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The Surface Recombination of H Atoms and OH Radicals

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A diffusion method of investigating surface recombination of atoms by substances of low catalytic power is presented. By this method we have evaluated the coefficient of recombination γ for H and OH on Pyrex for a temperature range of over 500°C. For smaller ranges of temperature we have found the recombination of H on a number of salts, and have found this recombination to be strongly dependent on the dryness of the surface. All salts investigated save KCl strongly recombined H when dry. Salts recombining H could not be investigated for OH recombination. However KCl, which did not recombine H, did recombine OH strongly. A number of strong dehydrogenating and dehydrating agents were tested for differences in H and OH recombination, but no difference was found.

INTRODUCTION

ALTHOUGH the investigation of surface recombinations of many atoms and radicals is still in the qualitative stage, quantitative results have already been obtained for the rate of recombination of H atoms on glass¹ and on certain metals.² By a modification in the experimental arrangement of previous investigators involving a change in the theory of the experiment, we have been able to extend these data and especially to find the variation of the coefficient of recombination γ (the fraction of times an atom striking the surface leaves as part of a molecule) with temperature.

1. EXPERIMENTAL PROCEDURE

The experimental procedure consists in allowing atoms that are formed by a low pressure gaseous discharge to diffuse through a side arm part of whose inner surface is coated with the material under investigation. Some of the atoms are lost to the coated walls and the remainder which succeed in passing through the side arm are detected by the heat of recombination they liberate at a small probe coated with some highly catalytic substance (Pt to detect H²; KCl to

detect OH).³ A high probe temperature indicates that few atoms are lost to the walls of the side arm, whereas a low probe temperature shows that many atoms are lost to the walls. By varying the probe distance, the decay in atomic concentration with distance from the juncture of discharge tube and side arm can be found, yielding an absolute measure of the coefficient of recombination; and with probe distance fixed, variation of the temperature of the coated section of the side arm yields the temperature dependence of the recombination coefficient.

Figure 1 is a diagram of the apparatus. The hydrogen was evolved electrolytically from a concentrated solution *S* of NaOH and passed through a water trap *T* which regulated the

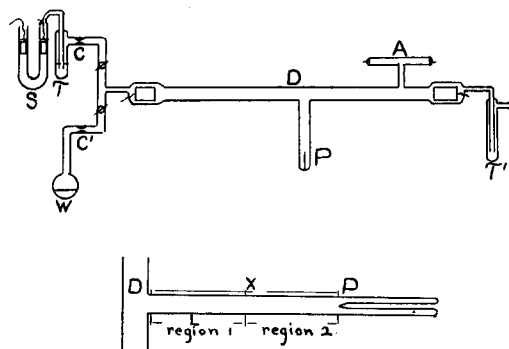


FIG. 1. Diagram of apparatus. *S* and *W* are sources of H₂ and H₂O, respectively. *T* and *T'* are traps. *C* and *C'* are capillary tubes restricting gas flow through discharge tube *D*. *A* is auxiliary discharge. *P* is probe at distance *X* from discharge. The temperature of region 1 of length *L* is varied. Region 2 is at room temperature.

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¹ H. G. Poole, Proc. Roy. Soc. **163**, 404 (1937); W. Steiner, Trans. Faraday Soc. **31**, 962 (1935). These values were obtained by complicated computations under conditions where the surface recombination was only a correction to a predominant volume recombination.

² K. F. Bonhoeffer, Zeits. f. physik. Chemie **113**, 199 (1924).

³ H. S. Taylor and G. I. Lavin, J. Am. Chem. Soc. **52**, 1910 (1930).

percent of water vapor in the gas.⁴ It was thence pumped through a capillary tube *C* and on through the discharge tube *D* by a Cenco Hyvac pump. A continuous flow of hydrogen through the discharge tube ensured freedom from impurities. The water vapor source was simply a bulb *W* of distilled water, the vapor of which was pumped through a capillary tube *C'* into the discharge tube. The trap *T'*, placed in dry ice, kept the water vapor out of the pump. A 100-milliamper current passed through the tube dissociated the gases respectively into $H+H$ and $H+OH$ ⁵.

The gases were investigated at pressures less than 0.1 mm, the pressure being governed by the capillary restriction and the pumping speed. The dark space of an auxiliary discharge *A* with plane electrodes was used to measure the pressure. It was calibrated against a McLeod gauge for hydrogen and against the vapor pressure of ice at known temperatures for water vapor. All stopcocks were lubricated with special low vapor pressure grease and were placed out of range of the atomic hydrogen.

The temperature of the probe *P* was measured by a copper-advance thermocouple with the cold junction 2 or 3 cm from the hot junction, thereby measuring the temperature difference of the gas and the heated probe. The whole thermocouple was separated from the low pressure gas by a glass wall, thin at the tip, so that the thermocouple junction (at atmospheric pressure) assumed the temperature of the platinum coating on the low pressure side of the glass. The probe was glass-blown to the side arm to avoid waxes or greases which might be attacked by atomic hydrogen.

The experimental procedure is based on the following considerations: The surface recombination of atoms must compete with recombination by triple collisions in the gas phase.

⁴ Addition of about two percent water vapor poisons the glass walls to H recombination. [R. W. Wood, *Proc. Roy. Soc.* **97**, 455 (1920).] Other poisoning agents such as metaphosphoric acid were avoided as they contain an indeterminate amount of water vapor and also make cleaning of the apparatus more difficult.

⁵ Spectroscopic observations have shown H and OH to be the only important decomposition products of an electric discharge through water vapor. [K. F. Bonhoeffer and T. G. Pearson, *Zeits. f. physik. Chemie.* **B-14**, 1 (1931).]

Simple calculations show that with γ of the order of 10^{-5} (the smallest value found was 2×10^{-5}), in apparatus of the dimensions used a pressure of 0.1 mm is sufficiently low to make volume recombination negligible.⁶ However at this low pressure diffusion becomes very rapid. Therefore, one cannot very well observe the recombination by the decay of concentration along a tube through which gas is flowing. A pumping speed high enough to make diffusion negligible is not practicable, particularly for H . Furthermore, the smaller γ , the smaller is the pumping speed required to produce a given concentration gradient of atoms along the side arm. Thus, rather than attempt cumbersome and inaccurate corrections for the influence of diffusion on flow velocity, it is far simpler to rely on diffusion alone to transport the atoms to the probe. It is in this reliance on diffusion rather than pumping that our experiment differs from previous ones.

Adoption of a diffusion scheme however requires that our detecting apparatus influence the atomic concentration as little as possible. Two techniques are available which have less disturbing influence than the one we adopted. They are the spectroscopic method of Steiner⁷ and the Wrede slit method.⁸ Both techniques are rather complicated however, the Wrede one especially so, and both have difficulties in interpretation, particularly the Steiner spectroscopic method. Simplicity of design was a consideration in our experiment as we investigated numerous different samples, necessitating frequent cleaning of our apparatus. Furthermore, we are able to show that most of our results are unaffected by the recombination at the probe.

⁶ Steiner (reference 1), reports volume recombination 3 times as effective as surface recombination for a pressure of 0.3 mm and tube diameter of 25 mm. This is not inconsistent with our criterion when due account is taken of his different pressure and diameter. Furthermore, his lower value of γ indicates better poisoned glass than that with which we worked.

⁷ Z. Bay and W. Steiner, *Zeits. f. physik. Chemie* **B3**, 149 (1929). The relative atomic concentration at points along a side arm from the discharge tube is deduced from the spectra of weak localized high frequency discharges induced at these respective points.

⁸ This method relies on the different velocities of effusion of molecules and atoms through a small slit. The differences in theoretical slit sizes necessary and the sizes used by experimenters has been criticized by Poole [*Proc. Roy. Soc.* **163**, 424 (1937)].

