 mm; He 3.7 mm; 1/[OH] in 1/standard pressure.

concentration obtained in this way for a single exposure is as follows: 0.64, 0.50, 0.50, 0.37, 0.46; average 0.49; mean deviation 12 percent. The results are not very precise but they are accurate enough for the present purpose of determining the order of the reaction.

IV. EXPERIMENTAL RESULTS

As is shown in the next section it is expected that for any set of conditions there should be a linear relation between 1/[OH] and the time. That this is true within the experimental error is shown in Fig. 1, in which are plotted the results for typical cases. The slope of the straight line represents an experimental rate constant $\bar{k}$ for the particular conditions employed. Table II is a summary of the experimental results as expressed by values of $\bar{k}$ corresponding to different values of H_2O and He pressure.

V. CHEMICAL KINETICS

The various possible processes leading to a long life of OH in the electric discharge through water vapor have been discussed at length in the preceding paper. For the present purpose we shall base our calculations on the following assumptions:

(a) The reacting mixture consists of H_2O, H and OH, with the addition of He in several runs. Ions will have recombined within a few thousandths of a second after the discharge. O atoms can be assumed to be present in negligibly small amounts if the current is not too high. The experimental arguments for this assumption have been summarized by Oldenberg. From the molecular structure it is plausible that the easiest dissociation process leads to H and OH, not to free O atoms.

(b) The probable reactions are:

$$\left.\begin{array}{ll}(1) & H+H+M\rightarrow H_2+M\\ (2) & H+OH+M\rightarrow H_2O+M\\ (3) & OH+OH+M\rightarrow H_2O_2+M\end{array}\right\}\text{Termolecular Processes where } M \text{ is any third molecule}$$

or instead of (2) and (3)

$$\left.\begin{array}{ll}(2a) & H+OH\rightarrow H_2O\\ (3a) & OH+OH\rightarrow H_2O_2\end{array}\right\}\text{Bimolecular Processes}$$

(c) H_2O is only to a small part dissociated so that $[M]$ will be approximately constant during the reaction.

For reactions (1), (2), (3) the rate of disappearance of OH is given by

$$-(d[OH]/dt)=k_2[OH][H][M]+k_3[OH]^2[M]$$

plus additional terms with different constants if more than one kind of molecule is effective as a third body. Since we assume the statement of Rodebush and Wahl that [H] and [OH] are the primary products, the reaction starts from equal concentrations [H] and [OH]. If we furthermore assume that H and OH disappear by triple collisions at not very different rates it follows that $[H]\simeq[OH]$ during the time through which

TABLE II.

Plate number	H_2O (mm Hg)	He (mm Hg)	$\bar{k}$ (standard pressure units^{-1} sec.$^{-1}$)
1	1.3	0	24
	2.6	0	24
	5.2	0	48
2	1.0	0	14
	2.0	0	17
	4.1	0	30
3	1.0	0	13
	1.0	7.2	31
4	1.45	0	17
	1.45	2.75	27
5	1.1	0	17
	1.1	3.7	31
6	0.75	0	18
	0.75	4.1	27

the reaction is observed. In this case the two terms may be combined and

$$-(d[\mathrm{OH}]/dt)=k[\mathrm{OH}]^2[M],$$

which may be integrated, M being constant with respect to the time:

$$(1/[\mathrm{OH}]_t)-(1/[\mathrm{OH}]_0)=k[M]t.$$

The corresponding treatment for OH reacting according to (2a) and (3a) would result in

$$(1/[\mathrm{OH}]_t)-(1/[\mathrm{OH}]_0)=k't.$$

The same equation would hold if the wall reaction is predominant. In any case there should be a linear relationship between $1/[\mathrm{OH}]$ and the time. This relationship has been used in the preceding section.

