Kinetics of OH Radicals as Determined by Their Absorption Spectrum III. A Quantitative Test for Free OH; Probabilities of Transition

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Kinetics of OH Radicals as Determined by Their Absorption Spectrum

III. A Quantitative Test for Free OH; Probabilities of Transition

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(1) In order to make the OH absorption bands applicable to a *quantitative* chemical test for free OH their probability of transition (f value) was measured by the concentration of "dispersion electrons" in a known concentration of OH. (2) This concentration of OH is produced by water vapor dissociated at 1473°C, the equilibrium of which was computed. (3) The concentration of the "dispersion electrons" was measured by photometry of the absorption lines photographed with high resolving power. (4) The f values of the various absorption lines are given in a table. The most intense lines have f values of the order of magnitude 2×10^{-4}. The accuracy is estimated to be 15 percent, the sensitivity (smallest detectable pressure under the conditions of the present experiment) 0.01 mm. (5) Comparison with other f values leads to the conclusion that the OH absorption band belongs to a half-forbidden transition. The lifetime of the excited state is computed as approximately 4×10^{-6} sec.

I. Problem

IN preceding papers[2–6] the absorption spectrum was applied as a chemical test for free hydroxyl radicals in gases. The purpose was to investigate some phases of the kinetics of the hydrogen-oxygen reaction, in particular to trace the progress of a fast reaction by snapshots. First, a *qualitative* test for OH was made in low pressure H_2O vapor, after interrupting an electric discharge which is known to dissociate H_2O into H and OH. The next step was a *quantitative* test in the *relative* sense in which the rotational lines, on the basis of the known thermal distribution of rotation, served as "concentration marks" to indicate the relative values of the hydroxyl concentration. This test was carried through by Frost and Oldenberg for various values of pressure. The result was that the rate of disappearance of OH increases with pressure and one infers that triple collisions are required for the reaction by which OH is consumed. In order to measure the rate constant of this reaction a *quantitative* test in the *absolute* sense had to be carried through. For this purpose the observed absorption spectrum of OH had to be calibrated against a known value of OH concentration which can be produced only by thermal dissociation of H_2O vapor into H+OH. This equilibrium was discovered and measured at temperatures between 1260 and 1590°C by Bonhoeffer and Reichardt.[7] For the purpose of this calibration, in the present paper, the *absolute* intensities of the absorption lines of OH, in thermally dissociated water vapor, are investigated by photographic photometry, and from these measurements their transition probabilities are computed or, in the conventional expression, their "f values" are determined.

Apart from the importance of the f value as leading to a quantitative test for free hydroxyl, such an investigation is of interest from the purely spectroscopic point of view. Although f values have been determined for many *atomic* absorption lines, very little is known about the f values of *molecules* (see Section VIa).

These f values apply also to problems of the solar spectrum. The presence of molecules in the

[1] The experiments reported in this paper were performed in 1936 (J. Phys. Chem. **41**, 293 (1937); Phys. Rev. **51**, 381 (1937)). The detailed computation was postponed in order to apply more accurate values of the equilibrium constants. In the meantime such values have been published by H. Zeise, Zeits. f. Electrochem. **43**, 704 (1937) and are applied in the present paper. For help in the preparation of the experiments reported here, we wish to express our appreciation to Dr. Martin Grabau.

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

[3] A. A. Frost and O. Oldenberg, J. Chem. Phys. **4**, 642 (1936).

[4] A. A. Frost and O. Oldenberg, J. Chem. Phys. **4**, 781 (1936).

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

[6] O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 169 (1938).

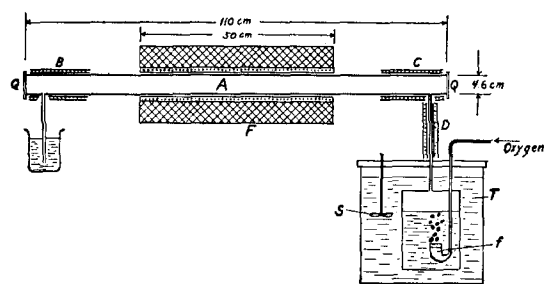[7] K. F. Bonhoeffer and H. Reichardt, Zeits. f. physik. Chemie **A139**, 75 (1928).

FIG. 1. Absorption experiment. A, absorption tube; F, high temperature furnace; B, C, D, auxiliary furnaces to prevent condensation; Q, quartz plates; T, constant temperature both; S, stirrer; f, porous filter.

solar atmosphere has been discussed by Russell[8] on the basis of their absorption bands. Russell based his estimates of concentration on the picture of an atmosphere of mean temperature and pressure for which he computed the thermal equilibrium. It is expected that the f values reported here will make possible a far more direct determination of the total concentration of OH in the solar atmosphere.

