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The Dissociation of H_2O into $H+OH$*

R. J. DWYER† AND O. OLDENBERG

Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts

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The energy of dissociation of H_2O into $H+OH$ was measured by an experiment developed from the method of Bonhoeffer and Reichardt. A spectrograph of high resolving power served for the measurement of the intensity of the absorption spectrum of OH in a heated mixture of water vapor and oxygen. The result (for $0°K$) was $H+OH \rightarrow H_2O - 118.2 \pm 0.7$ kcal. and $O+H \rightarrow OH - 100.1 \pm 0.9$ kcal. The probabilities of transition of the lines of the OH band were recomputed.

I. PROBLEM

THE energy of dissociation of H_2O molecules *into atoms* $H+H+O$ is known accurately. It is derived from the thermal measurement of the explosion $2H_2+O_2 \rightarrow 2H_2O$ and the spectroscopic investigation of the molecules H_2 and O_2. The energy of dissociation of H_2O *into H atoms and OH radicals*, or, closely connected with it, the energy of dissociation of free OH radicals, is much less accurately known. The importance of this latter dissociation process was first pointed out by Bonhoeffer and Reichardt.[1] They furnished the first determination of its energy by a method which basically still seems most reliable although it is subject to certain sources of error. Because of such errors, Gordon,[2] in his comprehensive treatment of dissociation energies, came to the con-

clusion that "unfortunately a reliable calculation of the hydroxyl dissociation is not possible at present because of the uncertainty as to the energy of dissociation."

In the measurement of Bonhoeffer and Reichardt there is a systematic error due to the lack of resolving power of the spectrograph. The absorption spectrum of free OH consists of rotational lines at irregular mutual distances, most of them widely separated from each other compared with the line width because of the small moment of inertia of OH (Fig. 1).[3] Consequently a spectrograph of small resolving power, as used by Bonhoeffer and Reichardt, which fails to resolve single lines but shows the whole band as a short, nearly continuous spectrum (see reproduction in reference 1), requires a relatively high concentration of OH. For a quantitative test by the absorption spectrum rather weak absorption is desired. But at this high concentration, although the *average* absorption observed with a spectrograph of poor resolving power may be weak, the *actual* absorption contains many lines each one of them at its middle almost completely absorbing the incident radiation; in this case the concentration of OH affects the total intensity transmitted only by the more or less extended wings of the lines. Therefore, the broadening of the lines is essential for the over-all absorption observed. In the method under discussion pairs of

[1] K. F. Bonhoeffer and H. Reichardt, Zeits. f. physik. Chemie **A139**, 75 (1928).

[2] A. R. Gordon, J. Chem. Phys. **1**, 308 (1933). The results of the various methods were recently surveyed by G. Damköhler and R. Edse, Naturwiss. **31**, 310 (1943).

[3] See O. Oldenberg, J. Chem. Phys. **3**, 270 (1935). The effect of the resolving power is discussed in J. Chem. Phys. **7**, 487 (1939).
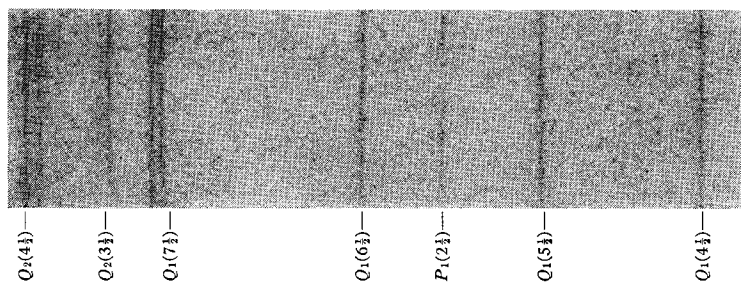
FIG. 1. Part of OH band 3064A (absorption, positive, 10 times enlarged).
For the reproduction a spectrum is selected with more intense absorption
lines than for the measurement.

absorption spectra are matched. The two members of such a pair, however, are subject to pressure broadening by widely different mixtures of O_2+H_2O (66.7 percent and 0.59 percent of H_2O, respectively) which may have different broadening effects. All that is known are the broadening effects on the mercury line 2537;[4] here H_2O has an effect stronger than O_2 by the factor 1.35. Therefore, two absorption spectra, taken at high concentration without resolving the lines, do not reliably indicate equal concentrations of OH by their equal intensities. Figure 1 shows that the single absorption lines are very narrow as compared with their mutual distances; this spectrum makes it evident that, for an accurate comparison of intensities, *single lines* should be observed rather than the *apparent continuum* produced by their broadening and lack of resolving power. It is not possible, however, to estimate the systematic error that may be caused by such a broadening. The ideal instrument would have a resolving power large as compared with the line width and so reveal the contours of the absorption lines.

As at this laboratory the absorption spectrum of free hydroxyl has been investigated with high resolving power for another purpose—the study of the kinetics of free hydroxyl—it seemed desirable to apply this technique to a more accurate measurement of the energy of dissociation of H_2O into H+OH, based on the work of Bonhoeffer and Reichardt. As will be shown in the survey of the different methods given in the following section, this method when carried out with a spectrograph of high resolving power gives the best prospect of high accuracy. This measurement is the subject of the present paper. The higher accuracy which is aimed at necessitates some other changes, in particular in the measurement of the temperature. A further improvement is due to the development of spectroscopic thermodynamics, which has taken place within

the last decade. Spectroscopy furnishes reliable data for the computation of the specific heats and the chemical constants of all molecules involved.

