

noted in this connection that any errors caused by thermal separation in the carbon dioxide-carbon monoxide mixtures in Fe-C-O equilibrium measurements¹⁰ would cause the values of K_3 calculated from the Fe-C-O and the Fe-H-O data to be low; accordingly the 2 or 3% difference between equation 38 and the values of K_2 thus indirectly calculated might easily be due to such errors in the Fe-C-O data. The direct calculations of K_3 based on our own data for the Sn-H-O system and those both of Eastman and Robinson (A) and Meyers and Scheffer (B) for the Sn-C-O system have been included since it is not possible at present to decide which of the two sets of experimental values of K_2 is the more reliable. It should be noted, however, that as pointed out above the 3 or 4% discrepancy between the values of K_3 in column B and those of equation 38 could be due entirely to thermal diffusion errors in the experiments of Meyers and Scheffer on the Sn-C-O system.

Summary

Values of the equilibrium constant $\text{H}_2\text{O}/\text{H}_2$ for the reaction $\frac{1}{2} \text{SnO}_2 + \text{H}_2 = \frac{1}{2} \text{Sn} + \text{H}_2\text{O}$ have been found to be 1.66, 2.22, 2.84, and 3.53 at 650, 700, 750 and 800°. These values are about 25% lower than the results of previous workers, and when combined with equilibrium data for the Sn-C-O system give values for the water gas constant that agree within a few per cent. with those obtained by direct measurements.

(10) See Eastman and Evans, *THIS JOURNAL*, **46**, 888 (1924).

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The Recombination of Hydrogen Atoms. I

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Introduction

The rate of recombination of hydrogen atoms has been measured by Smallwood,² Senftleben and Riechemeier³ and Steiner and Wicke.⁴ Kassel⁵ has summarized the results of these investigations. It seems fairly certain that the reaction takes place partly on the walls, although Senftleben and Riechemeier and Steiner and Wicke present some evidence to indicate that the wall reaction is not very significant, and partly as a trimolecular gas reaction. Opinion differs as to whether hydrogen atoms or hydrogen

(1) The material in this paper comprises a portion of a thesis presented by I. Amdur to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1932.

(2) Smallwood, *THIS JOURNAL*, **51**, 1985 (1929).

(3) Senftleben and Riechemeier, *Ann. Physik*, **6**, 105 (1930).

(4) Steiner and Wicke, *Z. physik. Chem.*, Bodenstein Band, 817 (1931).

(5) Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932, pp. 177-180.

molecules, or both, act as third bodies in the trimolecular gas reaction.⁶ Smallwood found atoms and molecules to be equally effective, Senftleben and Riechemeier found a much greater efficiency for collisions with atoms than with molecules and Steiner and Wicke concluded that atoms are relatively inefficient as third bodies, contributing at the most only ten per cent. of the effect attributed to hydrogen molecules. In view of the discrepancies reported, it seemed desirable to repeat certain portions of this work, using a large range of atomic hydrogen percentages. The effect of varying the total pressure through a twofold range was examined to determine, if possible, the influence of the wall. It is also shown that certain objections raised against the calorimetric method^{4,7} are invalid.

Experimental

Apparatus and Procedure.—The apparatus was essentially that used by Smallwood² with the following modifications.

The rate of inflow of molecular hydrogen was determined from the reading of a calibrated ammeter when the rate of generation of hydrogen equaled the rate of pumping as shown by the constant levels of liquids in the limbs of the H-shaped generator. A high rate of pumping was secured by using a large four-jet mercury pump⁸ connected in parallel with a single-jet pump. Three Hyvac pumps connected in parallel were used as fore pumps.

The temperature rise produced in the Dewar vessel, which served as a calorimeter, by the recombination of hydrogen atoms at the surface of the platinum catalyst was measured with a twenty-five junction copper-constantan thermocouple, the cold junction of which was immersed in a mush of ice and water in a Dewar vessel. The thermocouple was standardized against a Beckmann thermometer that had been calibrated by the U. S. Bureau of Standards. Between 20 and 30° the thermocouple voltage was a straight line function of the temperature with a value of 1006 microvolts per degree. Thermocouple voltages obtained during runs by means of a Leeds and Northrup Type K potentiometer were not converted to temperature rises since the heat capacity of the calorimeter was determined in terms of calories per millivolt rise of thermocouple voltage. Figure 1 shows a voltage-time plot for a typical run. The heat capacity of the calorimeter was determined at different positions along the recombination tube (with the discharge on and the platinum catalyst removed) for various rates of heating, corresponding to rates of heating observed during runs, by noting the increase in thermocouple voltage produced by passing a current through a constantan heating unit immersed in the calorimeter water, the energy input being measured potentiometrically.