Besides simplifying the mathematics, the diffusion method avoids stray discharges as there are no grounded points along the side arm. We wish to emphasize this point as it is particularly important if any significance is to be attached to low probe temperatures, which might otherwise be ascribed to the effect of stray discharges. With a flow through the side arm, which always ends with the pump as a grounded point, it is difficult to be sure stray discharges are avoided, especially when an alternating voltage is applied to the discharge.

2. THEORY OF THE EXPERIMENT

The atomic concentration at various distances from the discharge along a side arm will vary, as different parameters such as pressure, temperature, and degree of dissociation in the discharge are varied. The nature of this variation will differ according to the mechanism responsible for the recombination process. Four types of mechanisms are possible. They are:

1. A first-order wall effect with total recombination directly proportional to atomic concentration. Such an effect results from the assumption that each atom striking the wall has a definite probability of sticking to the wall and, once it sticks, is certain eventually to combine with a second atom and leave the wall as part of a molecule. This might be the mechanism of recombination on poor catalysts. The assumption of the wall being completely covered with a monolayer of atoms, independent of pressure, also results in first order recombination as in this case the number of molecules leaving the wall per second can vary only in direct proportion to the number of atoms striking the wall per second. Good catalysts, such as Pt, probably fall in this class. Whatever the mechanism responsible for such an effect, it can be described by assigning a coefficient of recombination γ to each atom striking the wall signifying the probability that the atom will eventually leave the wall as part of a molecule.

2. A second-order wall effect. Recombination proportional to the square of the pressure results from the assumption that each atom striking the wall adheres to it a short time only and that recombination will occur if, during this time,

another atom strikes the wall within a certain (small) distance of the first atom. Any practical case intermediate in pressure dependence between 1 and 2 can be resolved into these two parts.

3. Triple collisions in the gas phase.

4. Preponderant effect of the probe. If there were no wall recombination nor any losses of atoms by triple collisions, but only a large recombination at the probe, there would still be a variation of probe temperature with distance from the discharge as the transport of atoms to the probe is a function of the distance and the coefficient of diffusion. We cannot deduce from the small probe area ($5 \times 10^{-3} \text{ cm}^2$) that it is negligible, as the recombination is 10^4 or more times as great on Pt as on glass. (See Table II.)

From our measurements we want to decide between cases 1, 2, 3, and 4. For this purpose, we carry through the theory for each of the four cases and find which checks best with experiment.

Let n = number of atoms/cc

x = distance along side arm from junction with discharge tube

D = coefficient of diffusion

F = drift velocity of atoms along side arm

γ = coefficient of recombination

S = cross-sectional area of side arm

C = circumference of side arm

\bar{v} = average atomic speed

p = pressure.

The subscript 0 in the following derivations indicates the junction of the side arm with the discharge tube (Fig. 1).

We will assume the concentration is constant over the cross section so that $n = n(x)$ only. We assume also $F = F(x)$.⁹ Hence for all four cases

⁹ For the equation of diffusion to be applicable to our problem, we must have $2r \gg \lambda$. (r is the radius of the side arm; λ , the mean free path.) Also, n will equal $n(x)$ only if the diffusion is rapid enough to wipe out concentration gradients within any cross section which the losses to the walls tend to establish. A typical time for diffusion to wipe out these gradients is given by the relaxation time for diffusive equilibrium in an enclosure of dimensions r : $t = r^2/D \approx 3r^2/\lambda\bar{v}$. This time must be small compared to the time necessary for destruction of all atoms in the volume V , neglecting the effect of diffusion. It is

$$t = \frac{nV}{n\bar{v}S\gamma/4} = \frac{2r}{\bar{v}\gamma}$$

Therefore our complete condition for validity of our

the equation of diffusion applies in its simplest form:

$$nF = -D \frac{dn}{dx} \quad (1)$$

A second equation between n , F , and x is obtained by expressing the decay of the concentration n along the length x of the side tube in terms of the mechanism by which the atoms are removed. We may derive the dependence of n on x for cases 1 to 3 simultaneously, assuming constant temperature along the side arm. We first equate the number of atoms lost to the wall per cm per second to the gradient of atomic flow through the tube $[-S(d/dx)(nF)]$. The losses to the walls for the three cases are:

- (a) $\frac{n\bar{v}}{4} \gamma C$ for first-order wall recombination,
 (b) aCn^2 for second-order wall recombination, (2)
 (c) $bpSn^2 + cSn^3$ for volume recombination.

In (c) the first term is for molecules as third bodies and the second for atoms. As our partial pressure of atoms is in general small compared to the total pressure, we will ignore the second term.¹⁰ We then have

$$-S \frac{d}{dx}(nF) = \begin{cases} \frac{n\bar{v}}{4} \gamma C \\ aCn^2 \\ bpSn^2 \end{cases} \quad (3)$$

Combining this equation with (1) and solving subject to the boundary condition that $(dn/dx) = 0$ at $n=0$ [from Eq. (1), dn/dx is proportional to n and in particular approaches 0 as n approaches 0 since although F is variable, it remains

assumptions is $\lambda/2 \ll r \ll 2\lambda/3\gamma$. In practice we have $\lambda=0.2$ cm, $r=0.55$ cm, and $\gamma=10^{-3}$ to 10^{-5} . We see therefore that our assumptions $n=n(x)$ and $F=F(x)$ are valid.

¹⁰ The main conclusion of this derivation—that n/n_0 is a function of n_0 , approaching 1 for small n_0 , would still hold if this second term were included, but eliminating it simplifies the mathematics. (Data in the literature are not in agreement on the relative effectiveness of atoms and molecules as third bodies promoting volume recombination.)

finite] we have

$$n = \begin{cases} \frac{A \exp(\bar{v}C\gamma/4SD)^{1/2}x + B \exp(-\bar{v}C\gamma/4SD)^{1/2}x}{n_0} \\ \frac{n_0}{[1 + (n_0aC/6SD)^{1/2}x]^2} \\ \frac{n_0}{[1 + (n_0bp/6D)^{1/2}x]^2} \end{cases} \quad (4)$$

In the expression for first-order wall recombination, with a tube of finite length both A and $B \neq 0$. The negative exponent represents a component decreasing with increasing x . The positive exponent represents a stream of atoms reflected from the end of the tube and therefore increases with increasing x . We may however use the rule of thumb that for values of n/n_0 less than about $\frac{1}{4}$ (a condition satisfied by our experimental results) the atoms reflected from the tube end may be ignored; hence, $A \simeq 1$ and $B \simeq 0$. With obvious changes of constants, we therefore have

$$(a) \quad n = n_0 \exp(-\beta\gamma^{1/2}x)$$

for first-order wall recombination

with $\beta = (\bar{v}C/4SD)^{1/2}$,

$$(b) \quad n = \frac{n_0}{[1 + K \text{ (or } K')n_0^{1/2}x]^2} \quad (5)$$

for second-order wall recombination

(or for volume recombination).

We note that β is proportional to $D^{-1/2}$ and hence to $p^{1/2}$ as the coefficient of diffusion D is inversely proportional to the pressure.

To estimate the maximum influence of the probe alone on the concentration (case 4), we will make the assumption that all the atoms striking the cross section where the probe is located are eventually recombined at the probe. We will first analyze the problem under conditions of constant temperature along the side arm.