Apart from the chemical interest, this energy of dissociation enters into the measurement of the "*f* values" of OH radicals;[5] furthermore, it is of interest for the study of the solar atmosphere where Russell[6] found a discrepancy between the values of the abundance of OH estimated by different methods. This aspect will be discussed somewhere else.

II. PREVIOUS WORK

The work of Bonhoeffer and Reichardt,[1] which will be discussed in detail in Section III, gave the energy of dissociation of $H_2O \rightarrow H+OH$ as 115 kcal. with an estimated probable error of 2.5 kcal.; but this limit included only the *accidental* error, estimated by the conventional method, and did not take into account the *systematic* error pointed out in the preceding section.

Avramenko and Kondratjew[7] modified the method of Bonhoeffer and Reichardt by resolving the single lines of the OH band with a large Hilger quartz spectrograph. As a background they used the line spectrum from an electric discharge tube. They were forced to make rather arbitrary assumptions regarding the widths of their lines. Furthermore, they presupposed "weak absorption," although it may be difficult to decide whether weak absorption *observed with their inadequate resolving* power really indicates weak absorption *in the middle of the line*. Their

[4] C. Fuechtbauer, G. Joos, and O. Dinkelacker, Ann. d. Physik **71**, 220 (1923).

[5] O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 439 (1938).
[6] H. N. Russell, Astrophys. J. **79**, 325 (1934), Table III.
[7] L. Avramenko and V. Kondratjew, Acta Physicochimica **8**, 567 (1937). See O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 169 and 779 (1938).

accuracy was further impaired by a small temperature range (1200–1320°C). Their result for the energy, $H_2O \rightarrow H+OH-113.5$ kcal., was given without an estimate of the error, as this measurement was only incidental in an investigation largely concerned with other problems.

A different spectroscopic method was applied by Senftleben and his collaborators,[8] and by Wood and Gaviola.[9] In the most recent work of this group, Riechemeier, Senftleben, and Pastorff illuminated water vapor, to which a trace of mercury vapor was added, with the resonance line of mercury and so produced gaseous hydrogen. In accord with the work of Cario and Franck,[10] they assumed that the excited mercury atoms transferred their energy of 4.86 ev to the water molecules and so caused their dissociation into H+OH. This process requires slightly more energy than is available as excitation energy of the mercury atoms. Therefore, it can occur only at collisions with excess thermal energy. The authors measured the yield of H_2 as a function of the temperature and compared their results with the theoretical expression based on the Boltzmann formula. Thus for the energy of $H_2O \rightarrow H+OH$ they obtained 5.07 ± 0.04 ev or 117.0 ± 0.9 kcal. (For the excitation energy of Hg atoms, the authors applied 4.9 instead of 4.86 ev. For this reason we corrected their final result by -0.04 ev. $= -1$ kcal. However, their method is such that an additive correction is not strictly correct.)

Two objections to this argument may be raised. First, it is not certain whether the hydrogen is formed by the dissociation process just mentioned or, instead, by the intermediate formation of HgH molecules in the process $Hg'+H_2O \rightarrow HgH+OH$ followed by a reaction in which the rather unstable HgH molecules give off their H atoms. (The analogous formation of HgH is well established in the collisions of excited mercury atoms with hydrogen molecules.) This intermediate process would require less energy by the energy of formation of HgH ($=0.369$ ev). If such molecules are formed, the numerical result given above would be too low.

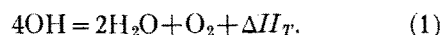The other objection is more fundamental in that it applies to all methods in which a *non-equilibrium* is observed. In this method it is presupposed that for any thermal collision taking place above the energy of dissociation the intrinsic probability of the reaction is the same. On this basis the temperature effect on the rate of the reaction is determined only by the Boltzmann factor. It is disregarded that the intrinsic probability of collisions of the second kind may gradually vary with the excess energy of the collisions. Conventionally such a variation is described by the "excitation function." This function is unknown. It should not affect the result of the equilibrium method; but if, for example, the intrinsic probability is *increasing* with increasing energy, the non-equilibrium method would yield *too large* a value for the limiting energy. It is true that, for the non-equilibrium method under discussion, the excitation function needs to be considered only for the narrow energy range of thermal motion. On the other hand, at least for *atomic* energy levels, the excitation functions are known to vary rapidly within a narrow range right above the limit.[11]

Finally, the energy of dissociation $H_2O \rightarrow H+OH$ has been determined by the explosion method.[12] The most recent and accurate experiment was performed by Lewis and von Elbe. This method is subject to many corrections.[13] Lewis and von Elbe derived the energy 114000 ±1000 kcal. for the same dissociation process.

The survey of various methods given here seems to indicate that the method of Bonhoeffer and Reichardt, when applied with a spectrograph of high resolving power, offers the best prospect for high accuracy.

III. THE EQUILIBRIUM 4OH⇌2H₂O+O₂

Following Bonhoeffer and Reichardt, we consider the thermal dissociation of H_2O vapor with excess O_2 added:[14]

$$4OH = 2H_2O + O_2 + \Delta H_T. \tag{1}$$

[8] O. Riechemeier, H. Senftleben, and H. Pastorff, Ann. d. Physik 19, 202 (1934).