. Finally, these f values are of interest because they yield a value for the lifetime of the excited state of OH. In preceding papers *collisions during the lifetime* were discussed as explaining the intensity distribution of OH bands excited in an electric discharge through H_2O with various amounts of He added. The value of the lifetime determined here leads to an estimate of the efficiency of such collisions (Section VIb).

The OH bands, in spite of their complicated structure of twelve branches, are suitable for an investigation of their intensities since, on the basis of the theory of Hill and Van Vleck,[9] the intensity relations between the various branches are well known.

The probability of transition, that is, the "f value," is a constant characteristic for each single line. It is determined as the number per cc of "dispersion electrons" (derived from the intensity of the absorption line) divided by the number of OH radicals able to absorb this individual line (derived from the thermal equilibrium). The determination of these two quantities will be discussed in the following sections.

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[8] H. N. Russell, Astrophys. J. **79**, 317 (1934).

[9] E. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928). The general formulae have been adapted to the special case of OH by L. T. Earls, Phys. Rev. **48**, 423 (1935).

II. CONCENTRATION OF THE INITIAL STATE OF ABSORPTION

(a) Experiment

As discovered by Bonhoeffer and Reichardt, water vapor is thermally dissociated—in addition to the well-known process $2H_2O \rightleftarrows 2H_2 + O_2$ (equilibrium constant $K(O_2)$)—by the process $2H_2O \rightleftarrows H_2 + 2OH$ (equilibrium constant K_{OH}), both equilibrium constants being of the same order of magnitude.

In order to make the absorption spectrum of OH observable with a medium-size quartz spectrograph, Bonhoeffer and Reichardt produced a comparatively high degree of dissociation by a temperature as high as 1590°C. Our purpose has been to investigate smaller concentrations of OH in electric discharges with an instrument of higher sensitivity, that is, to observe individual absorption lines with a spectrograph of far higher resolving power. Hence for the calibration a lower temperature was sufficient to dissociate the water vapor partially.

The absorption tube, A (Fig. 1), 110 cm long and 4.6 cm wide, made of "Pythagoras composition" was used.[10] Short glass tubes with side tubes for inlet and outlet and with plane flanges were cemented on the ends. Plane quartz windows, Q, were pressed against the flanges by springs. It was not necessary to make them vacuum tight since the vapor in the tube had a slight excess pressure. A furnace, F, 50 cm long, wound with Nichrome V wire, covered the middle section of the tube. This oven could be heated without difficulty for many hours to 1200°C. The temperature distribution along the axis of the oven was measured with a Pt/Pt-Rh thermocouple, calibrated against the melting point of Cu. The Cu sample was furnished by the National Bureau of Standards.

Since pure water vapor under the conditions described gives only weak absorption lines, the mixture $\frac{2}{3}H_2O + \frac{1}{3}O_2$ was applied; this mixture, containing equal numbers of H and O atoms, gives a maximum concentration of OH. The mixture was prepared largely as described by Bonhoeffer and Reichardt. In order to secure saturation of the oxygen, bubbling through

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[10] Manufactured by W. Haldenwanger, Spandau, Germany.

water at 89°C, very small bubbles were produced by passing the oxygen through a fine porous filter, F. The resulting mixture, after passing through the absorption tube, was analyzed. One can easily derive from the mass action law that the composition of the mixture is not critical since the dissociation yielded by the mixture described represents a maximum.

(b) Computation

(α) *Pressure of OH.*—The total pressure of the mixture studied must be one atmosphere, for technical reasons. For a given total pressure the maximum value of p_{OH} occurs, according to Bonhoeffer and Reichardt, when $p(H_2O) = 2p(O_2)$. Since the degree of dissociation is very small at the temperatures used in our experiments, the pressure $p(O_2) = \frac{1}{3}$ atmos. and $p(H_2O) = \frac{2}{3}$ atmos. can be considered as constant. Then p_{OH} follows from

$$\frac{K_{OH}^2}{K(O_2)} = \frac{27}{4} \cdot \frac{p_{OH}^4}{(1-p_{OH})^3},$$

where $K(O_2)$ and K_{OH} are functions of the temperature (p_{OH} in atmos.). In our case p_{OH} is so small (1/2000 atmos.) that in the denominator p_{OH} is negligible as compared to 1.

While the values of $K(O_2)$ as a function of temperature are well known, the values of K_{OH} are less certain, largely because the energy of dissociation of H_2O into $H+OH$ is not known with sufficient accuracy.[11] We applied the most recent values published by Zeise[12] which do not differ much from the results of Bonhoeffer and Reichardt.