At X we have destruction of atoms at a rate $(n\bar{v}/4)S$. These atoms are being supplied by diffusion down the side arm at a rate SnF . Therefore at X

$$F = \bar{v}/4. \quad (6)$$

In the region from $x=0$ to $x=X$, where there are assumed to be no losses of atoms by recom-

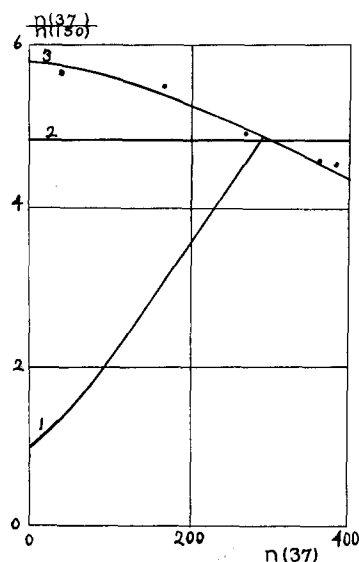


FIG. 2. Variation in the ratio of temperatures of two probes plotted against the temperature of one of these probes. Discharge in H_2 ; pressure = 78μ . 1 = Theoretical curve for loss of H by three-body collisions. 2 = Theoretical curve for first-order wall recombination of H. 3 = Observed data. (The constants of the theoretical curves were chosen to fit the observed data at the point of intersection.)

bination, we must have conservation of mass transport along the tube, hence

$$\frac{d}{dx}(nF) = 0. \quad (7)$$

Combining (7) with the equation of diffusion (1) we get

$$n = n_0 - Kx/D, \text{ where } K \text{ is some constant.} \quad (8)$$

This means that there is a linear fall of atomic concentration along the side arm furnishing a gradient to transport atoms to the probe by diffusion. From Eqs. (1), (6), and (8), we therefore derive

$$(F)_x = \frac{K}{n(X)} \frac{\bar{v}}{4}, \text{ whence } K = \frac{n(X)\bar{v}}{4}. \quad (9)$$

Substituting this value of K in (8) and evaluating at $x = X$, we have

$$n(X) = n_0 - \frac{n(X)\bar{v}}{4D} X = \frac{n_0}{1+GX} \text{ where } G = \frac{\bar{v}}{4D}. \quad (10)$$

Assuming that not all the atoms crossing X recombine on the probe, but that a large fraction do so (the condition in actual practice) has the effect of making G smaller. We will therefore

take the magnitude of G as unknown and examine only the dependence of our equation on X , pressure, and temperature. The latter will prove most useful for correlation with experiment. For this purpose, we will want a solution for the case where the temperature of a portion of the side arm far from the probe is varied (thus changing the density and the coefficient of diffusion). The calculation for this case is straightforward though a bit tedious. The resulting formula is

$$n = \frac{n_0}{1 + G \left(X - L + \frac{T_1 D_0}{T_0 D_1} L \right)}. \quad (11)$$

Here T_1 and D_1 are temperature and coefficient of diffusion in region 1 and T_0 and D_0 are the corresponding values in the discharge tube and in region 2. (See Fig. 1.)

To interpret our results, we must relate probe temperature to atomic concentration. Let us define "probe temperature" $t = T_p - T_0$ where T_p is the actual equilibrium temperature of the probe and T_0 is the temperature of the side arm in which the probe is located. We assume

$$\frac{n\bar{v}}{4} Aq = kt, \quad (12)$$

where A is the probe area, q the heat generated per atom striking the probe, and k the conduction-convection constant. Heat loss of the probe by radiation [which would introduce a term $k'(T_p - T_0)^4$] is neglected.

A complication in our investigation is the necessity of *assuming* this linear relation between probe temperature and atomic concentration, as we cannot divorce the investigation of loss of atoms along the tube from a simultaneous investigation of probe response. Such an assumption is reasonable however, particularly in the case of recombination of H on Pt as it is known that metals are quickly covered with a monolayer of atoms at temperatures ranging from below room temperature to several hundred degree centigrade. If this monolayer is maintained over the partial atomic pressure range investigated, the number of molecules leaving the surface per second must be proportional to the number of atoms striking the surface per second. In any case, a small deviation from linearity in response

would not be serious as most of the concentration variations are exponential in character.

3. RECOMBINATION OF H ON PYREX—DISCHARGE IN H_2

All the samples of Pyrex used were cleaned by scrubbing and rinsing in distilled water, as preliminary investigations showed no difference in results even at high temperatures using other methods of cleaning such as washing in KOH, $KHCrO_4$, H_2SO_4 , or HF.

A. Check on Three-Body Collisions and Second-Order Wall Effects

In order to distinguish between Eqs. (5a) and (5b), we note that (5a) predicts n/n_0 independent of n_0 , whereas (5b) predicts n/n_0 strongly dependent on n_0 , and indeed approaching the value 1 as n_0 approaches 0. The following experiment was therefore performed. Two parallel side arms of equal diameter were attached to the discharge tube, terminating in probes respectively 37 cm and 150 cm from the discharge. The atomic concentration was varied over wide ranges without materially changing the pressure or the coefficient of diffusion by simply varying the current through the discharge tube. The ratio of the two probe readings was then plotted against the temperature of the probe closest to the discharge (Fig. 2). The observed approximate constancy of this ratio, at a value far from 1, is ample evidence that n/n_0 is not dependent on n_0 . We conclude therefore that neither three-body collisions nor second-order wall recombination on moist Pyrex walls are important factors in H recombination at the pressure and temperature investigated (78 microns, and 23°C).

B. Check on the Effect of the Probe

If the probe recombination predominates, a change of temperature of region 1, Fig. 1, should have an effect predicted by Eq. (11). This is checked in Fig. 3 where the probe temperature, indicating the number of H atoms arriving per second, is plotted against the temperature of section L of the side arm. For comparison the theoretical curves derived from Eq. (11) (predominant probe recombination) are also plotted. These theoretical curves are adjusted to fit the experimental values at room temperature.

Obviously at temperatures other than room temperature the probe recombination does not predominate. However as the surface recombination is lowest at room temperature (see Fig. 6), this argument does not eliminate the possibility of important disturbance from the probe at room temperature. Values of γ calculated by ignoring the probe effect may however be considered maximum values, and all results for various surfaces at various temperatures yielding a γ considerably larger than the least of these values may be considered reliable. Furthermore, the assumption of negligible probe effect appears justified even at room temperature in view of the agreement between experiment and theory shown below in Figs. 4 and 5. This result is plausible since the pressure is kept so low and the probe area so small that we should expect the first-order wall effect to predominate.

C. Computation of γ at Room Temperature

1. Computation from the Decay in Atomic H Concentration Along the Side Arm. (Fig. 4)

From Eqs. (5a) and (12) we have

$$t = \frac{n_0 \bar{v} A q}{4k} \exp - (\beta \gamma^{\frac{1}{2}} x). \quad (13)$$

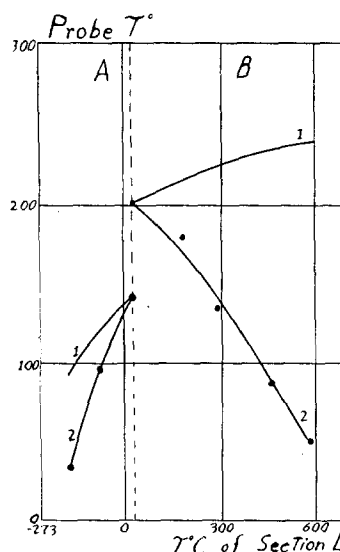


FIG. 3. Variation of probe temperature with temperature of furnace located at region 1 of Fig. 1. H_2 pressure = 80μ . 1 = Theoretical curve for atomic gradient caused by recombination at probe, normalized to observed data at 20°C. 2 = Observed data. A: $L = 58$; $X = 70$. B: $L = 20$; $X = 50$.

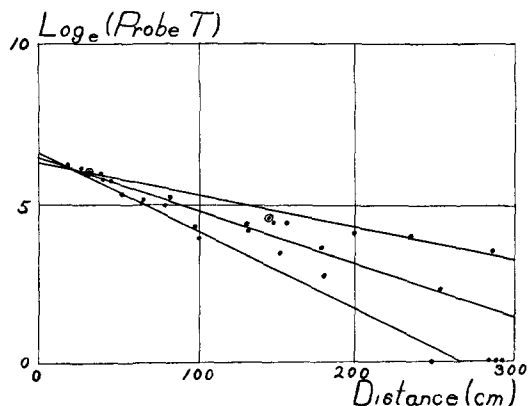


FIG. 4. Variation of probe temperature with distance from a H_2 discharge. Pressure = 75μ . Circled points correspond to circled point of Fig. 5.