[9] R. W. Wood and E. Gaviola, Phil. Mag. 6, 1191 (1928).

[10] G. Cario and J. Franck, Zeits. f. Physik 11, 161 (1922).

[11] W. Hanle, Zeits. f. Physik 54, 848 (1929); 56, 94 (1929); 65, 512 (1930).

[12] K. Wohl and M. Magat, Zeits. f. physik. Chemie B19, 117 (1932); B. Lewis and G. von Elbe, J. Chem. Phys. 3, 63 (1935).

[13] See A. Eucken, "Energie und Waermeinhalt," *Handbuch der Experimental-Physik* 8, Part 1, 369 (1929); K. Wohl and G. von Elbe, Zeits. f. physik. Chemie B5, 241 (1929).

[14] We follow the notation of S. Glasstone, *Textbook of Physical Chemistry* (D. Van Nostrand Company, Inc., New York, 1940).

From this energy ΔH_T, reduced to zero degrees, and certain other known energies, we shall derive the energy $\Delta U_0{}^0$ of the reaction we are interested in,

$$H + OH = H_2O + \Delta U_0{}^0. \qquad (2)$$

A. Theory

1. The Measurement of ΔH_T

As the underlying theory presented here largely follows the argument given by Bonhoeffer and Reichardt,[1] we shall omit the detail of the computations.

When we write the partial pressures of H_2O, O_2, and OH as x, y, and z, respectively, the equilibrium constant of reaction (1) is

$$K = x^2 y / z^4. \qquad (3)$$

While we can vary x and y at will, we want to determine z by the intensity of the absorption spectrum of OH. The experiments are carried out at constant pressure ($P = 775$ mm). We restrict ourselves to temperatures so low that the hydroxyl pressure z is very small as compared with x and y. We can vary at will the ratio of x to y at constant T and P; thus the partial pressure z of OH varies and reaches a maximum for $x = \frac{2}{3}P$ and $y = \frac{1}{3}P$, that is, for equal numbers of bound H atoms and O atoms. This is called the "optimum mixture."

ΔH_T is derived from the Van't Hoff isochore, which, when integrated between the temperatures T_1 and T_2, with the application of Eq. (3), leads to Eq. (4):

$$\Delta H_T = [4RT_1T_2 \ln (z_2/z_1)]/(T_1 - T_2). \qquad (4)$$

In this integration we assume that ΔH_T does not vary between T_1 and T_2; this will be checked later. (Subscript 1 indicates the higher and 2 the lower temperature.)

The most satisfactory application of absorption spectra consists of matching two absorption lines of *equal intensity* and so testing the two absorbing mixtures for *equal density* of the absorbing molecules. In order to apply this method to two gas mixtures at different temperatures Bonhoeffer and Reichardt[1] reduced the partial pressure of OH at the higher temperature T_1 by adding more oxygen and so changing the mixture from its optimum composition, at constant total pressure

P. Thus they reduced the OH partial pressure to such a value z_1' that, in spite of the high temperature T_1, the absorption spectrum was only as intense as that of the optimum mixture at the low temperature. The ratio z_1'/z_1 follows from the mass action law:

$$z_1'/z_1 = \{[27x_1'^2(P - x_1')]/4P^3\}^{\frac{1}{2}}. \qquad (5)$$

The partial pressure x_1' of the water vapor is at our disposal, the total pressure P being constant. (The prime indicates the equilibrium shifted by the excess of oxygen, while letters without a prime indicate optimum mixtures; hence $x_1 = 2P/3$.)

By matching absorption lines we identify a pair of mixtures with equal *density* of OH. Hence this experiment, in which two mixtures are compared at different temperatures, gives the following evidence regarding *partial pressures:*

$$z_1'/z_2 = T_1/T_2. \qquad (6)$$

In order to apply Eq. (4) we wish to know z_2/z_1. This follows by dividing the last two equations. Introducing the result into (4) we obtain:

$$\Delta H_T = \frac{4RT_1T_2 \ln \left(\dfrac{z_1'}{z_1} \times \dfrac{T_2}{T_1} \right)}{T_1 - T_2}. \qquad (7)$$

This theory leads to the following procedure: Select the total pressure P a little higher than one atmosphere so that inside the chamber there is always a slight excess pressure. Select T_2 as the minimum temperature at which, with the optimum mixture, the absorption spectrum of OH is still observable. Select an arbitrary value of x_1' considerably smaller than the optimum value of $\frac{2}{3}P$. Next determine the corresponding temperature T_1, defined as the temperature of equal intensities of absorption lines; experimentally this temperature is found by taking absorption spectra at various temperatures. For the highest accuracy, a value of x_1' must be determined by trial and error so that the temperature T_1 is as high as can be reached with the oven. (Our present knowledge of ΔH_T may serve for predicting a reasonably good value of x_1', once T_1 is given as the highest temperature to be reached.) These are the temperatures and pressures which must be introduced into the above equation (7).

2. Corrections

Errors may be caused by (a) the non-uniform temperature distribution, (b) the difference in the Boltzmann distributions between the two temperatures, and, finally, (c) the variation of ΔH_T over the temperature range $T_1 - T_2$.

(a). Introducing $z_2/z_1 = (z_1'/z_1)(T_2/T_1)$ into Eq. (5) involves an error in that a uniform temperature over the length of the oven is presupposed. For non-uniform temperature equal absorption lines indicate that the integrals of the densities of OH, taken over the length of the tube, are the same for both absorbing mixtures. For this case Bonhoeffer and Reichardt, who used a graphite tube resistance furnace along which the temperature could not be equalized, applied a method of successive approximations.