Variations in pressure were obtained by decreasing or eliminating the heat input to the mercury pumps.

The walls of the recombination tube and discharge tube (both of Pyrex glass) were coated with sirupy phosphoric acid⁷ made by dissolving c. p. phosphorus pentoxide in distilled water. As a result reproducible results were obtained when the apparatus was used continuously and runs at a given temperature were made in as short a time interval as possible.

(6) For a discussion of the improbability of two atoms uniting to form a molecule as a result of a binary collision, see Boltzmann, "Gastheorie II," Leipzig, 1912; Polanyi, *Z. Physik*, **1**, 337 (1920); Herzfeld, *ibid.*, **8**, 132 (1922); Born and Franck, *Ann. Physik*, **76**, 225 (1925); Jeans, "Dynamical Theory of Gases," fourth edition, Cambridge University Press, p. 195.

(7) Von Wartenberg and Schulze, *Z. physik. Chem.*, **B2**, 1 (1929).

(8) Ho, *Rev. Sci. Instruments*, **3**, 133 (1932).

Throughout the investigation the potential across the discharge tube electrodes was 6600 volts and the primary current of the transformer was 32 amperes.

Results

The corrected thermocouple voltage increase was obtained by extrapolating the final cooling curve and the initial warming curve until the extrapolated lines intersected the ordinate drawn at the mid-point of the time abscissa which represented the duration of the discharge. The height

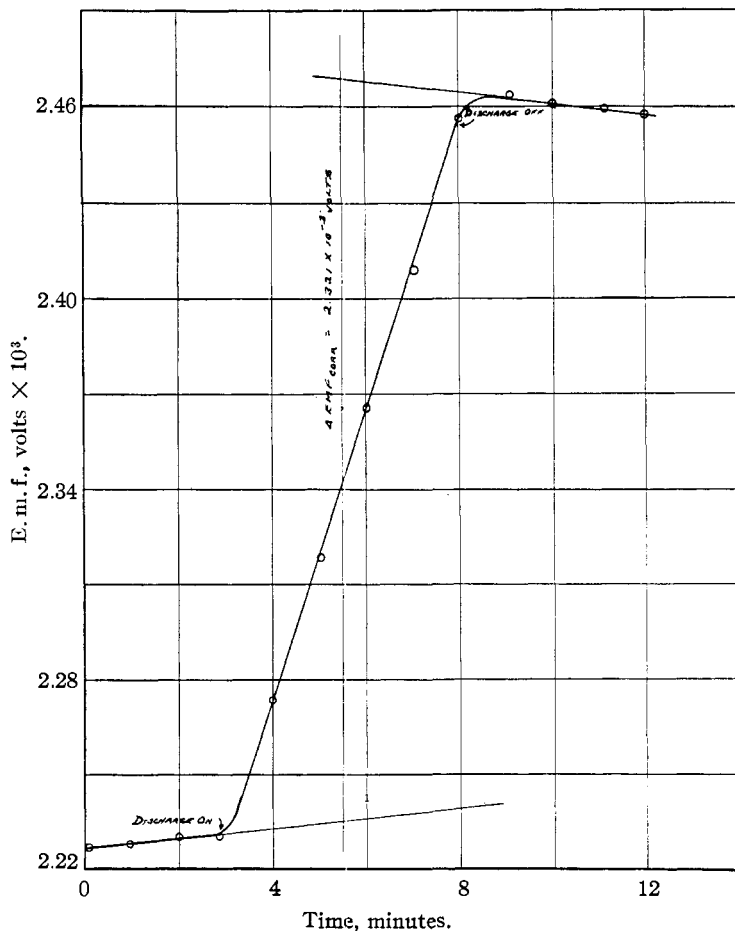


Fig. 1.—A voltage-time plot for a typical run.

of this ordinate gave the corrected voltage as shown in Fig. 1. The fraction of atomic hydrogen at any point along the recombination tube is given by

$$\alpha = \frac{C \Delta e. m. f._{corr}}{60n \Delta H} \tag{1}$$

where C is the heat capacity of the calorimeter in calories per millivolt,⁹ ΔH is the heat of formation of one mole of molecular hydrogen from the atoms and was taken to be 102,800 calories per mole as reported by Richardson and Davidson,¹⁰ and t is the time in minutes during which the discharge was on. The other symbols have the meanings designated in Table I. The runs in a single set in this table were all made in one day and fit a smooth curve well (Fig. 2).