Therefore in a series of experiments in which n_0 , \bar{v} , etc., are kept constant, we derive

$$\log_e t = -\beta_0 \gamma^{\frac{1}{2}} x + C', \quad (14)$$

where C' = some constant.

For $p = 75\mu$, $\beta_0 = 3.73$ (see Section D).

Three lines are drawn through the points in Fig. 4 showing the mean and extreme values of the slope. The corresponding values of γ calculated are

$$\gamma = \left. \begin{array}{l} 0.75 \\ 2.01 \\ 4.56 \end{array} \right\} \times 10^{-5}. \quad (15)$$

The variations in γ are of the order of 2 or $\frac{1}{2}$ from the mean. As numerous different samples of Pyrex were used the variation in γ is reasonable.

2. Computation from Pressure Variation of n_0/n

Equation (5a) may be written

$$\log_e (n_0/n) = \left(\frac{\beta' x_0 \gamma^{\frac{1}{2}}}{75^{\frac{1}{2}}} \right) p^{\frac{1}{2}} \quad (16)$$

where p is in microns and β' is the value of β at 75μ pressure.

In Fig. 5, $\log_e n(30)/n(145)$ is plotted against $p^{\frac{1}{2}}$. The theoretical curve 16, a straight line through the origin, gives a good fit to the experimental points. Some deviation is observed at pressures below 80 microns. This is possibly caused by a breakdown in the assumption of uniform drift velocity F along the tube cross section since for these pressures the mean free

path (1.1 mm at 80μ) is no longer negligible compared to the tube diameter (1.1 cm).

The value of γ calculated from 16 and Fig. 5 is

$$\gamma = 1.05 \times 10^{-5}. \quad (17)$$

The probe temperatures at 30 and 145 cm used in Fig. 5 for a pressure of 75μ are also plotted on Fig. 4 (the circled points). They are seen to represent a value of γ nearer the lowest value than the mean value deduced from Fig. 4. These values (see 15) are 0.75×10^{-5} and 2.01×10^{-5} . The check of 1.05 with 0.75 is excellent.

3. Comparison with Other Values

Steiner¹ reported γ on moist glass varying between 2×10^{-6} and 9×10^{-6} . Poole¹ reported a value of γ of 1.6×10^{-4} . Our values lie between these two extremes. Poole's results are for glass under the actual conditions of the discharge however, for which γ is to be expected comparatively large. The agreement of these values with ours is very good in view of the complicated mathematics used in the work of the other two investigators where the wall recombination was a minor effect. The simplicity of interpretation of our results plus the fact that the wall recombination was the preponderant agent removing the atoms in the pressure region we investigated would seem to give greater confidence to our results.

D. Experiments at Other Temperatures

In these experiments, the pressure, tube current, and distance X are kept constant while the temperature of a section L near the discharge is changed by means of a furnace or low temperature bath (see Fig. 1). In some runs a parallel check side arm and probe was used to see if the atomic H production remained constant during the run. It was found that the probe temperature in this check side arm would vary by a factor of 2 or $\frac{1}{2}$ for the first few hours and then remain constant often to 10 percent for over twelve hours. Occasional larger fluctuations seemed to be caused by local variations in the check side arm or check probe and to have no relation to the H concentration near the main side arm, as this probe did not show fluctuations at the same time. The best check on our temperature variation curves however is their reversibility. In

runs extending even over several days, with furnace temperature raised from 20°C to 580°C, the probe temperature would drop to $\frac{1}{4}$ its original value or less, and on returning the furnace to 20°C, the probe temperature would return to within 20 percent of its original value.

From the known rate of loss of atoms to the walls at room temperature and the observed change in probe temperature with temperature of section L of the side arm, the variation in γ may be found by a simple computation providing we assume we can piece together solutions of the form $n = n_0 \exp -\beta\gamma^{\frac{1}{2}}x$ rather than complete solutions of the form

$$n = A \exp \beta\gamma^{\frac{1}{2}}x + B \exp -\beta\gamma^{\frac{1}{2}}x.$$

This assumption is valid however whenever we are sure that we can neglect the reflection of atoms beyond the length L , and can therefore attribute all changes of n to the change of decay along the heated tube. Actually the length L is long enough so that at room temperature the value of n falls to a small fraction of its original value at the far end of L , and as actually the recombination coefficient was in all cases observed to rise with temperature, this condition is even better fulfilled at higher temperatures. At temperatures below room temperature, γ remains nearly constant, again introducing no appreciable error. We therefore derive

$$t_1 = k' \exp (-\beta_1\gamma_1^{\frac{1}{2}}L) \cdot \exp [-\beta_0\gamma_0^{\frac{1}{2}}(x-L)]$$

where k' is some constant

$$t_0 = k' \exp (-\beta_0\gamma_0^{\frac{1}{2}}x)$$

whence

$$t_0/t_1 = \exp (\beta_1\gamma_1^{\frac{1}{2}}L - \beta_0\gamma_0^{\frac{1}{2}}L),$$

$$\log_e (t_0/t_1) = \beta_1\gamma_1^{\frac{1}{2}}L - \beta_0\gamma_0^{\frac{1}{2}}L,$$

$$\gamma_1 = \left(\frac{\beta_0\gamma_0^{\frac{1}{2}}L + \log_e (t_0/t_1)}{\beta_1L} \right)^2,$$

$$t_0 = \text{probe } T \text{ for } L \text{ at } T_0,$$

$$t_1 = \text{probe } T \text{ for } L \text{ at } T_1. \quad (18)$$

TABLE I. Variation of β with temperature.

$T^\circ\text{C}$	β	$T^\circ\text{C}$	β
-180	7.26	180	2.91
- 80	4.70	300	2.55
15	3.73	450	2.28
		590	2.09

The variation of β with temperature must also be computed. We remember

$$\beta = (\bar{v}C/4SD)^{\frac{1}{2}}. \quad (19)$$

With $p = 75\mu$, using Amdur's¹¹ value for D , we obtain Table I for β .

The experimental runs were taken by varying the furnace temperature in steps of about 120°, allowing from one hour to five hours or more for the furnace to reach equilibrium. A minimum of

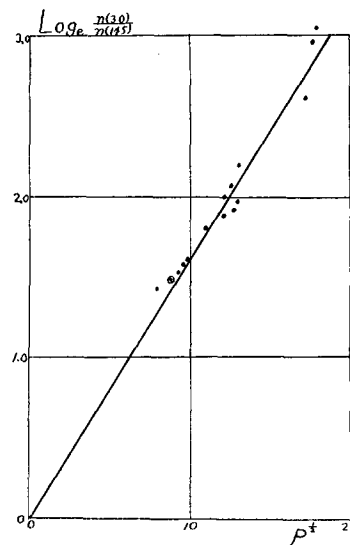


FIG. 5. Variation with pressure (in μ) in the ratio of temperatures of two probes at two different distances from a H_2 discharge. Circled point corresponds to circled points of Fig. 4.

one hour was found necessary for any approach to equilibrium, and several runs were made leaving the furnace at various temperatures overnight to be sure a close approach to equilibrium was attained. As the variation of probe temperature with furnace temperature was reversible, the values obtained do represent equilibrium values. Several different pressures near 75 microns were used, and since the results for all the different runs showed more random variations than systematic variations, all were averaged and plotted in Fig. 3. The low temperature portion of the experiment was conducted with the section L bent into a U tube and immersed in dry ice or liquid air.

¹¹ I. Amdur, J. Chem. Phys. 4, 339 (1936).