The first application of their method to our experiment resulted in a very small correction for ΔH_T, less than 0.3 percent. The constancy of the temperature along the oven was responsible for this favorable result. Another procedure to simplify the labor required in the calculation of the other plates immediately suggested itself. As the correction was so small, much smaller than the probable error estimated below, and as all plates were taken at nearly the same two temperatures, it may be assumed that the same correction applies to all plates. Consequently, Eq. (7) may be written in the corrected form

$$\Delta H_T = \frac{4RT_1T_2 \cdot \ln \left(\dfrac{Cz_1'}{z_1} \right)\left(\dfrac{T_2}{T_1} \right)}{T_1 - T_2}.$$

The correction factor C, taken from the first plate, was 0.993.

(b). In the theoretical discussion (Section III, A1) we assumed that *equal intensities of absorption lines indicate equal densities of the absorbing gas.* As we were observing single absorption lines, unlike Bonhoeffer and Reichardt, this statement applied to the density not of OH, but only of the rotational level responsible for the absorption line under observation. From the energy levels (electronic, vibrational, and rotational) the populations of the various rotational levels (zero vibration, electronic level $^2\Pi_{1i}$) which absorb the Q_1 branch were computed for $T_1 = 1360°K$ and

$T_2 = 1176°K$. As stated in a preceding paper,[3] the line $Q_1(6\frac{1}{2})$ served best, because it is near the intensity maximum and has only a weak satellite.

As will be described below, the matching was not so accurate that for one pair matched other pairs could be observed as non-matched, that is, the difference between the thermal distributions at 1176°K and 1360°K could not be noticed. As the procedure involves no preference for one or the other spectrum, no *systematic* error is to be expected. The spread of results (Table I) is due to *accidental* errors in the matching of absorption lines.

(c). At the integration of the Van't Hoff isochore we put ΔH_T in front of the integral and so assumed its constancy between T_1 and T_2. The change in ΔH as a function of temperature is expressed by Kirchhoff's formula,

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_p dt.$$

The value of ΔC_p for the reaction of Eq. (1) is

$$\Delta C_p = 2C_{H_2O} + C_{O_2} - 4C_{OH}.$$

These specific heats (all taken at constant pressure) have been calculated from spectroscopic data and published for O_2 by Johnston and Walker,[15] for OH by Johnston and Dawson,[16] and for H_2O by Gordon.[17] Gordon's calculations assumed a rigid molecule, so the correction formula for rotational distortion given by Wilson[18] was applied, using the correction term obtained by Stephenson and McMahon.[19] In this manner it was calculated that the value of ΔH changed only 130 calories per mole between 900°C and 1100°C, the range of temperatures used in the experiment. As this is less than 0.1 percent of the total value, the assumption of constant ΔH in the integration was clearly justified.

3. Reduction to Standard Pressure and Temperature

While we measured the energy ΔH_T at 775 mm pressure, we want to determine the energy $\Delta H_T{}^0$

[15] H. L. Johnston and M. K. Walker, J. Am. Chem. Soc. 55, 172 (1933).
[16] H. L. Johnston and D. H. Dawson, J. Am. Chem. Soc. 55, 2744 (1933).
[17] A. R. Gordon, J. Chem. Phys. 2, 64 and 549 (1934).
[18] E. B. Wilson, J. Chem. Phys. 4, 528 (1936).
[19] C. C. Stephenson and H. O. McMahon, J. Chem. Phys. 7, 614 (1939).

at the standard pressure of 760 mm. Both energies are equal.[20]

Finally, the reduction to zero temperature is to be carried out with the formulas and tables of spectroscopic thermodynamics as follows. The entropy S and the free energy function $-(G^0 - U_0^0)/T$ have been tabulated[21] as functions of the temperature for all molecules involved. Surveys of this field have recently been given by Wilson and by Zeise.[22]

The entropies and free energies were obtained from the tables of Johnston and Dawson[16] on OH, Johnston and Walker[15] on O_2, and Gordon[17] on H_2O. As in the case of specific heats, Gordon's values were corrected for rotational distortion by Wilson's[18] formula using the correction constant of Stephenson and McMahon.[19]

The heat of reaction at absolute zero ΔU_0^0 is[23]

$$\Delta U_0^0 = \Delta H_T^0 - T\Delta S_T^0 + T\Delta\left(-\frac{G_T^0 - U_0^0}{T}\right). \quad (8)$$

In this equation ΔH_T^0 is taken from our measurements and the other quantities from tables.

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[20] See S. Glasstone, reference 14, p. 230, Eq. (149), applied to the ideal gas law.

[21] The formulas are given by S. Glasstone, reference 14, for the entropy S on p. 865, Eq. (179); for the free energy function $(G^0 - U_0^0)/T$ on p. 865, Eq. (180).

[22] E. B. Wilson, Chem. Rev. 27, 17 (1940). H. Zeise, Zeits. f. Electrochemie 43, 704 (1937); 48, 425, 476, and 693 (1942).

[23] S. Glasstone, reference 14, p. 866, Eq. (182).