TABLE I

MEASUREMENTS AT ROOM TEMPERATURE ($25 \pm 2^\circ$)Internal diameter of recombination tube, 1.066 cm.; length ab,^a 174 cm.

Set 1

 $P_a^b = 0.375$ mm., $P_b = 0.162$ mm. Rate of flow of $H_2 = n_0 = 0.881 \times 10^{-5}$ mole/sec.

Distance from a to bottom of catalyst x. cm.	Time of discharge t, min.	E. m. f. (corr.) volts $\times 10^3$	Dissociation 100%
13.7	5	2.321	94.0
38.3	5	1.916	80.9
66.0	5	1.643	69.6
92.9	5	1.499	63.5
116.4	5	1.399	59.2

Set 2

 $P_a = 0.466$ mm., $P_b = 0.245$ mm. $n_0 = 0.863 \times 10^{-5}$ mole/sec.

14.1	5	2.133	87.9
38.0	5	1.702	73.8
63.0	5	1.381	59.5
87.5	5	1.114	48.3
112.0	5	0.994	42.8

Set 3

 $P_a = 0.648$ mm., $P_b = 0.485$ mm. $n_0 = 0.891 \times 10^{-5}$ mole/sec.

13.1	5	1.933	76.8
38.7	5	1.138	47.3
63.2	5	0.779	32.4
87.6	8	.883	23.2
112.4	10	.874	18.5

Set 4

 $P_a = 0.802$ mm., $P_b = 0.682$ mm. $n_0 = 0.835 \times 10^{-5}$ mole/sec.

14.1	5	1.537	65.7
38.8	6	0.870	32.6
64.0	10	.874	19.6
88.7	14	.889	14.2
111.0	15	.719	10.6

^a a and b are positions of the taps to the McLeod gage from the lower and upper ends of the recombination tube, respectively. ^b P_a and P_b are averages for separate runs in a set (measured at least twice during each run). The maximum deviation of the individual values from the recorded average was 3%.

(9) When the calorimeter was quite close (10 to 15 cm.) to the discharge tube, this value was 110 calories per millivolt as compared to 115 calories per millivolt for all other positions along the recombination tube ab. The lower value is no doubt due to heat conduction from the discharge tube.

(10) Richardson and Davidson, *Proc. Roy. Soc. (London)*, **A123**, 466 (1929).

To calculate reaction velocity constants for the various possible kinetic processes, a knowledge of the variation of pressure along the vertical recombination tube is necessary. Smallwood attempted to measure the change of pressure with distance by sealing in pressure taps at points along the tube and connecting the taps to the McLeod gage. He was unsuccessful, probably because of a catalytically active tube. We were

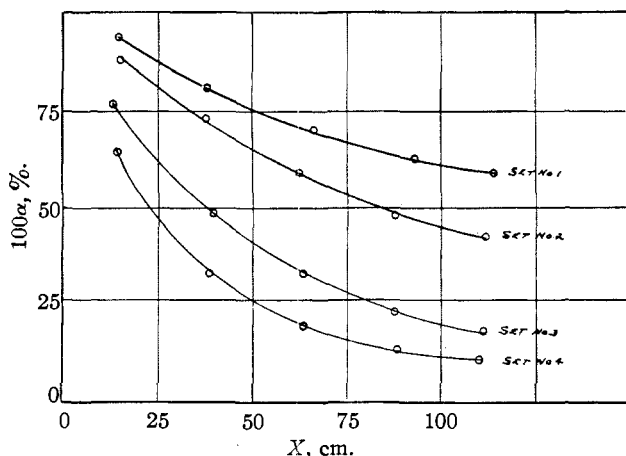


Fig. 2.—Percentage of atomic hydrogen vs. distance from discharge.

more fortunate in our attempt. In Fig. 3 are shown the experimental values and smoothed curves for the variation of pressure along the recombination tube for the conditions corresponding to sets 1-4 of Table I. The pressure values as read from these curves check within 0.5 to 3% the values given by the approximate formula of Smallwood, namely

$$P = (P_a^2 - \beta x)^{1/2} \quad (2)$$

and justify the assumption of viscous flow in the gas stream. The following derivation of the differential equation for the rate of decrease of hydrogen atoms is chiefly that used by Steiner and Wicke,⁴ modified to take account of the variation of pressure along the tube. In the experiments of Steiner and Wicke this variation was small (about 10%) and consequently was neglected.^{10a}

Assuming the absence of a wall reaction the variation of the number of hydrogen atoms with time may result from the following three processes (1) by recombination in triple collision

$$\left(\frac{\partial[\text{H}]}{\partial t}\right)_x = -k[\text{H}]^2([\text{H}] + [\text{H}_2]) \quad (3)$$

(10a) For a criticism of the equation of continuity used by Steiner and Wicke see Amdur, *Phys. Rev.*, **43**, 208 (1933).