The temperature distribution along the axis of the furnace was determined with the thermocouple, the corresponding distribution of p_{OH} was computed and, by graphical integration, an equivalent value of $p_{OH} = 0.35$ mm was determined, which, over a tube length of 44 cm would represent the same absorbing layer. The number of OH per cc follows from the kinetic theory.

(β) *Population of the individual initial states.*—The energy levels of OH were computed from the band spectrum as analyzed by Fortrat[13] on the basis of the energy level diagram for $^2\Sigma - \Pi^2$ bands. The rotational terms of the lowest electronic term are given in Table I, neglecting Λ type doubling, which is only of the order of magnitude of a few cm^{-1}. By the Boltzmann formula the thermal distribution was determined over both electronic levels $^2\Pi_i$ and $^2\Pi_{1i}$, the various rotational levels, and the vibrational levels $v=0$ and $v=1$. (The term $v=1$ (3568 cm^{-1}) contributed only three percent and $v=2$ was negligible.) The Λ type doubling is so small as compared to kT that, for the computation of the thermal distribution it can first be neglected and finally taken into account by assuming that all levels split into doublets of equal statistical weight. (In this computation of the thermal equilibrium it was assumed that no more low electronic levels exist which may be unknown, since they fail to emit bands in the easily accessible spectral range. Such unknown levels would reduce the population of the levels considered here.) The result of this computation was the population N_{rad} per cc of OH radicals of any initial state for which the absorption intensity was measured.

III. Concentration of Dispersion Electrons

(a) Experiment

For the measurement of the intensity of individual absorption lines the light traversing the absorption tube described had to be analyzed with a spectrograph of a resolving power higher than the width of the lines. Here a major experi-

TABLE I. *Rotational terms (cm^{-1}) of the lowest electronic term of OH.*

J	$^2\Pi_i$	$^2\Pi_{1i}$	J	$^2\Pi_i$	$^2\Pi_{1i}$
$\frac{1}{2}$	138		$9\frac{1}{2}$	2068	1656
$1\frac{1}{2}$	199	0	$10\frac{1}{2}$	2464	2021
$2\frac{1}{2}$	300	84	$11\frac{1}{2}$	2895	2421
$3\frac{1}{2}$	441	203	$12\frac{1}{2}$	3360	2855
$4\frac{1}{2}$	620	356	$13\frac{1}{2}$	3858	3321
$5\frac{1}{2}$	836	545	$14\frac{1}{2}$	4388	3821
$6\frac{1}{2}$	1090	770	$15\frac{1}{2}$	4951	4354
$7\frac{1}{2}$	1380	1030	$16\frac{1}{2}$	5544	4918
$8\frac{1}{2}$	1706	1325	$17\frac{1}{2}$	6168	5514

[11] See A. R. Gordon, J. Chem. Phys. **1**, 311 (1933).
[12] See reference in footnote 1 and B. Lewis and G. von Elbe, J. Chem. Phys. **3**, 63 (1935).

[13] Fortrat, J. de phys. **5**, 20 (1924). W. Jevons, *Report on Band Spectra of Diatomic Molecules* (The Physical Society, Cambridge, 1932), p. 164.
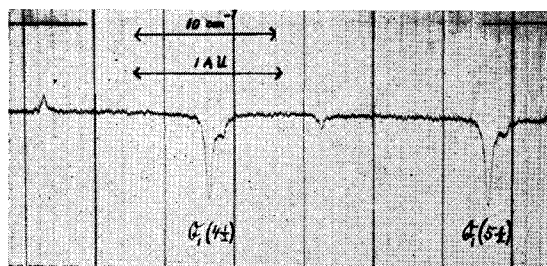
FIG. 2. Section of densitometer trace.

mental difficulty arose because of the small width of the OH absorption lines. We could not increase their width by pressure broadening, as Füchtbauer did for alkali lines, for that would have required a pressure of many atmospheres—too difficult a problem to handle for high temperatures and a large volume.

The second order of a 21-foot concave Rowland grating, mounted at this laboratory by Dr. F. H. Crawford and Mr. D. W. Mann, proved sufficient for the present purpose. The intensity of illumination was increased by a factor of about 16 by a cylindrical quartz lens in front of the photographic plate. A lens 5×5 cm^2 is large enough to cover the Q_1 and Q_2 branches of the OH band which, because of their high intensity, best lend themselves to observation. Eastman IV$-$O plates were used because of their fine grain and high contrast, both properties being of the greatest importance for the investigation of narrow and faint absorption lines; their very low speed was not a serious obstacle because of the gain of intensity by the cylindrical lens. The continuous spectrum of hydrogen served as a background. The hydrogen discharge tube was developed for the purpose of these investigations by Dr. N. D. Smith.[14] Fig. 2 shows a small section of the densitometer trace.