B. Experimental Procedure

1. The Oven and the Measurement of the Temperature

The oven (Fig. 2) consisted of a ceramic tube (length 5 feet, o.d. 6 cm), wound with Nichrome V ribbon, thermally insulated to about 3'' from the ends. In order to equalize the temperature over as long a section as possible, the heater winding was provided with nine taps, in addition to the free ends. The end sections from which the dissipation of heat was greatest carried the full current; toward the middle of the oven the current was adjusted to smaller values by shunts. With this arrangement it was possible to equalize the temperature to within 2°C over a central portion 85 cm in length. It then dropped off rapidly toward the ends.

The oven was provided with a thermostat which was built by Dr. H. S. Sommers, Jr., following the design given by Bancroft.[24] A thin platinum wire, embedded in the oven, formed one branch of a Wheatstone bridge. By its change of resistance it operated a thyratron which, in turn, regulated the heating current. This regulator is capable of holding the temperature of the oven constant to a fraction of a degree.

The temperature distribution along the oven was measured by a platinum, platinum-rhodium

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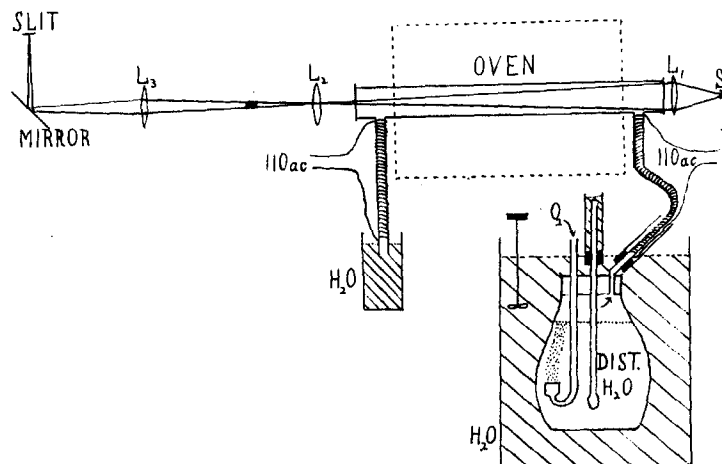[24] D. Bancroft, Rev. Sci. Inst. 13, 24 and 114 (1942).

Fig. 2. Experimental arrangement for the measurement of the absorption spectrum of heated water vapor.

thermocouple. Within the oven the thermocouple was protected by a long, narrow quartz tube.

Considerable trouble was experienced because of the deterioration of the quartz tube in the heated mixture of H_2O and O_2. After some weeks of heating the quartz turned brittle. As soon as a leak developed, the thermocouple was exposed to the vapors and so deteriorated. For the final measurements a new quartz tube was used, also a new thermocouple which was exposed to the high temperature for as short periods as possible; its wires were insulated from each other by a thin quartz tube since the Alundum tube used in the first experiments seemed to affect the wire. Moreover, insulating by means of a thin quartz tube is advantageous because of its small thermal inertia.

One end of this tube inside the oven was closed and so prevented direct contact of the thermocouple with the water vapor; the other end was sealed through one of the quartz windows and was open so that the thermocouple could slide in and out. The thermoelectric force was measured by a potentiometer against a standard cell which, in turn, was calibrated against another cell recently checked by the Bureau of Standards.

The thermocouple wires were checked for homogeneity[25] at intervals during the progress of the experiment. At no time did they develop electromotive forces sufficient to cause errors of over half a degree at the highest temperatures used. The thermocouple was calibrated against the melting point of pure gold.

For the accuracy of the method, the ease with which the temperature can be adjusted and measured is of importance. Here again the high resolving power of the grating is responsible for a marked improvement in the method. The reason is that it brings down the highest temperature applied from 1590° to 1100°C. Here the temperature of the oven can more easily be measured and kept constant over its length.

2. The Mixtures of Water Vapor and Oxygen

In order to be independent of the daily variations of the atmospheric pressure, we maintained a constant pressure of $P = 775$ mm, slightly above the ordinary pressure. This pressure was easily kept constant by adjusting the height of the water level (Fig. 2) through which the mixture

[25] W. F. Roeser and H. T. Wensel, National Bureau of Standards, Research Paper RP768 (March, 1935).

bubbled at the outlet side of the large tube. With this arrangement, minor leaks could not disturb the content of the tube, any leakage being from inside to outside.

The *optimum mixture* of H_2O and O_2 was produced by the apparatus shown in Fig. 2. The water vapor pressure had to be $\frac{2}{3}P = 516\frac{2}{3}$ mm. This was produced by bubbling oxygen in very small bubbles through distilled water of 89.53°C. The temperature of the distilled water was kept constant by a water bath, permanently stirred, the temperature of which was controlled through a mercury thermostat. The temperature of the distilled water was measured by a mercury thermometer calibrated against a standard thermometer which, in turn, was calibrated by the Bureau of Standards. It was possible to estimate to 0.01°C. (In order to apply the proper correction, the temperature of the stem was kept constant by a coaxial tube containing water, a stirrer, and another small thermometer.) The principal difficulty in maintaining the temperature of the distilled water constant was in maintaining the rate of flow of the oxygen constant, a precaution necessary because of the cooling by evaporation. Therefore a standard rate of flow was maintained by observing the rate of bubbling at the exit jar. Experiment showed that this was proportional to the rate of flow. The rate corresponded to a velocity of approximately 0.23 cm/sec. through the tube, or 16 liters/hour for the mixture. The temperature of the distilled water was constant within 0.04°. In order to prevent condensation of the water vapor, every part of the system was maintained at a temperature higher than that of the bath in which the mixture was formed.