The experimental constant $\bar{k}$ is to be compared with the constants $k[M]$ or k' of the theory. If $\bar{k}$ is independent of the H_2O and He concentrations the reaction proceeds according to (2a), (3a). On the other hand, if $\bar{k}$ increases with the H_2O and He concentrations in such a way that

$$\bar{k}=k_{\mathrm{H_2O}}[\mathrm{H_2O}]+k_{\mathrm{He}}[\mathrm{He}],$$

then the reaction is termolecular according to (2) and (3). That the latter is the case may be seen at least qualitatively in Fig. 1 where it is noticed that the addition of He increases the rate of the reaction. The constant $k_{\mathrm{H_2O}}$ may be calculated directly from data on the reaction in the absence of He. Fig. 2 is a plot of $\bar{k}$ against H_2O pressure based on the experiments with a wide variation of H_2O up to 5.2 mm (plates 1 and 2 of Table II). The rate does definitely increase with increasing $[\mathrm{H_2O}]$. The fact that the best straight line does not go through the origin seems to indicate the simultaneous occurrence of a slow bimolecular reaction, presumably at the surface. More evidence of a surface reaction is given in the next section.

The value of $k_{\mathrm{H_2O}}$ as given by the slope of the line of Fig. 2 is

$$k_{\mathrm{H_2O}}=6.8;\quad \mathrm{H_2O}\text{ in mm Hg}.$$

The constant k_{He} is most easily obtained by dividing the increase in the constant $\bar{k}$ due to the addition of He by the pressure of He added. The four last plates of Table II give the four values 2.5, 3.6, 3.8, 2.2, the average of which is $k_{\mathrm{He}}=3.0$. These results for $k_{\mathrm{H_2O}}$ and k_{He} are based on the same "standard units" of [OH].

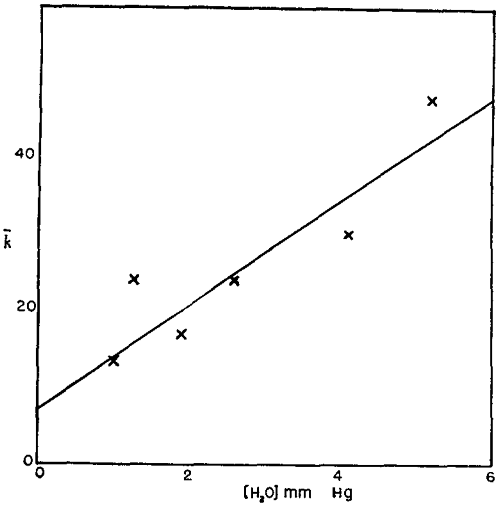

FIG. 2. Dependence of experimental rate constant $\bar{k}$ upon H_2O pressure; $\bar{k}$ in standard pressure units^{-1} $\times$sec.$^{-1}$.

In order to determine whether or not these are reasonable values for triple collision rate constants the absolute concentration of OH must be known or estimated. If we assume that the maximum OH concentration obtained with the present apparatus, defined as a standard in section III, is about 0.1 mm so that the large majority of molecules is not dissociated, then the reaction constants are

$$k_{\mathrm{H_2O}}=68 \quad\text{and}\quad k_{\mathrm{He}}=30 \quad (\mathrm{mm}^{-2}\ \mathrm{sec.}^{-1})$$

$$\text{or}\quad k_{\mathrm{H_2O}}=2.4\times10^{16}\quad\text{and}\quad k_{\mathrm{He}}=1.1\times10^{16}\quad(\mathrm{cc}^{-2}\ \mathrm{mole}^{+2}\ \mathrm{sec.}^{-1}).$$

These values although being very approximate compare favorably with rate constants for similar third order reactions such as

$$\mathrm{H}+\mathrm{H}+M\rightarrow\mathrm{H_2}+M^{8}$$

$$\text{and}\quad \mathrm{Br}+\mathrm{Br}+M\rightarrow\mathrm{Br_2}+M^{9}$$

with values ranging from 10^{15}–10^{16}.

Obviously the problem remains of determining the *absolute* concentration of OH which in this argument is rather arbitrarily assumed. The only

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[8] H. M. Smallwood, J. Am. Chem. Soc. **51**, 1985 (1929) and **56**, 1542 (1934).