(b) **Computation**

The classical electron theory attributes the integrated absorption coefficient of a single observed absorption line to the number per cc N_{el} of vibrating "dispersion electrons." This number is derived from the absorption measurements as follows: For each frequency within the line the intensity transmitted is given by $i(\nu) = i_0 \cdot e^{-\alpha_\nu l}$ ($i_0 =$ uniform incident intensity of

[14] N. D. Smith, J. Opt. Soc. Am. **28**, 40 (1938).

background; $\nu =$ frequency in cm^{-1}; $\alpha =$ absorption coefficient per unit length; $l =$ length of absorbing layer). From the densitometer curve i/i_0 is derived as a function of ν and α_ν is computed. The number of dispersion electrons characteristic for this line is

$$N_{el} = \frac{mc^2}{\pi e^2} \int_0^\infty \alpha_\nu d\nu$$

($m =$ mass of electron; $e =$ charge on electron in e.s.u.; $c =$ velocity of light).[15]

$\int_0^\infty \alpha_\nu d\nu$ was derived from the densitometer traces by the following procedure. The $Q_1(6\frac{1}{2})$ line has only a weak satellite. For this line the logarithm of the ratio i_0/i was plotted against the wave number and the area under the curve taken as the quantity $l \int_0^\infty \alpha_\nu d\nu$. However, the remaining lines are in more complex groups which must be resolved by graphical methods in order to yield the above integral for each line of the group. Since the absorption coefficients for overlapping lines are additive, the graphical separation into component lines was conveniently carried out with a plot of $\log i_0/i$ against ν. The contour of the $Q_1(6\frac{1}{2})$ line was taken as a standard. By trial and error, lines of this shape were given separations and heights which would add to fit the observed contour of the group. The actual computation is simplified because in the range of photographic densities used, the relation between density and $\log I$ is accurately represented by a straight line. In this case, $\log I$ varies linearly with $\log d$ where d is the galvanometer deflection read from the microphotometer trace. The above procedure may be carried out with plots of $\log d$ against positions along the trace, and the areas derived for the individual lines converted to give $l \int_0^\infty \alpha_\nu d\nu$ by means of a constant multiplier which involves the contrast of the photographic plate and the dispersion on the trace. Typical contours are illustrated in Fig. 3.

[15] This formula follows from the one applied by Füchtbauer, Joos and Dinkelacker (Ann. d. Physik **71**, 222 (1923)), when one considers that their q is identical with $i(\nu)/i_0$; hence $4\pi nkl/\lambda$ is identical with $\alpha_\nu l$. We applied cm^{-1} instead of Füchtbauer's sec.$^{-1}$.

For frequencies of the OH band considered and with a length of 44 cm of the absorbing layer the result was

$$N_{el} = 2.54 \times 10^{10} \times l \int_0^\infty \alpha_\nu d\nu \, (\text{cm}^{-3}).$$

IV. RESULTS

(a) Uncorrected; correction for lack of resolving power

The numerical results are given in Table II. Column I gives the line observed. The lines belong to the branches Q_1, R_2, P_1, and $^QP_{21}$. Column II gives the integrated absorption coefficient $l\int\alpha_\nu d\nu$, derived from the photometry of the absorption lines, as it is needed for the computation of the number of dispersion electrons. These integrals may be considered as expressing line intensities.

The values of column II indicate by a systematic defect that a correction must be applied. The outstanding difficulty in the measurement of the intensities of narrow absorption lines is due to lack of resolving power. This is evident from the limiting case, the complete disappearance of absorption lines in spectrographs of poor resolving power. The intensities of such lines can be measured only with a spectrograph of a resolving power considerably higher than the width of the lines. Technically it seems possible to approach this condition reasonably well for the OH bands in the furnace. The resolving power of the grating in the second order is, theoretically, 0.145 cm^{-1}. It seems hardly possible to apply a still higher resolving power. The third-order grating spectra have so much less intensity that they cannot very well be used in this experiment. Furthermore, Fabry-Pérot plates or similar instruments of highest resolving power cannot be used for absorption spectra with a continuous background because of the very close proximity of adjacent orders. The Rowland grating at our disposal is supposed to have a resolving power nearly equal to its theoretical value of 0.145 cm^{-1} as tested in investigations on band spectra and Zeeman effects. It was used with its full aperture as the knife-edge method failed to reveal deficiencies of any zones. On the other hand the ob-
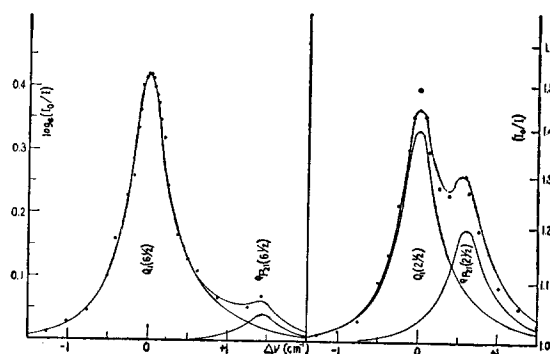

FIG. 3. Intensity curves.

served line width of OH in the furnace was 0.58 cm^{-1}, that is, four times the resolving power.