The flowing mixture had a measurable effect on the end of the oven it entered first, so the shunting resistors were adjusted to equalize this temperature while the mixture was flowing at the standard rate. In order to check the apparatus, the resulting mixture was analyzed and found satisfactory.

The *non-optimum mixture* should deviate strongly from the optimum mixture which had a water vapor pressure of $516\frac{2}{3}$ mm. We chose the water vapor pressure at 0°C, that is $x_1' = 4.58$ mm. As found by trial and error, this mixture needed a temperature well within the reach of a

Nichrome wound oven (around 1100°C) in order to produce the same intensity of absorption lines as the optimum mixture at 900°C. This partial pressure of water vapor was produced by bubbling oxygen of slightly more than 1 atmos. through two successive deep vessels containing water of 0°C, the temperature of which was kept constant with an ice bath.

This choice of x_1' leads to the ratio of the two OH partial pressures, non-optimum and optimum, z_1'/z_1 by Eq. (5).

$$\log (z_1'/z_1) = -0.9066.$$

3. The Optical Arrangement

The OH absorption band at 3064A was observed in the second order of a 21-foot concave grating. In order to increase the intensity, the grating was covered with a thin coating of aluminum evaporated in vacuum.[26] The grating at our disposal, ruled by Rowland, had nearly the theoretical resolving power, which was not impaired by the aluminum plating. At the spectral range near 3000A this resolving power was 0.015A. It permitted a wide separation of the single lines of the absorption band (Fig. 1). It almost permitted a resolution of the contour of each single absorption line, its width being 0.054A. These figures show that the apparatus nearly reached the ideal case of a resolving power high as compared with the width of the absorption line.

A hydrogen discharge tube, constructed by N. D. Smith,[27] furnished the continuous background. Eastman Spectroscopic Plates III-O were used as the best compromise between resolution and exposure time, which was 30 min.

First one exposure of the OH absorption spectrum was taken with the optimum mixture and the temperature near 900°C, then a series of six or seven was taken with the non-optimum mixture causing the oven temperature to vary in steps of five to ten degrees. After the development the plate was split, the 900° exposure being separated from the series taken around 1100°. The object then was to match one of this series with the exposure at 900°C.

We agree with Bonhoeffer and Reichardt in that the eye is well able to match absorption spectra, so that the densitometer does not improve the results. For the visual matching of absorption lines rather low intensities of absorption turned out to be useful. The order of magnitude was 8 percent absorption at the middle of the lines. For such lines densitometer traces are less satisfactory because the grain is prominent. Two plates were matched by placing them so that the lines on one plate appeared to run into the same lines on the other plate. Where the backgrounds of the two plates were equal, it was convenient to match the lines under a binocular microscope possessing a broad field of view which permitted the entire spectrum on the plates to be seen as a whole. Where the backgrounds were slightly different, it was better to match the lines with a special comparator,[28] with which background variations could be compensated. In general, if one line on one plate was stronger than the same line on the other plate, one could observe that all lines on the one were stronger than the same lines on the other. This indicated that the variation with rotational distribution between the temperatures of 900° and 1100°C was not noticeable; so no correction for this was made.

C. Results

The lowest temperature at which the absorption spectrum of free OH showed up clearly was 768°C. Incidentally, this figure indicates how much more sensitive the test for free OH is with the large grating spectrograph than with the medium-size quartz spectrograph used by Bonhoeffer and Reichardt,[1] who report barely observable absorption at 1150°C. Computed for absorption tubes of equal length, the sensitivity is increased by the factor 45.

The main experimental problem consisted of finding the high temperature T_1 at which the non-optimum mixture (water vapor pressure $x_1' = 4.58$ mm) produced as intense absorption lines as the optimum mixture ($x_2 = 516.7$ mm) at the low temperature T_2. Because of the even temperature distribution along the oven, it was possible to let

[26] We appreciate the help and advice of Mr. John Gilroy who allowed us to use his vacuum evaporation apparatus.
[27] N. D. Smith, J. Opt. Soc. Am. **28**, 40 (1938).

[28] A. A. Frost, D. W. Mann, and O. Oldenberg, J. Opt. Soc. Am. **27**, 147 (1937).

T_1 and T_2 represent the average value of the temperature over a length of 88 cm in the middle portion (see Section III, A2).

Table I gives the results of eight plates. Some other plates had to be discarded because the intensities of either the background or the absorption spectrum turned out to be unfavorable for the photometric comparison.

The formula for the "probable error of the mean" applied to Table I leads to a value of less than 1 kcal. Considering the difficulty of the photometric work, we prefer to give ±2.6 kcal. as what seems to us a liberal estimate of this probable error. This leads to the result for an average temperature of 1250°K:

$$\Delta H_T = 157.5 \pm 2.6 \text{ kcal.}$$

As discussed above (Section III, A2), ΔH_T is practically constant over the whole range of

TABLE I. Survey of results.