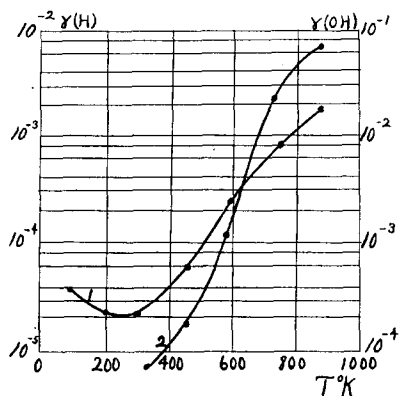


FIG. 6. 1, $\gamma(H)$ on Pyrex in H_2+2 percent H_2O at 75μ pressure as a function of temperature. 2, $\gamma(OH)$ on Pyrex in H_2O at 50μ pressure as a function of temperature.

The value of γ may be calculated from Fig. 3, Eq. (18), and Table I. The results are plotted in Fig. 6, together with those for $\gamma(OH)$ on Pyrex (see Section 5). We may note that the observed variation cannot be simply explained by any mechanism involving some single energy of activation or heat of reaction as the resulting equations will predict $\log \gamma$ inversely proportional to temperature rather than almost directly proportional as observed in the high temperature region of Fig. 6. So simple an explanation could not be expected however as the temperature is sure to modify the properties of the surface, in particular the layer of adsorbed water.

E. Variation of γ with Water Vapor Content

Three runs were made with respectively $\frac{1}{2}$ percent, 2 percent, and 9 percent water vapor added to the hydrogen. It was found that the probe temperature increased with increasing water vapor content for all furnace temperatures, but especially at the higher temperatures. The results are plotted in Fig. 7. A pressure of 60 microns was employed, and at least three hours were allowed for equilibrium at each temperature. The three curves were obtained in one continuous run of over 200 hours; curves 2, 1, and 3 consecutively. In such a long run, the probe is apt to change its sensitivity somewhat and there is reason to believe curve 2 should be more nearly intermediate between 1 and 3 than it is, as a check point taken at room temperature with H_2+2 percent H_2O just before the run 3 gave a probe temperature of 175° . The general nature

of the variation with water vapor content is however unmistakable.

Increasing water vapor content in the discharge may mean either better poisoning of the walls or increased OH concentration (see Part 5) or both. In Part 5 it will be shown that the uncertainty in OH decay is such that OH radicals might still reach the Pt probe. However, using the most probable value of OH decay, the OH concentration at the Pt probe may be neglected, and the observed variation may be attributed entirely to better poisoning of the glass walls for H recombination.

4. RECOMBINATION OF H ON OTHER SUBSTANCES

Substances investigated include quartz, combustion tubing, and K_2SiO_3 chosen for their similarity to Pyrex; KCl because of its importance in certain investigations of OH recombination; Al_2O_3 as a typical dehydration catalyst; $ZnO \cdot Cr_2O_3$ as a typical dehydrogenation catalyst; Pt; and also KOH, K_2CO_3 , metaphosphoric acid, and Na_3PO_4 .

Two arrangements were used in the investigation. The first is the same as was used in Section 1 on Pyrex—an *indirect method*, good for substances of low catalytic power. In this method, the atoms diffuse down a side arm coated in part with substances under investigation, and the atoms passing through this coated section are detected by a Pt coated probe (see Fig. 1). The coated

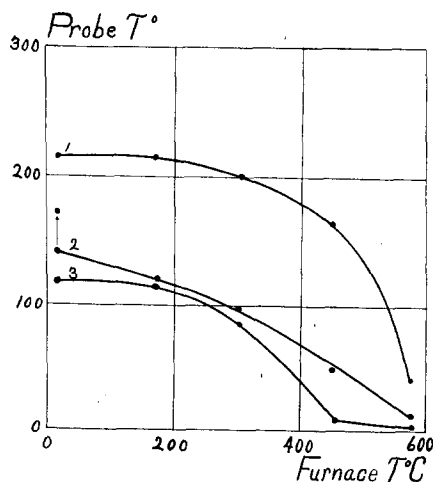


FIG. 7. Variation of Pt probe temperature with water vapor content of discharge. Arrow points to an independent check of first point of curve 2. 1 = H_2+9 percent H_2O . 2 = H_2+2 percent H_2O . 3 = $H_2+\frac{1}{2}$ percent H_2O .

TABLE II. H recombination on various substances. We may note from the close check between the values of the last two rows that γ (Pt)200° is nearly equal to 1.

Substance	Sample length L probe dist. x	Condition	Furnace temp.	Pt probe temp. (indirect method)	Probe U temp. (direct method)	Probe U temp. corrected for changing atomic concentration and speed	γ (indirect method)	γ/γ Pt (direct method)
Quartz	$L=20$ $x=30$	erratic behavior	15	45	—	—	$7.0 \cdot 10^{-4}$	—
			300	22	—	—	$2.6 \cdot 10^{-3}$	—
			500	15	—	—	$3.4 \cdot 10^{-3}$	—
Combustion Glass	20 30		15	70	—	—	$4.6 \cdot 10^{-4}$	—
			300	50	—	—	$1.8 \cdot 10^{-3}$	—
			500	30	—	—	$2.8 \cdot 10^{-3}$	—
K_2SiO_3	6 30	moist	15	200	0	0	10^{-4}	$1.7 \cdot 10^{-3}$
		dry	15	10°	—	—	$7 \cdot 10^{-2}$	—
		dry	200	4°	35	47	$7 \cdot 10^{-2}$	$1.6 \cdot 10^{-1}$
		dry	500	2°	—	—	$1 \cdot 10^{-1}$	—
KCl ¹	6 30		15	350	0	0	$2 \cdot 10^{-5}$	—
			400	240	0	0	$2 \cdot 10^{-4}$	—
KOH	6 30	moist	15	200	0	0	10^{-4}	10^{-3}
		dry	15	0	—	—	$\geq 10^{-1}$	—
		dry	200	0	20	27	—	$9 \cdot 10^{-2}$
		dry	300	0	—	—	$\geq 2 \cdot 10^{-1}$	—
K_2CO_3	6 30	moist	15	200	0	0	10^{-4}	10^{-3}
		dry	15	0	14	14	$\geq 1 \cdot 10^{-1}$	$5 \cdot 10^{-2}$
		dry	200	0	10	13	$\geq 2 \cdot 10^{-1}$	$4 \cdot 10^{-2}$
		dry	400	0	—	—	$\geq 2 \cdot 10^{-1}$	—
Metaphosphoric acid	20 30	moist	15	350	0	0	$2 \cdot 10^{-5}$	—
Sodium Phosphate	6 30	moist	15	200	0	0	10^{-4}	$\leq 10^{-3}$
		moist	300	150	—	—	$5 \cdot 10^{-4}$	—
		dry	15	0	20	20	$\geq 1 \cdot 10^{-1}$	$7 \cdot 10^{-2}$
		dry	200	0	15	20	—	$7 \cdot 10^{-2}$
		dry	300	0	—	—	$\geq 2 \cdot 10^{-1}$	—
Al_2O_3	2.5 30	moist	15	20	20	20	$9 \cdot 10^{-2}$	$7 \cdot 10^{-2}$
		moist	200	—	10	13	—	$4 \cdot 10^{-2}$
		dry	15	0	100	100	—	$3.3 \cdot 10^{-1}$
		dry	200	0	60	80	—	$2.7 \cdot 10^{-1}$
		dry	400	0	25	67	—	$2.2 \cdot 10^{-1}$
$ZnO \cdot Cr_2O_3$	2.5 30	moist	15	0	160	160	—	$5.3 \cdot 10^{-1}$
		or	200	0	120	160	—	$5.3 \cdot 10^{-1}$
		dry	400	0	65	170	—	$5.6 \cdot 10^{-1}$
Pt	2.5 30	moist	15	0	300	300	—	1
		or	200	0	250	330	—	1.1
		dry	400	0	120	320	—	1.1

¹ Numerous other runs established that within experimental error the catalytic effect of KCl on H recombination cannot be distinguished from that of Pyrex. As the KCl coating did not completely shield the glass surface from the discharge, it is therefore possible that KCl is even less catalytic to H recombination than Pyrex. This is hard to establish definitely as measuring the recombination coefficient on glass represents about the limit of our experimental technique with the present method of investigation.

sections were 11 mm inside diameter, glass blown to the system save for quartz, combustion tubing, Al_2O_3 , $ZnO \cdot Cr_2O_3$ and Pt. (These latter substances were of 8 mm inside diameter tubing slipped inside the main side arm where they fitted snugly.)