Obviously it is desirable to check whether the results were affected by a lack of resolving power. First we applied the method of Slater [16] by which the contour of a line may be corrected for the lack of resolving power. We assumed that the actual resolving power was given by the theoretical resolving power of the grating and the slit width applied at the densitometer. This procedure resulted in a correction of at most a few percent at the center of the absorption coefficient contour.

However, a second method yielded corrections so much larger that we were led to the conclusion that the over-all resolving power is considerably less than we had assumed. Without extensive tests it is impossible to decide if the discrepancy lies in the grating, the densitometer, or in the inability of the photographic plate to reproduce accurately steep intensity gradients[17] (the half-value width of the lines measures only 0.06 mm on the plate). The second method was a modification of the one applied by Bourgin[18] in his work on the intensity of infra-red absorption spectra. The eventual error was expected to be larger the steeper the line contour, that is,

[16] J. C. Slater, Phys. Rev. **25**, 783 (1925).

[17] The "Eberhard effect" is expected to be appreciable only for densities higher than 1 (*Handbuch der Experimentalphysik*, Vol. 26, p. 693); our background density was about 0.7; the plate was brushed during development. The resolving power of the Eastman IV–0 plate is estimated at 1/85 mm using white light. Using ultraviolet light, it is probably 1.5 or 2 times as great. Judged by these figures, the plate should reproduce the contour of a line, 0.06 mm wide, quite well.

[18] D. G. Bourgin, Phys. Rev. **29**, 794 (1927).

the more abrupt the change of intensity with frequency. Bourgin took this error into account by varying the depth of the absorbing layer. For ideal resolving power the intensity (integrated absorption coefficient) per unit length ought to remain constant. Actually the long tube yielded an apparently smaller intensity per unit length because the spectrograph failed to show the steeper line contour. The absorption line seemed to be too shallow. In order to obtain a correction factor, Bourgin plotted the observed intensity per unit length against the observed total intensity. He extrapolated this curve for smaller intensities and thus determined the corrected value as the limit for zero tube length.

In our case of the OH bands, we could not easily vary the tube length. But, instead, we could predict the various intensities of single lines, on the basis of the theory of Hill and Van Vleck, in conjunction with the populations of the various initial states determined in Section IIb(β). Actually the observed intensities given in Table II, column II, failed to come in the ratios theoretically predicted; there was a *systematic* deficiency of the more intense lines. By plotting the ratio (intensity observed)/(intensity predicted) against the intensity predicted (Fig. 4) a straight horizontal line was not actually obtained, as would be expected for ideal resolving power. Instead, the line had a definite slope which indicated that the observations were too small for the strongest absorption lines, as is characteristic for lack of resolving power. The line was reasonably smooth and straight and covered so wide a range of intensities that a minor extrapolation led to the limiting value for zero intensity. (If, instead, the ratio (intensity observed)/(intensity predicted) was plotted against the rotational quantum number J, the points scattered and failed to show a regularity.) Hence this extrapolation yields a corrected value for $l\int\alpha_\nu d\nu$. The correction does not change the order of magnitude. It is negligible for weak lines, but for the strongest lines the observed intensity seems to be only a little more than 50 percent of the real intensity.

(b) Corrected results

The corrected values of $l\int\alpha d\nu$ are given in Table II, column III. From this value the con-

centrations of dispersion electrons given in column IV were deduced. The concentrations N_{rad} of OH radicals for the lower state of the absorption lines, computed from the OH pressure and the Boltzmann distribution (Section IIIb) are given in V. Finally, column VI gives the principal result, the f values $= N_{el}/N_{rad}$ for the various absorption lines for which column I gives the lower level.

The quantum theoretical expression for the probabilities of spontaneous transition are Einstein's a_{ki} values. Their relation to the f values, as discussed by Ladenburg,[19] is given by $a_{ki} = g_k/g_i \times (8\pi^2 e^2 \nu^2)/mc \times f$ (notation the same as in Section IIIa; ν in cm⁻¹; g_k and $g_i =$ statistical weights of upper and lower levels, respectively). Column VII gives the a_{ki} values of the various lines.