[9] K. Hilferding and W. Steiner, Zeits. f. physik. Chemie **B30**, 399 (1935); E. Rabinowitsch, Zeits. f. physik. Chemie **B33**, 275 (1936).

method to apply is a comparison of the OH observed at the discharge with a known concentration as it was observed by Bonhoeffer and Reichardt[10] in water vapor partially dissociated at temperatures above 1150°C. An experimental difficulty turns up, however, in that the two absorption experiments to be compared are carried through at temperatures different by a factor 5 and pressures by a factor 1000, so that the line widths are quite different. But the total energy absorbed within a spectral line of a certain coefficient of absorption depends upon the width of the line—apart from the properties of the spectrograph. Hence the comparison requires a special study of the pressure broadening of the OH lines. For this purpose even the second order of the 21-foot grating is not adequate. An attempt will be made to solve this problem and so determine the absolute values of the reaction rate constants k_{H_2O} and k_{He}.

VI. SURFACE REACTION

The pressure effect reported definitely indicates a gas reaction. If the surface reaction were prominent He would decrease rather than increase the rate, contrary to the values of Table II. In the following experiments a potassium chloride surface was studied for various reasons. KCl is known not to catalyze the recombination of hydrogen atoms. Hence any positive effect in the discharge through water vapor must be due to the adsorption of OH radicals. A very strong effect of KCl was discovered by Pease[11] in the slow combustion of H_2 at temperatures of 520–550°C. This is known to be a chain reaction. When the glass walls are covered with KCl the rate is reduced by a factor of about 1000. Since chain reactions are easily broken by surface reactions removing one chain carrier, the effect of a KCl surface on radicals is of interest. Taylor and Lavin[12] observed the heating of thermometers covered with various substances in the flowing gases pumped out of the discharge through H_2O; they inferred adsorption and recombination of OH on a KCl surface.

The rate of disappearance of OH, observed by the decay of the absorption spectra, was compared for a glass surface carefully cleaned with cleaning solution, boiling water and distilled water, and on the other hand for the same surface covered with KCl. In both cases, of course, the surface was moist. The KCl surface increases the rate materially. While for the glass surface the absorption spectrum of OH is easily traced through 8/15 sec., it disappears completely for the KCl surface in the same time interval. Furthermore, since the discharge proper producing OH is not instantaneous but lasts through 1/15 sec. it is noticeable that, right after interrupting it, more OH is present in the case of the clean glass than in the case of the KCl surface.

The obvious interpretation of this experiment is that the KCl surface adsorbs OH radicals and so catalyzes their reaction, in agreement with the result of Taylor and Lavin.

The noticeable increase of the surface reaction caused by the KCl surface indicates that for clean glass the surface reaction is not predominant. Whether or not in the experiment of Pease the same effect takes place, i.e., whether OH is one of the chain carriers, remains uncertain. An endeavor will be made to obtain further evidence.

VII. ABSORPTION SPECTRUM OF H_2O_2

In section 5 it was shown that OH disappears largely by triple collisions. It remained uncertain whether H_2O or H_2O_2 is formed, that is, whether reaction (2) or (3) takes place. The results of Rodebush and Wahl seemed to indicate an overwhelming probability for the formation of H_2O_2 since concentrations of nearly 50 percent H_2O_2 were obtained in the gases pumped out of the discharge. It should be possible to measure a concentration as high as that by the absorption spectrum. Rodebush and Wahl failed in doing this. They explained that their failure was caused by lack of sensitivity of the experiment. Since the absorption spectrum of OH proved to be valuable for the study of kinetics, it seemed worth while to improve the sensitivity with which the absorption spectrum of H_2O_2 was to be observed.

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[10] K. F. Bonhoeffer and H. Reichardt, Zeits. f. physik. Chemie **139**, 75 (1928).

[11] R. N. Pease, J. Am. Chem. Soc. **52**, 5106 (1930).