The *indirect method* is obviously not good for substances of high catalytic power such as

K_2CO_3 , KOH, etc., because few atoms would reach the probe, but we have used it as a very rough estimate of γ . Where zero probe readings were observed, we have assumed the probe T to be equal to or less than one-half degree and we have assumed that the probe T at the discharge end of the tube would be at least 500°. These assumptions yield our lower limits of γ listed in

Table II. γ is calculated from the probe temperatures, the data for Pyrex, and the obvious equation¹²

$$\log_e(i) = -(\beta\gamma^{\frac{1}{2}}L)_z - [\beta\gamma^{\frac{1}{2}}(X-L)]_{\text{Pyrex}} + C' \quad (20)$$

where z is the substance under investigation.

The second system of probes, utilizing a *direct method* of comparing different substances, is illustrated in Fig. 8. It is good for substances of high catalyzing power.

The unknown substance is coated on probe "U." Probe "T" is coated with Pt as an indicator of the minimum H concentration near "U." (The actual concentration near "U" is of course in general much greater than that indicated by "T," and the reading of "T" was never interpreted quantitatively. In some runs however, a portion of the active substance coated on probe "U" would become dislodged or would be sublimed onto the surface of the side arm. This coating then would decrease the total H concentration as measured by "T" without increasing the reading of "U." The presence of the check probe "T" was useful in eliminating these runs.)

Probe "U" is inserted in the middle of a 20 cm long furnace whereby the temperature variation in the response of "U" can be measured. To correlate the readings of probe "U" at different furnace temperatures, the change in heat loss of the probe with temperature of the surrounding furnace must be known. Calculations of heat losses, including radiation losses,—necessarily rough because of the comparatively long mean free path (of the same order of magnitude as the probe diameter) and the inaccurately known accommodation coefficient—show that this heat loss does not vary very greatly with temperature over the range from 20°C to 450°C. That is, in Eq. (12), the term A/k may be taken as constant over this temperature range, and q will be proportional to γ . In this equation however, the factor $n\bar{v}$ varies with temperature. We assume n is not different for different coatings on the probe. This assumption is only a first approximation, and as n will actually be somewhat larger in the presence of less catalytic substances, a direct comparison of these with a Pt coating on "U" will make the unknown

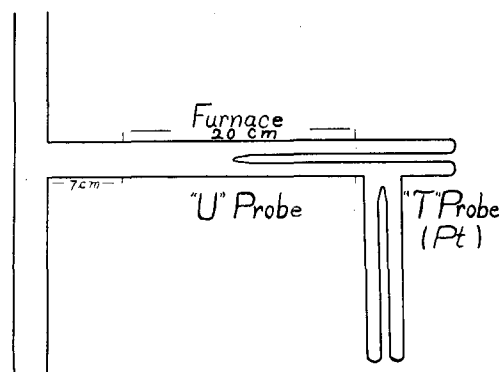


FIG. 8. Direct method of investigating γ . Substance to be investigated is coated on "U" probe.

substance appear more catalytic than it really is. N also varies with temperature however due to losses to the clean glass walls of the side arm. This correction may be computed from Eq. (20), substituting $L=10$, $X=17$ (here z is Pyrex at the furnace temperature), the observed temperature variation of γ (Fig. 6), and the computed values of β (Table I). These changes in n and \bar{v} are corrected for in Table II.

The data in this section are not as accurate as in Section 1. In the first place, the salts at high temperatures (around 500°C) sublimed somewhat to different parts of the side arm, and even a slight invisible layer of salt on the glass completely changes its catalytic effect. In the second place, certain salts such as KCl were reduced in or very near the discharge. Also, some substances lost water of crystallization in violent miniature explosions which spread the coating. Most important of all, however, was the fact that the catalytic effects of almost all these substances depended far more on their moisture content than on their temperature. Moist salts were non-catalytic; dry ones (save KCl) catalytic to H recombination. As a result, the data obtained with these salts with varying temperature are in general non-reversible, low catalytic effect being initially observed, increasing as the increasing furnace temperature dries out the salt, and remaining high when the furnace temperature is again lowered.

5. EXPERIMENTS WITH WATER VAPOR

When a discharge is passed in water vapor, the molecules are dissociated into H atoms and OH

¹² Derived analogously to Eq. (14).

radicals. There is a negligible concentration of O atoms.⁵ Three possible two-body surface recombinations can occur.

- 1— $\text{H} + \text{H} + M \rightarrow \text{H}_2 + M + 4.3 \text{ ev},^{13}$
- 2— $\text{H} + \text{OH} + M \rightarrow \text{H}_2\text{O} + M + 5.5 \text{ ev},$
- 3— $\text{OH} + \text{OH} + M \rightarrow \text{H}_2\text{O}_2 + M + 3.1 \text{ ev}.$

M is the surface catalyzing the recombination. All three reactions are strongly exothermic. No previous work has been done to distinguish between recombination processes 2 and 3.

The state of knowledge with respect to these three recombinations prior to these experiments may be briefly summarized. All the data were known only at room temperature. At this temperature Pyrex glass was known to catalyze 1 very poorly and 2 and 3 also poorly, although it was thought to be somewhat more catalytic for one or both of the latter reactions than for reaction 1. Numerous substances—such as Pt, $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$, KOH, etc., were known to catalyze 1 strongly, but their effect for 2 or 3 was unknown. Al_2O_3 was known to catalyze 1 strongly and was thought to catalyze 2 also. KCl was known to be quite ineffective in catalyzing 1, and quite effective in catalyzing either 2 or 3 or both. All these conclusions may be drawn from the work of Taylor and Lavin,³ although they do not try to distinguish the two possible types of OH recombination.

The present investigation has added to the existing data and narrowed down the possible interpretations, but has not succeeded in uniquely distinguishing between recombination processes 2 and 3. We have succeeded in obtaining a rough estimate of the recombination coefficient γ for process 2 or 3 on glass, and have found its change with temperature. We have also investigated the effect of temperature on other substances, especially KCl.

The experimental arrangement is indicated in Fig. 1. Water vapor is pumped through the discharge tube from the water reservoir. The OH concentration is detected by the heating of probes coated with KCl. (Note that Pt probes could not be used as Pt recombines atomic H. KCl does not recombine H and does recombine

OH—see below.) The response of these KCl surfaces was quite erratic, and they almost always required activation for 15 minutes at 250°C to manifest their catalytic power. The probe response was fairly reproducible for an average of about 5 runs, after which it would usually become very erratic. The glass walls near the probe were observed to become coated with KCl in patches by fragments exploded from the probe in the course of repeated activation. This coated section robbed the probe of OH and caused part at least of the erratic nature of the probe response. Because of this effect, probe temperatures below 10° were considered unreliable.

To avoid possible reduction of the KCl by the discharge, the probe was always kept at least 10 cm distant from the discharge.

A. Pyrex

1. Investigation of γ (OH) at Room Temperature

Figure 9 is a logarithmic plot of KCl probe temperature against distance from the discharge. The scattering in observed points is very large. A greater range of distance could not be investigated as for shorter distances there was danger of reduction of KCl by the discharge and for larger distances the probe temperature was so small as to be unreliable. The scattering here, in contrast to that in Fig. 4, is believed due more to variation in probe response than in surface conditions of the glass. One sequence of points (the circled values) was taken with the same KCl coating on the probe, readings at small and large values of x alternating.