The relation of our results to the recent results of Avramenko and Kondratjew,[20] although apparently contradictory, yet furnishing a good confirmation, will be discussed in a subsequent paper.

(c) Accuracy and sensitivity

(α) *Accuracy.*—Errors were due to the uncertainty of the equilibrium constant and to the imperfections of the spectrograph.

The *equilibrium constant* is uncertain largely because of the uncertainty in the energy of dis-

TABLE II. f values.

I	II	III	IV	V	VI	VII
Line	$l\int\alpha d\nu$ uncorrected (cm⁻¹)	$l\int\alpha d\nu$ corrected (cm⁻¹)	$N_{el} \times 10^{-10}$ (cm⁻³)	$N_{rad} \times 10^{-13}$ (cm⁻³)	$f \times 10^4$	$a_{ki} \times 10^{-6}$ (sec.⁻¹)
$O_1(1\frac{1}{2})$	0.226	0.268	0.681	4.16	1.64	1.15
$(2\frac{1}{2})$	0.286	0.465	1.18	5.74	2.06	1.44
$(3\frac{1}{2})$	0.354	0.613	1.56	6.83	2.28	1.60
$(4\frac{1}{2})$	0.388	0.708	1.80	7.32	2.46	1.73
$(5\frac{1}{2})$	0.376	0.731	1.86	7.28	2.55	1.79
$(6\frac{1}{2})$	0.358	0.708	1.80	6.83	2.64	1.85
$R_2(\frac{1}{2})$	0.068	0.070	0.18	1.83	0.97	0.69
$(1\frac{1}{2})$	0.122	0.140	0.36	3.42	1.04	0.73
$(2\frac{1}{2})$	0.165	0.203	0.51	4.66	1.10	0.77
$P_1(1\frac{1}{2})$	0.218	0.280	0.71	4.16	1.71	1.20
$(2\frac{1}{2})$	0.272	0.348	0.88	5.74	1.54	1.08
$QP_{21}(1\frac{1}{2})$	0.136	0.187	0.47	4.16	1.14	0.80
$(2\frac{1}{2})$	0.152	0.168	0.43	5.74	0.74	0.52
$(3\frac{1}{2})$	0.120	0.130	0.33	6.83	0.48	0.34
$(4\frac{1}{2})$	0.094	0.101	0.26	7.32	0.35	0.24
$(5\frac{1}{2})$	0.053	0.077	0.20	7.28	0.27	0.19
$(6\frac{1}{2})$	0.036	0.056	0.14	6.83	0.21	0.15

[19] R. Ladenburg, Zeits. f. Physik 4, 451 (1921). These a_{ki} values differ from the probability values, introduced by Füchtbauer (Physik. Zeits. 21, 822 (1920)) and applied in the recent review of Margenau and Watson (Rev. Mod. Phys. 8, 29 (1936)).
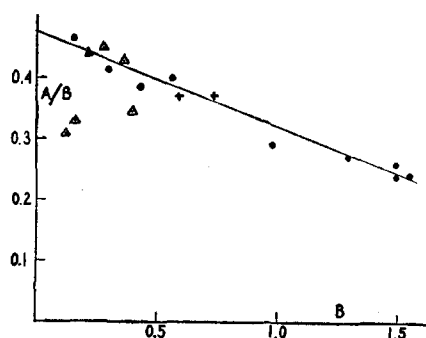[20] L. Avramenko and V. Kondratjew, Acta physicochem. U. S. S. R. 7, 567 (1937).

FIG. 4. Correction for lack of resolving power. A, observed values of $1\int\alpha_\nu d\nu$; B, Boltzmann factor $\times$ Hill and Van Vleck intensity factor; solid circle, Q_1; open circle, R_2; cross, P_1; triangle, $^QP_{21}$. (The two points farthest from the curve are derived from weak lines close to strong ones, and are accordingly of low weight.) Corrected values of $l\int\alpha_\nu d\nu = 0.475B$.

sociation $H_2O \rightarrow H + OH$. How large an effect this uncertainty has on the concentration of OH becomes evident from a table computed by Avramenko and Kondratjew.[20] A more accurate determination of this constant may necessitate a recomputation of N_{rad} of Table I, but not a repetition of the experiment. In the estimate of accuracy, we disregard this source of error; it is hardly possible to estimate the limit of this error; moreover we believe that the spectroscopic determination of the energy of dissociation may be improved so that this error may be eliminated in the future.

Scattered light in the spectrograph is negligible for large concave gratings, and is much fainter than that of plane gratings in a Littrow mounting in which reflection on the lens may be responsible for a considerable fog. In the concave grating even intense and rich emission spectra produce no appreciable diffuse light, presumably less than in any other instrument.