(2) by the streaming of atoms from the discharge tube

$$\left(\frac{\partial[\text{H}]}{\partial t}\right)_x = -\frac{\partial(V_x[\text{H}])}{\partial x} \quad (4)$$

where v_x is the linear velocity (in centimeters per second) of the gas at the point x

$$V_x = \frac{n_0}{\pi r^2([\text{H}_2] + 0.5[\text{H}])} \quad (5)$$

(3) by diffusion of atoms

$$\left(\frac{\partial[\text{H}]}{\partial t}\right)_x = D \text{ div. grad. } [\text{H}] \quad (6)$$

where D is the diffusion coefficient for atomic and molecular hydrogen.

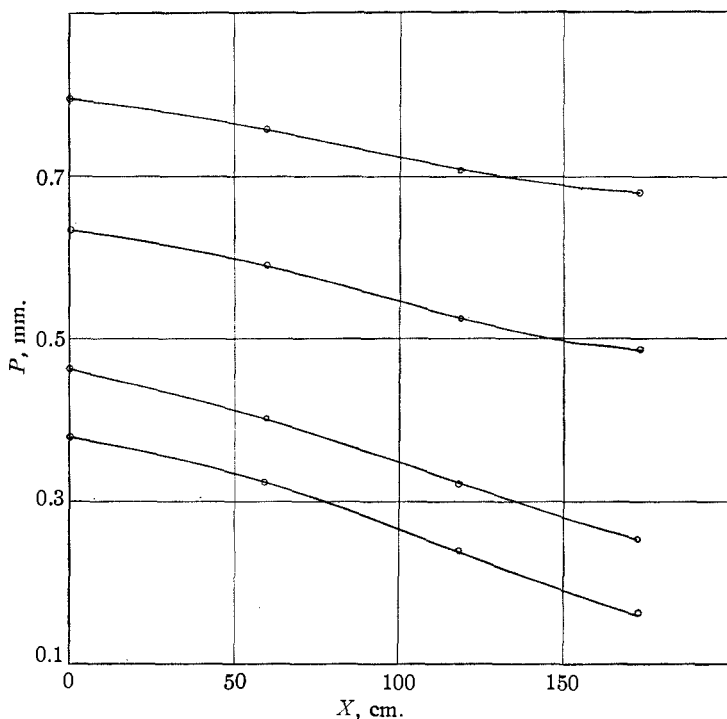


Fig. 3.—Pressure variation along the recombination tube.

Since the system represents a steady state in which $(\partial[\text{H}]/\partial t)_x = 0$, we obtain from equations 3, 5 and 6

$$D \text{ div. grad. } [\text{H}] - \frac{\partial(V_x[\text{H}])}{\partial x} - k[\text{H}]^2([\text{H}] + [\text{H}_2]) = 0 \quad (7)$$

Assuming that the concentrations of atoms in a plane perpendicular to the tube ab at any given point is essentially constant, Equation 7 takes the form

$$D \frac{\partial^2[\text{H}]}{\partial x^2} - \frac{\partial(V_x[\text{H}])}{\partial x} - k[\text{H}]^2([\text{H}] + [\text{H}_2]) = 0 \quad (8)$$

In order to obtain the value of k from experimentally determined data Equation 8 must be integrated. This is not readily accomplished by the ordinary methods for solving differential equations. If, however, one uses the differential equation directly by substituting slopes¹¹ determined graphically from experimental curves, and neglects the term $D\partial^2[H]/\partial x^2$ (since its magnitude is only about 10^{-8} times that of $\partial(V_x[H])/\partial x$), the expression for k becomes

$$k_1 = \frac{-\frac{\partial(V_x[H])}{\partial x}}{[H]^2([H] + [H_2])} = \frac{-\partial\left(\frac{n_0[H]}{\pi r^2([H_2] + 0.5[H])}\right)}{[H]^2([H] + [H_2])} \quad (9)$$