Plate No.	T_1 (deg. K)	T_2 (deg. K)	$-\Delta H_T$ (kcal.)	Weight
1	1379	1194	158	$\frac{1}{2}$
2	1371	1188	158	$\frac{1}{2}$
3	1361	1178	156	1
4	1340	1166	159	1
5	1346	1166	155	1
6	1319	1145	154	$\frac{1}{2}$
7	1339	1160	154	1
8	1366	1191	165	1
			average 157.5	

temperatures applied. Hence the reduction to zero temperature by Eq. (8) can be applied to this average value. The result for $T=0°$K is $\Delta U_0^0 = -153.4$ kcal. or

$$4OH = 2H_2O + O_2 - 153.4 \pm 2.6 \text{ kcal.}$$
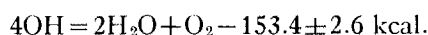
The only source of a *systematic* error which we know of is the lack of resolving power of the spectrograph, as even the large grating at our disposal does not permit a reliable measurement of the complete contours of the absorption lines. In a previous investigation[5] it was found that the widths of these lines are due only one-third to Doppler effect, the other two-thirds representing pressure broadening. Here the lines are observed at a pressure of nearly one atmosphere, this pressure being composed in one experiment of $\frac{2}{3}H_2O + \frac{1}{3}O_2$, and in the other experiment, of

$0.006H_2O + 0.994O_2$. This gives a chance for comparison of the broadening effects of the molecules H_2O and O_2 on the absorption lines of OH. A difference in the widths of the absorption lines is barely noticeable, H_2O causing a broadening just slightly stronger than O_2.[29] The difference is so small that at first it was overlooked. It can hardly affect the comparison to a considerable extent.

IV. THE EQUILIBRIUM H₂+2OH⇌2H₂O

A. The Energy H+OH→H₂O

As an intermediate step, we compute the energy of $H_2 + 2OH \rightarrow 2H_2O(g)$ which will be needed in the following section. To the result of the experiments reported, we add the equation for the combustion of molecular hydrogen[30] forming water vapor, which is known from thermochemistry with higher accuracy. The result is

$$H_2 + 2OH = 2H_2O(g) - 133.8 \pm 1.3 \text{ kcal.}$$
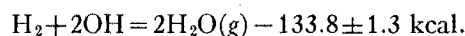
Beutler[31] calculated the energy of dissociation of hydrogen molecules (normal mixture of ortho and para) from spectroscopic data as 102.48 ± 0.03 kcal. This leads to the energy of dissociation we are mainly interested in,

$$H + OH = H_2O(g) - 118.2 \pm 0.7 \text{ kcal.}$$
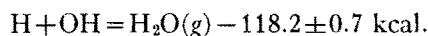
This result agrees, within the limit of error, with the less accurate result of Bonhoeffer and Reichardt,[1] which (applying the more recent value of the energy of dissociation of H_2) is 115.3 ± 2.5 kcal. Furthermore, the result agrees with the result of Senftleben and collaborators[8] (5.07 ± 0.04 ev $= 117.0 \pm 0.9$ kcal.). However, as discussed in Section II, we hesitate to consider this agreement as a confirmation, since their non-equilibrium method is subject to two sources of systematic errors. We are not sure whether the accuracies warrant more detailed conclusions regarding the possible processes involved.

Our value is larger than the upper limit which Damköhler and Edse[2] derived from the work of

[29] The mercury line 2537 is broadened by H_2O more strongly than by O_2; see reference 4.
[30] A. R. Gordon, J. Chem. Phys. 1, 310 (1933). This value is not appreciably affected by Wilson's correction for the stretching of the rotating molecule. The probable error is negligible as compared with the error of our measurements.
[31] H. Beutler, Zeits. f. physik. Chemie B29, 315 (1935).

Sharma.[32] We do not believe, however, that it is safe to derive quantitative conclusions from Sharma's experiment. In the ultraviolet absorption spectrum of H_2O_2 he observed a continuous band with an abrupt high frequency limit at 2055A. He attributed this limit to the dissociation process $H_2O_2 + h\nu \rightarrow H + H + O_2$ and computed the energy required for this dissociation from the wave-length. This interpretation may be questioned. From the investigation of diatomic molecules it is known that a dissociation process becomes evident, not by a sharp limit of the absorption spectrum, but rather by a transition from a discrete to a continuous spectrum. The reason is that the probabilities of transition (explained by the Franck-Condon principle) do not abruptly vary when, by increasing frequency of light, the final state of the absorption process changes from high vibration to dissociation.[33] It seems hardly possible to invent potential curves for the normal and excited states such that

FIG. 3. The equilibrium constants K_{OH} and K_{O_2} as functions of the temperature.

dissociation is connected with a sharp *high frequency* limit of a *continuous* spectrum.

The energy of formation of H_2O from the atoms is 218.3 ± 0.2 kcal. Together with the last equation this leads to the energy

$$O + H = OH - 100.1 \pm 0.9 \text{ kcal.}$$
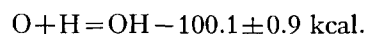
These energy values apply for 0°K. For higher temperatures, the energies can be computed with the help of the tables referred to in Sections III and IV.