Whether OH disappears by process 2 or 3 is immaterial in the calculation of γ as γ is defined as the fraction of times the OH radical strikes the wall and is recombined there *by any process*. We have therefore the same equation as for $\gamma(\text{H})$. [Eq. (14)], but in this case $\beta_0 = 4.63$ (see Section 2). From Fig. 9, we get therefore

$$\gamma = 8 \times 10^{-5}. \quad (21)$$

The small range in probe temperatures (a factor of 10) and distances (a factor of 5) available (compare factors of several hundred and 20 respectively in experiments on H recombination)

¹³ Energies of recombination calculated from data of Int. Crit. Tab. V, p. 176, and A. v. Engle and M. Steenbeck, *Electrische Gasentladungen* I, p. 43.

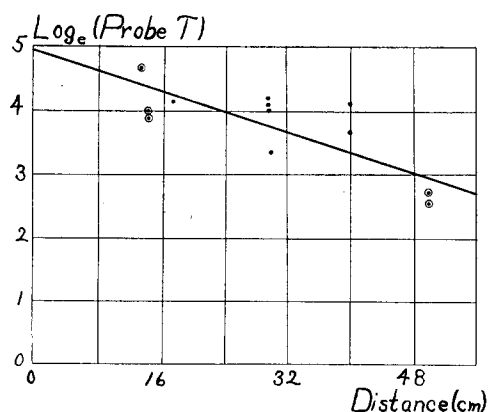


FIG. 9. KCl probe temperature as a function of distance from a water vapor discharge. Pressure = 50μ . Circled points are for one sequence of runs with the same KCl surface on probe.

together with the relative unreliability of the KCl probes rendered attempts to distinguish between surface recombination and losses of OH by three-body collisions useless. However as the pressures are even lower than in the work on H recombination, surface effects probably preponderate. The nature of the temperature variation in probe response (Fig. 10) evidently precludes the possibility of recombination at the probe overshadowing losses of radicals to the Pyrex walls.

2. $\gamma(\text{OH})$ at Other Temperatures

Investigations were made in the temperature range from 15°C to 590°C . The experimental set-up is the same as that in Fig. 1 except that two probes " U_1 " and " U_2 " in two independent side tubes were used instead of one. The double probe system was used to eliminate random fluctuations. An average of several runs is plotted in Fig. 10. Here the temperature of the 7 cm furnace was varied by jumps of 150° every two hours. Reversibility of probe response with furnace temperature showed that probe readings represented equilibrium values. The short reliable life of the KCl probes made it impossible to vary the furnace temperature more slowly.

Computation of β for OH diffusion is not accurate as no data are available on the coefficient of diffusion of OH. We may get a rough estimate however by assuming that the coefficient of diffusion of OH nearly equals the self-diffusion

coefficient of H_2O . This we compute from the viscosity data by means of the equation

$$D = C\eta/\rho \quad (22)$$

where we take $C = 1.36$ as a compromise between the hard sphere and inverse fifth power repulsion values of C (1.200 and 1.543, respectively). The resulting values of β , calculated from equations analogous to those of Part 3, are given in Table III.

The values of γ computed from this table and the data of Fig. 10 are plotted in Fig. 6.

3. $\gamma(\text{H})$ on Pyrex in H_2O

In Part 3 we have measured $\gamma(\text{H})$ on Pyrex in moist H_2 . Here we may do the same for H atoms produced in a water vapor discharge. Different values of coefficient of diffusion, etc., make this determination of γ an interesting check with the previous ones. Furthermore, if the recombination $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$ is considerably stronger than either $\text{H} + \text{H} \rightarrow \text{H}_2$ or $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$, a large value of γ should result as the initial dissociation of H_2O yields equal amounts of H and OH.

OH disappears more rapidly with distance from the discharge along the side arm than does H. This is known from the data of Taylor and Lavin,³ and also from the large value of $\gamma(\text{OH})$ which we have found. It is not known whether

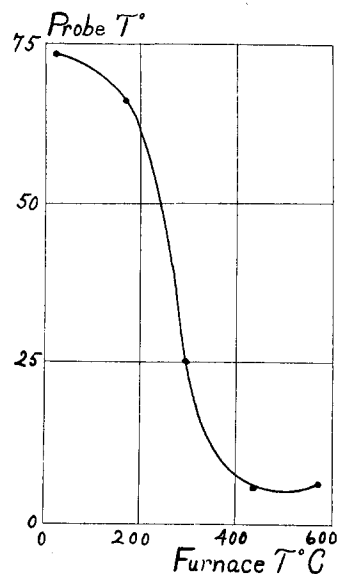


FIG. 10. KCl probe temperature as a function of furnace temperature in a water vapor discharge. Pressure = 40μ .

OH recombines on Pt or not, but presumably it does. Consequently the Pt probe is affected by both H and OH. However, for distances sufficiently far from the discharge (around 50 cm), the larger recombination of OH on Pyrex assures small concentrations of OH compared to H, and thus the decay of H alone may be measured.

Pt probe readings in H₂O are therefore plotted logarithmically in Fig. 11 for a pressure of 50 μ . The scattering of points is not great. The deviation from a straight line shown by the initial group of points is presumably from the effect of OH on the probe. The final two points near 300 cm are zero probe readings whose logarithms are plotted arbitrarily as zero (equivalent to a temperature of 1°), and their deviation from linearity is not significant.

The following equation¹⁴ holds for the diffusion of molecular H₂ into H₂O.

$$D = 0.7516(T/273)p/160 \quad (p \text{ in mm of Hg}). \quad (23)$$

As H has nearly the same diameter as H₂¹⁵ and as for large differences of masses of the inter-diffusing molecules, D is proportional to the velocity of the lighter component, we can conclude that for the diffusion of atomic H into H₂O,

$$D = 2^{1/2} \cdot 0.7516(T/273)p/760. \quad (24)$$

With this value of D , for a pressure of 50 μ , at room temperature, we get $\beta = 3.72$, whence, using Fig. 11 and Eq. (14), we get

$$\gamma(\text{H}) = 1.9 \times 10^{-5}. \quad (25)$$

The agreement with values of γ for moist hydrogen is surprisingly good and indicates that the recombination $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$ on Pyrex is weaker than $\text{H} + \text{H} \rightarrow \text{H}_2$ or $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$.

Experiments similar to those in Part 3 showed three-body collisions to be negligible compared to the surface recombination of H.

TABLE III. Values of β for OH diffusion.

$T^\circ\text{C}$	β	$T^\circ\text{C}$	β
20	4.63	450	2.08
180	3.16	590	1.89
300	2.53		

¹⁴ Int. Crit. Tab. V, p. 62.

¹⁵ Calculations from Amdur's viscosity data (reference 11) for atomic H give this result.

B. Other Substances

1. KCl

Numerous experiments with alternating H₂ and H₂O discharges establish definitely that KCl coated probes are heated appreciably—up to around 100°—at 10 cm from a H₂O discharge and are not heated above 1°–2° at the same distance from a discharge in moist H₂. We may therefore conclude that KCl catalyzes OH

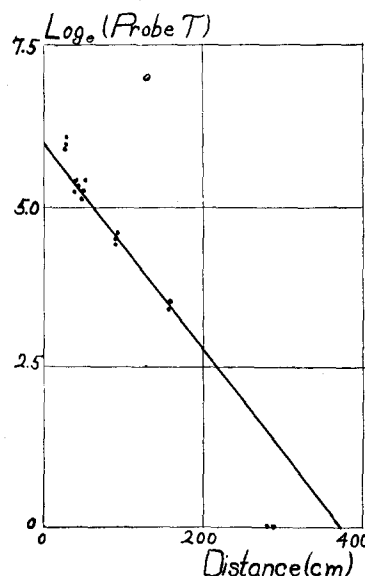


FIG. 11. Pt probe temperature as a function of distance from a water vapor discharge. Pressure = 50. O probe temperatures plotted as 1°.

recombination and does not catalyze H recombination. This is important because it establishes a test for free OH which is not affected by H. Our conclusion agrees with the results of Taylor and Lavin³ and Frost and Oldenberg.¹⁶

Similar experiments with a furnace surrounding the probe have been carried out. At a furnace temperature of 180°C, the KCl response decreased by a factor of two. Possibly this was due to some KCl sputtered onto the walls. Insertion of a check probe beyond the furnace proved useless as the OH concentration was too small to be accurately detected.