One might expect "ghosts," caused by imperfections of the grating, to affect the absorption lines because the ghost from the surrounding emission may raise the intensity at the bottom of the absorption line and so reduce the intensity of the observed absorption. That this is not the case in our spectrograph becomes evident from the following consideration. In the first place the Rowland grating used is known to have ghosts of negligible intensity, even in the neighborhood of over-exposed emission lines. Moreover, it can be shown that if a grating shows

ghosts in *emission*, an absorption spectrum taken with the same grating must show ghosts as apparent *absorption* lines at the same distance and relative intensity. Actually the observed absorption spectra failed to show even the slightest traces of such ghosts. Their absence is evident on the densitometer trace (Fig. 2). As faint absorption lines may be lost on the densitometer record, it is more critical that no trace of a ghost can be seen on the absorption spectrum. It is concluded that the intensities of the absorption lines are not seriously obscured by a ghost background.

A source of error, the effect of which could be quantitatively estimated, was the lack of resolving power. There is no doubt that the resolving power of the grating approaches reasonably well the theoretical value. A possible effect of a deficiency was corrected in Section IVa. This correction leads to f values defined well within 15 percent. We do not believe that the error is much larger, since there is a great difficulty only in the investigation of *intense* absorption lines where a small change of the intensities observed at the bottom strongly affects $\int\alpha d\nu$. On the other hand, for absorption lines that are inherently *weak at the center* the resolving power of the spectrograph does not cause a *systematic* error, because it makes no difference whether or not the spectrograph shows the absorption spreading over too wide a range, provided that the intensity dip remains deep enough for measurement.

It seems impossible in the investigation of the OH bands to duplicate the high accuracy with which f values of a few outstanding *atomic* lines are known. This difficulty, however, does not make the investigation of the OH bands useless. Its chief aim is its application to reacting gases for the purpose of determining the probabilities of elementary reactions. For this end our accuracy, estimated at 15 percent, is sufficient, because in chemical investigations other major difficulties enter—such as possible wall reactions—which affect our spectroscopic investigation of the reaction as well as the chemical approaches to the same problem.

(β) *Sensitivity.*—The minimum concentration detectable is estimated as follows. The faint absorption line $R_2(\frac{1}{2})$ shows up quite well on the

densitometer trace. It is estimated that a line of $\frac{1}{3}$ this intensity would still be observed by direct scrutiny of the photographic plate, although it might be difficult to locate on the trace. This corresponds to an integrated absorption coefficient $l \int \alpha d\nu = 0.023$ cm^{-1}. The most intense line $Q_1(5\frac{1}{2})$ would show up with the same intensity for a partial pressure of OH $= 0.01$ mm. This applies to a furnace of 44 cm length.

In other experiments which were made with electric discharges through H_2O vapor[21] the absorbing layer was 150 cm long. Furthermore the temperature was nearly room temperature so that the rotational distribution was restricted to a smaller range. In a subsequent paper it will be shown that partial pressures of hydroxyl as low as 0.0008 mm are detectable with absorption spectra taken with the 21-foot grating.

It is evident that for other molecules for which the transitions observed are not half-forbidden, the absorption spectra may provide far more sensitive tests.

VI. DISCUSSION

(a) Comparison with other f values

The f values of the principal absorption lines of *atoms* are of the order of magnitude of unity if the transition is not restricted by a selection rule; for example, 0.25 and 0.5 are the f values for the two D lines of Na. For the line 2537 of Hg, the f value is only 0.03, indicating a half-forbidden intercombination line.

In *molecular* spectra the f values are not diminished by the fact that a single line can be absorbed only by a small percentage of all molecules; this reduction is fully taken into account by the thermal distribution (Section IIIb(β)).

The only band spectrum for which the f value has been measured is closely related to the D lines of Na; it is the principal absorption band of the Li_2 molecule, $^1\Sigma \rightarrow ^1\Sigma$, which in the limit of dissociation corresponds with the $^2P \rightarrow ^2S$ transition of the Li atom.[22] For single lines of this spectrum Ladenburg and Levy found f values between 0.008 and 0.045. These small values are

partly explained by the fact that in the molecule each initial state has more possible transitions than in the atom because of the simultaneous changes of rotation and vibration. In particular the changes of vibration may spread over a considerable range of quantum numbers as explained by the Franck-Condon rule.

For the visible I_2 bands Füchtbauer and Hofmann[23] reported an f value of the order of magnitude 10^{-6}. However, they compared the "number of dispersion electrons," derived from the intensity of the absorption spectrum, with the *total* number of I_2 molecules present, irrespective of the thermal distribution over vibration and rotation, as the analysis of band spectra was still unknown. The rotational energy distribution in I_2 near room temperature includes so many quanta that the individual quantum may have a probability of 1/100. But, in any case, an f value is obtained which is small as compared to unity.