B. The Equilibrium Constant

We are interested in the thermal dissociation of H_2O, without the addition of O_2 which, in the experiments reported, was added for technical reasons. The equilibrium in water vapor is given by

$$H_2 + 2OH = 2H_2O(g) - 133.8(\pm 1.3) \text{ kcal.}$$
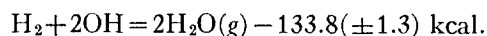
The equilibrium constant K_p which applies to this equilibrium is

$$K_{OH} = [H_2O]^2 / [H_2] \times [OH]^2.$$

Its numerical value is derived from the equation (see Section III, A3):

$$\log_{10} K_{OH} = T\Delta\left(-\frac{G^0 - U_0^0}{T}\right) \cdot \frac{0.434}{RT} - \Delta U_0^0 \frac{0.434}{RT}.$$

Tables for the free energy functions $-(G^0 - U_0^0)/T$ have been computed for all molecules involved on the basis of data derived from molecular spectra.[34] The resulting values of K_{OH}, extended up to 3000°K, are given in Table II and Fig. 3.[35]

The accuracy of $\log_{10} K_{OH}$ depends upon the accuracy with which the energy ΔU_0^0, determined in the present paper, and the free energy function $-(G^0 - U_0^0)/T$ are known. The papers referred to above give estimates of the accuracy of the free energy functions.
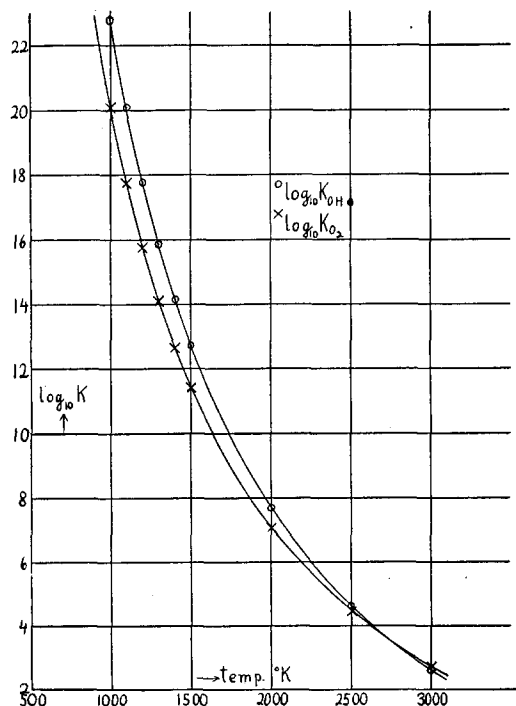
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[32] R. S. Sharma, Proc. Ind. Acad. Sci. **4**, 51 (1934).
[33] See G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 409.

[34] The thermodynamic functions for H_2 were obtained from Giauque's table [J. Am. Chem. Soc. **52**, 4821 (1930)] of the free energy function and Davis and Johnston's table [J. Am. Chem. Soc. **56**, 1045 (1934)] of entropies. All the tables used in the present calculation excluded the nuclear contribution except Giauque's table for the free energy function; so in order to use it with the others his values were all reduced by 2.775, the amount he gives as the nuclear contribution.
[35] Zeise computed values of K_{OH} [Zeits. f. Electrochemie **48**, 23 (1942)] on the basis of our preliminary publication of the energy of dissociation [Phys. Rev. **59**, 928 (1941)].

These values of K_{OH} are larger than the ones derived by Bonhoeffer and Reichardt, indicating less hydroxyl dissociation. The values are only slightly beyond the limit estimated by these authors. In order to compare the *"hydroxyl dissociation"* with the well-known *"oxygen dissociation"* of water vapor

$$2H_2+O_2 \rightleftharpoons 2H_2O \quad (K_{O_2} = [H_2O]^2/[H_2]^2[O_2]),$$
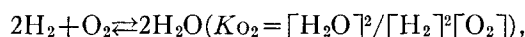
the values of K_{O_2} are given in the same table and graph. K_{O_2} is smaller than K_{OH} up to about 2600°K where the two curves intersect. This means that below this limit the dissociation into hydroxyl is less than that into oxygen, but above this limit the hydroxyl dissociation prevails.

V. PROBABILITIES OF TRANSITION

In the measurement of the probabilities of transition (*"f values"*) of the various OH lines given by O. Oldenberg and F. F. Rieke,[5] the greatest uncertainty was caused by the computation of the equilibrium. The present results permit a more accurate computation. It leads to the conclusion that the f values published (Table II of reference 5) must be multiplied by 4.2.

From the comparison with related reactions known from thermochemistry or band spectra (see Section IV, A), it is evident that their energies are known with higher accuracy. Considering the importance of the H₂O molecule, a more accurate determination would be desirable. But it is difficult to suggest improvements in the

TABLE II. Equilibrium constants K_{OH} and K_{O_2}.

$T°K$	$\log_{10} K_{OH}$	$\log_{10} K_{O_2}$
400	67.62	58.53
600	42.81	37.30
800	30.35	26.60
1000	22.80	20.14
1100	20.07	17.79
1200	17.78	15.82
1300	15.85	14.15
1400	14.18	12.71
1500	12.74	11.46
2000	7.69	7.10
2500	4.66	4.47
3000	2.63	2.71

complicated method. The largest error comes from the matching of absorption lines. Therefore the results would be improved by the application of a still more powerful spectrograph which would give evidence of the contour of each single absorption line and make the application of the densitometer more reliable. Unfortunately, Fabry-Pérot plates are not well applicable to absorption spectra because they require a background continuous over the width of the absorption line, yet narrow enough so that adjacent orders of interference do not overlap.[3] As the second order of the 21-foot grating is not far below the requirements, a larger concave grating (35-foot) may be expected to help; but it would necessitate a more intense source of a continuous background.