To estimate the magnitude of $\gamma(\text{OH})$ on KCl, we observe that a KCl coated probe 20 cm from a H₂O discharge heats up to 65° whereas a Pt

¹⁶ A. A. Frost and O. Oldenberg, J. Chem. Phys. 4, 642 (1936).

TABLE IV. Comparative probe temperatures with H_2 and H_2O discharges.

Gas	Al_2O_3 (unactivated)	Al_2O_3 (activated)	$ZnO \cdot Cr_2O_3$	Pt
H_2	290	315	290	580
H_2O	80	180	220	415

probe 20 cm from a H_2 discharge heats up to 500° . As $\gamma(OH)$ on Pyrex is greater than $\gamma(H)$ on Pyrex, the OH concentration near a H_2O discharge surely does not exceed the H concentration near a H_2 discharge. Furthermore the mean of the heats of recombination by the processes $H+OH \rightarrow H_2O$ and $OH+OH \rightarrow H_2O_2$ is nearly the heat of recombination of atomic H. We may therefore conclude that $\gamma(OH)$ on KCl is surely greater than 0.1 times $\gamma(H)$ on Pt.

The temperature variation of OH recombination on KCl could not be followed closely, but since a KCl probe located 10 cm beyond a 6 cm section of the side arm coated with KCl showed no response for any temperature of the 6 cm section up to and including $400^\circ C$, evidently KCl remains catalytic to OH recombination at high temperatures.

2. KOH , K_2CO_3 , K_2SiO_3 , Na_3PO_4

These substances all have the property of recombining atomic H strongly when dry and poorly when wet. Measurements of OH recombination by the *direct method* therefore are useless as the H recombination masks the OH response, and any systematic variations between response in H_2 and in H_2O are as easily ascribed to varying catalytic effect for H (because of the strong dependence of H catalysis on surface dryness) as to some catalytic recombination of OH.

Measurements by the *indirect method* with KCl coated probes are useless if the KCl catalyzed recombination is by the process $H+OH \rightarrow H_2O$, as no H passes the coated section of the side arm. Similarly, measurements with a Pt probe are valid only if the reaction $OH+OH \rightarrow H_2O_2$ proceeds strongly on Pt. The nature of OH recombination on KCl and Pt is not known however. Furthermore, a positive response with a Pt probe can also be interpreted as a change in $\gamma(H)$ on the coatings on the Pyrex walls with increased H_2O content of the discharge.

We have nonetheless made these measurements, as a positive response of the KCl probe in any case where no H passes the coated section would establish the reaction $OH+OH \rightarrow H_2O_2$ on KCl, and a null response with the Pt probe shows $\gamma(H)$ is still large on the wall coatings investigated.

The substance under investigation was coated inside the 7 cm length of side arm in the furnace. Probes " U_1 " and " U_2 " were located 5 cm beyond the furnace, and were coated with KCl. Probe " T " was located 5 cm beyond U_1 and U_2 and was coated with Pt. Alternate runs were taken with a clean glass side arm to check the response of the KCl.

Positive readings on U_1 or U_2 were found only with a Na_3PO_4 coated side arm at temperatures below $400^\circ C$ —i.e., in an unactivated condition where H recombination was known to be uncatalyzed. This therefore established only the fact that unactivated Na_3PO_4 catalyzes neither H recombination nor OH recombination.

Null readings were found with " T " for activated coatings, except that readings of a few degrees were observed with a K_2SiO_3 coated side arm even at high furnace temperatures. This behavior is the same as with moist hydrogen, showing that for the substances investigated it is a function of *surface* wetness, not H_2O concentration in the gas.

3. Pt, Al_2O_3 and $ZnO \cdot Cr_2O_3$

Indirect measurements with these substances (3 cm samples) established zero KCl probe readings which proved little (see previous section). The Pt probe response was the same as with H_2 (part 4) except that with an Al_2O_3 sample, Pt probe readings of 1° – 2° were observed at room temperature even after activation of the Al_2O_3 at high temperatures (at which temperatures the Pt probe response was zero). Probable interpretation of this result is that there is greater poisoning of Al_2O_3 for H recombination in H_2O than in moist H_2 at the pressures employed. (See below for confirmation of this interpretation).

Direct measurements at 17 cm from the discharge established the data in Table IV for alternate H_2 and H_2O discharges. (The data are aver-

age values for several runs. H_2 pressure 75μ ; H_2O pressure 50μ).

To obtain high readings with an H_2O discharge, it was necessary to heat the Al_2O_3 probe in a furnace to $320^\circ C$ for 30 minutes. As even after this activation the Al_2O_3 probe temperature slowly decreased over the course of 30 minutes to 125° , it seems probable that the lower ratio of readings with H_2O to readings with H_2 for Al_2O_3 compared with $ZnO \cdot Cr_2O_3$ and Pt is caused by increased poisoning of the Al_2O_3 surface by water vapor.

Our observation that Al_2O_3 does not heat up more with a H_2O discharge than with a H_2 discharge disagrees with that of Taylor and Lavin. However if the ratio of their Al_2O_3 probe readings

to their silver probe readings is examined, it is seen not to change appreciably with changing H_2O concentration in the discharge. Their data, together with ours, therefore show no significant difference in relative heating of Al_2O_3 , $ZnO \cdot Cr_2O_3$, Pt, and Ag with H_2O and H_2 discharges—and therefore no measurable difference in the *relative* catalytic effect of the dehydration catalyst Al_2O_3 and the dehydrogenation catalyst $ZnO \cdot Cr_2O_3$ for H and OH recombination.

The author wishes to express his appreciation to Professor O. Oldenberg for suggesting this problem and for his continued interest and help in its development. He is also indebted to Professor W. H. Furry for clarification of many aspects of the diffusion problems considered.

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Mechanical Properties of Polymeric Materials

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A molecular model in terms of which the elastic viscous properties of rubber-like substances can be interpreted is presented. Experiments on stress relaxation at constant extension, creep under constant load, extrusion, vibration, and breaking are discussed in terms of a mathematical formulation of this molecular model.

A VERY large class of substances composed of large molecules, such as nylon and other fibers, natural and synthetic rubbers, muscle tissue, and so on, exhibit elastic-viscous properties that are qualitatively similar, which fact reflects an over-all similarity in molecular structure.

These substances are composed of long chain molecules linked together at some points by primary cross bonds and at other points by bonds of a secondary nature such as strong Van der Waals' bonds (as in regions of local crystallinity) dipole-dipole bonds, etc. The cross linking bonds give these polymers an effective network structure. Between the cross bonds there is a rather long length of coiling, twisting molecular chain, the segments of which are rotating more or less freely. This amorphous liquid-like structure comprises the bulk of the

polymer, when the latter is in the temperature range of the rubbery state of aggregation.

Because of statistical considerations, the molecular chains spend most of their time in very coiled configurations when no external stresses are acting. When the polymeric network is rapidly stretched, the molecular chains are stretched and thereby have fewer conformations that are consonant with this extended state. The probability of a unit cell of the network having dimensions x, y, z is^{1,2}

$$P_{(xyz)} = A \exp [-\beta(x^2 + y^2 + z^2)]. \quad (1)$$

The entropy is related to the probability by

¹ E. Guth and H. M. James, *Ind. Chem.* **33**, 624 (1941). See also earlier work of Meyer, Mark, Kuhn, and Guth referred to in this paper.

² Tobolsky, Powell, and Eyring, Chapter on "Elastic Viscous Properties of Matter" in *Frontiers of Chemistry*, Interscience Publishers (in press).