[12] H. S. Taylor and G. I. Lavin, J. Am. Chem. Soc. **52**, 1910 (1930).

According to Urey, Dawsey and Rice,[13] H_2O_2 has a continuous absorption spectrum extending from about λ3100 with increasing intensity to short waves beyond the range of the quartz spectrograph. No other molecule present in this experiment shows continuous absorption in the same range. In particular OH has the major intensity in the 0→0 band so that no continuous OH spectrum beyond a convergence limit of vibrational quanta is to be expected which might obscure the H_2O_2 spectrum. The difficulties of the two absorption experiments are entirely different. While for the absorption spectrum of OH because of the exceedingly narrow lines high resolving power is necessary, the absorption spectrum of H_2O_2 can be observed with any small quartz spectrograph because of its continuous nature. In order to detect small traces of H_2O_2 a very accurate measurement of the light intensity passing through the vapor is necessary, hence a very steady source of light is required.

In order to take advantage of the strong absorption at short wave-lengths, some experiments were made with an electric discharge through Cd vapor, the resonance line of which at λ2280 is rather isolated in its spectrum. However, the mercury line λ2537 emitted from an ordinary arc proved about as effective and easier to apply. Instead of using a monochromator in order to separate the line λ2537 from the intense long wave-length spectrum which is not absorbed by H_2O_2, a chlorine filter was applied, consisting of a layer of chlorine gas of 1 atmosphere, 30 cm long. The intensity of the light passing the H_2O_2 was measured by a photoelectric cell which indicates small changes of intensity much better than the photographic plate. A cadmium cell, argon filled, in a quartz bulb, made in this laboratory by Mr. H. W. Leighton, was used. The visible light transmitted by the chlorine filter has no effect on the cadmium cell since its long wave-length limit is λ3100. The current was amplified with a type 32 tube and measured with a microammeter. This system—lamp, chlorine filter, cadmium cell—was calibrated for its power to indicate the presence of H_2O_2 by H_2O_2 vapor of known concentration.[14] The calibration showed that in the same absorption tube of 150 cm length H_2O_2 of 1/100 mm could be detected.

We are interested as to whether or not in the electric discharge through water vapor the OH radicals when recombining form H_2O_2. The absorption experiment gave no trace of H_2O_2. This result indicates that the considerable amount of H_2O_2, frozen out in the experiment of Rodebush and Wahl in the liquid-air trap, is formed in the trap, not in a gas reaction.

The formation of H_2O_2 *in the trap* was mentioned as an alternative explanation by Rodebush and Wahl themselves. That this actually takes place was concluded by Campbell and Rodebush[15] from recent experiments. Their result has recently been confirmed by Geib,[16] who found hydrogen peroxide in the gases pumped out of the discharge tube only under conditions which according to his own experiments are favorable for the formation in the trap of H_2O_2.

In the interpretation of the experiments by Rodebush and Wahl the difficulty remains that the concentration of H_2O_2 observed in the trap does not appreciably change, while the time of flow between discharge bulb and trap (velocity of flow and distance) is varied. It must be concluded that no appreciable combination of OH+H takes place during the time of flow. This might be largely due to the fact that they worked with pressures as low as 0.1 or 0.2 in the discharge tube, hence still somewhat lower in the flowing system, so that triple collisions consuming the OH radicals are still less probable than in the experiments reported above. Furthermore the 50 percent yield of H_2O_2 reported in their experiments means the value relative to H_2O, not to the total gas content pumped out of the discharge. At any rate, their observation confirms the conclusion of section 6 that no fast combination of OH on a clean glass wall takes place since even the gas slowly flowing through long glass tubes shows the same yield of H_2O_2 in the trap.

VIII. PROCESSES IN THE DISCHARGE THROUGH H_2O

It remains to summarize the chemical processes taking place after interrupting the discharge

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[13] H. C. Urey, L. H. Dawsey and F. O. Rice, J. Am. Chem. Soc. **51**, 1371 (1929).

[14] Concentrated H_2O_2 was made for other experiments which will be described in another paper.