The OH bands have f values much smaller than the Li_2 bands. This is explained—as Professor Van Vleck pointed out to us—by the property of the corresponding transition belonging to the pair of dissociated atoms. The dissociation products of the normal state are probably $O^3P + H^2S$, and of the excited state $O^1D + H^2S$.[24] The $^3P \rightarrow ^1D$ transition of the O atom is forbidden and so explains the small probability of transition of the molecule. The high intensity by which the OH bands intrude as an impurity effect in discharge tubes does not point to high probability of transition but to the tendency of the H_2O molecule to cover all surfaces and come off gradually under the effect of the discharge.

(b) Lifetime of the excited state

The *lifetime* of the excited state is of interest for experiments in which *collisions during the lifetime* affect the observed spectrum. This lifetime is the reciprocal of the probability of transition expressed by Einstein's a_{ki} value, provided that there is only one transition possible, for example, for each of the D lines of Na. If several transitions can occur from the same

[21] To be published.
[22] R. Ladenburg and S. Levy, Zeits. f. Physik **88**, 449 (1934).

[23] C. Füchtbauer and W. Hofmann, Ann. d. Physik **43**, 127 (1914).
[24] H. Sponer, *Molekulspektren* (Julius Springer. 1935). p. 27.

excited level the lifetime is derived from the *total* probability of transition, that is, the sum of the a_{ki} values.

The computation of the lifetime, which is nearly the same for all initial levels of the same band, was carried through for the initial level of $Q_1(4\frac{1}{2})$. From the same level the fainter lines $R_1(3\frac{1}{2})$ and $^QR_{12}$ $(4\frac{1}{2})$ originate (neglecting two very faint satellites). From the intensity formulae of the Hill-Van Vleck theory the relative intensities of these lines follow, respectively, as 2.10; 0.63; 0.24. The next change of *vibrational* quantum number which belongs to the 0→1 emission band is very improbable, as indicated by the relatively very small intensity of the 3428 band; hence all transitions from $v'=0$ to higher vibrations of the lower electronic level can be disregarded. In this respect the computation of the lifetime is much simpler for OH than for many other molecules. Furthermore, we assumed that there is no other *electronic* transition competing with the 3064 band since no other band system of the neutral hydroxyl is known.

The resulting lifetime is 3.8×10^{-6} sec. On the other hand the lifetime to be expected at the wave-length 3100A, computed from the radiation damping of the corresponding electromagnetic

dipole, is 0.4×10^{-8} sec. The smaller value of the actual lifetime indicates a half-forbidden transition.

This long lifetime has a bearing on certain results on the persistence of rotation in collisions. In preceding papers abnormal rotation of OH as produced by the discharge and its persistence in collisions was discussed.[25] A few cm of He added hardly affected the observed abnormal rotation. In all the estimates a normal lifetime of the order of magnitude 10^{-8} sec. was assumed. On the basis of our present results the lifetime is much longer and therefore the chance for collisions during the lifetime much higher. Lyman and Jenkins,[26] in careful photometric work, found that the addition of 2 cm He to a discharge through H_2O caused only a minor reduction of the high rotation. With our value of the lifetime (applying the gas kinetic cross section of the water molecule to the excited OH radical), we computed that 570 collisions during the lifetime are rather inefficient in bringing about thermal equilibrium.

[25] O. Oldenberg, Phys. Rev. **46**, 210 (1934).
[26] E. R. Lyman and F. A. Jenkins, Phys. Rev. **53**, 214 (1938).

The Absolute Rates of Heterogeneous Reactions

I. The General Theory of Adsorption*

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The statistical theory of reaction rates, developed by Eyring for homogeneous reactions, is extended to include heterogeneous reactions. It is shown that rates of adsorption and desorption are governed by the same form of mathematical expression in terms of partition functions of the system as rates of homogeneous reactions, provided only that for the activated state a "super-partition function," formed by adding together the partition functions for all the active spots, is used. The pseudothermodynamical form of the rate constant form is discussed, and illustrated by applications to special cases.

IT has been shown by Eyring[1] that the rate constant k_1 of a homogeneous chemical reac-

[1] Eyring, J. Chem. Phys. **3**, 107 (1935); Eyring and Wynne-Jones, J. Chem. Phys. **3**, 492 (1935).

tion may be represented by an expression of the form

$$k_1 = \kappa \frac{kT}{h}, \frac{Z^*}{\Pi_i Z_i},\qquad(1)$$