[15] R. W. Campbell and W. H. Rodebush, J. Chem. Phys. **4**, 293 (1936).

[16] K. H. Geib, J. Chem. Phys. **4**, 391 (1936).

through water vapor or else in the gases pumped out of the discharge. We are not concerned with the discharge proper in which reactions may be caused by ions as discussed in detail by Brewer.[17]

Again we assume H and OH as primary products, since O is produced at a comparatively small concentration. The main result of the present paper is that the disappearance of OH is largely due to a termolecular gas reaction. From our failure to observe the absorption spectrum of H_2O_2 and from the results of Campbell and Rodebush and of Geib, $H+OH+M\rightarrow H_2O+M$ is to be assumed as the most plausible process. A wall reaction is certain not to play a predominant part for a clean glass surface but to become important at the KCl surface.

In addition it is possible that H_2O_2 is produced but rapidly decomposed so that no appreciable concentration builds up, since H atoms and OH radicals are both able to decompose it.[18]

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[17] A. K. Brewer, J. Phys. Chem. **38**, 1051 (1934).

[18] Cf. K. H. Geib, Zeits. f. physik. Chemie **A169**, 161 (1934). Evidence for the decomposition process $OH+H_2O_2$ will be presented in another paper.

OCTOBER, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

The Crystal Structure of Polonium by Electron Diffraction

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Electron diffraction photographs ($\lambda=0.062$A) were obtained from about 10^{-7} g of polonium that had been volatilized in a stream of hydrogen and condensed over an area of about 3 mm² on a thin collodion film. Diffraction patterns were also obtained from bismuth and tellurium since it was expected that polonium would have a similar crystal structure. Analysis of these patterns shows that the structure of polonium closely resembles that of tellurium, the lattice being pseudohexagonal with $a=4.25$A, $c=7.06$A, or 14.12A, and the calculated density 9.39 assuming 3 Po in the pseudo unit of structure. The true lattice is probably monoclinic with $a=7.42$A, $b=4.29$A, $c=14.10$A and β quite close to 90°, a suggested value being $\beta=92°$; the calculated density for 12 Po in the unit of structure is 9.24. A structure, based upon the space group $C_2{}^3-C2$, in which each polonium atom has four nearest neighbors gives moderate agreement between observed and calculated intensities of reflection.

Introduction

Polonium is the superior homolog of tellurium in the periodic system of the elements and immediately follows bismuth in atomic number. It resembles both these elements in its chemical properties but, of course, differs from them in being radioactive. The crystal structure of the element could be expected to be similar to that of tellurium or bismuth.

Sufficiently large amounts of polonium have not yet been available for x-ray diffraction experiments and thus no information is available on its crystal structure or its density. A strong source of polonium for radioactive work contains *ca.* 10^{-6} g of material, which is quite sufficient to give electron diffraction photographs provided that it can be obtained as a thin film.

Preparation of the Polonium Film

Pure polonium was prepared from old radon bulbs[1] under the supervision and with the constant help of Dr. L. R. Hafstad[2] who has developed a technique for the production of strong polonium sources after the method used by Mme. I. Curie.[3] According to this method

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* On leave of absence from the University of Milan. I am particularly indebted to Professor Dr. G. Bruni, Dr. Charles L. Parsons, Dr. H. G. Knight and Dr. C. H. Kunsman for making arrangements necessary for the successful culmination of this work and for their many courtesies.

[1] We are indebted to Dr. C. F. Burnham and Dr. F. West of the Kelly Hospital, Baltimore, Maryland, for the liberal supply of old radon bulbs that they placed at our disposal. The purification of the polonium was carried out at the National Bureau of Standards. Successful completion of the work was due in a large part to the cooperation of Dr. Hafstad, of the Department of Terrestrial Magnetism, Carnegie Institution of Washington.

[2] L. R. Hafstad, J. Frank. Inst. **221**, 191 (1936).

[3] I. Curie, J. chim. phys. **22**, 471 (1925).