Equation 9 assumes that the wall effect is absent and that hydrogen atoms and molecules are equally efficient third bodies. If only hydrogen molecules are considered as possible third bodies, the above expression becomes

$$k_2 = -\frac{\partial\left(\frac{n_0[H]}{\pi r^2([H_2] + 0.5[H])}\right)}{\frac{\partial x}{[H]^2[H_2]}} \quad (10)$$

and for atoms as the only possible third bodies

$$k_3 = -\frac{\partial\left(\frac{n_0[H]}{\pi r^2([H_2] + 0.5[H])}\right)}{\frac{\partial x}{[H]^3}} \quad (11)$$

In the above expressions the concentrations of atoms and molecules in moles per cc. are given by the relations

$$\begin{aligned} [H] + [H_2] &= \frac{1332 P}{RT} = P(5.42 \times 10^{-8}) \\ [H] &= \frac{1332 P}{RT} \frac{2\alpha}{1 + \alpha} = \frac{P(5.42 \times 10^{-8})2\alpha}{(1 + \alpha)} \\ [H_2] &= \frac{1332 P}{RT} \frac{1 - \alpha}{1 + \alpha} = \frac{P(5.42 \times 10^{-8})(1 - \alpha)}{(1 + \alpha)} \end{aligned}$$

where P , taken from the curves of Fig. 3, is expressed in mm. The values of R and T are 8.32×10^7 ergs per mole per degree and 296°K ., respectively. Making the proper substitutions, Equations 9, 10 and 11 take the forms

$$\begin{aligned} k_1 &= -\frac{\frac{\partial\alpha}{\partial x} 2n_0(1 + \alpha)^2}{\pi r^2 P(5.42 \times 10^{-8})^2 4\alpha^2} \\ k_2 &= -\frac{\frac{\partial\alpha}{\partial x} 2n_0(1 + \alpha)^3}{\pi r^2 P(5.42 \times 10^{-8})^2 4\alpha^2(1 - \alpha)} \\ k_3 &= -\frac{\frac{\partial\alpha}{\partial x} 2n_0(1 + \alpha)^3}{\pi r^2 P(5.42 \times 10^{-8})^2 8\alpha^3} \end{aligned}$$

The units of the constants calculated in this manner are $\text{cc.}^2 \text{mole}^{-2} \text{sec.}^{-1}$.

(11) The use of slopes is probably more accurate than Steiner and Wicke's use of increments.

TABLE II
SUMMARIZED VALUES OF REACTION VELOCITY CONSTANTS

x	$\frac{\partial \alpha}{\partial x}$	α	P	$k_1 \times 10^{-15}$	$k_2 \times 10^{-15}$	$k_3 \times 10^{-15}$
25	0.00527	0.868	0.358	16.8	238	18.1
45	.00406	.773	.338	17.4	136	20.0
65	.00324	.702	.316	18.9	108	22.9
85	.00239	.647	.292	19.6	91	24.9
105	.00175	.606	.262	21.4	87	28.4
25	.00612	.808	.438	11.3	106	12.6
45	.00556	.689	.421	13.8	75	16.9
65	.00480	.581	.399	17.2	65	23.4
85	.00378	.494	.371	20.8	61	31.5
105	.00202	.441	.342	16.6	43	27.1
25	.0108	.597	.617	10.5	42	14.0
45	.00664	.426	.603	10.8	26.8	18.0
65	.00479	.316	.587	13.0	25.0	27.2
85	.00285	.233	.569	13.2	21.5	34.2
105	.00180	.194	.540	13.8	20.5	42.5
25	.0118	.452	.779	7.7	20.4	12.4
45	.00580	.287	.769	7.6	13.7	17.1
65	.00330	.196	.754	8.6	12.8	26.2
85	.00199	.146	.737	9.1	12.2	35.7
105	.00139	.113	.716	10.9	13.7	53.6

The constants in Table II were calculated for the reaction at 23°.

The accuracy of the experiments was limited by the reproducibility of results and the usual errors of calorimetry. Each of these sources it is estimated might contribute a maximum error of about 2%, making the combined effect about 4% at the most. The question as to whether all atoms collide with the catalyst¹² is settled definitely by the Einstein-Smoluchowsky formula for the time required for a particle in the center of a tube of radius r to diffuse to the walls. The formula is

$$t = \frac{3\pi r^2}{4Lc}$$

where L is the mean free path under existing pressure conditions and c is the mean molecular velocity at the temperature in question. Substitution of approximate values in the above expression shows that the time required for an atom in the flowing gas stream to hit the wall (or interior of the cylindrical catalyst) is small enough to insure complete recombination of all the atoms on less than 4 mm. of catalyst, if the catalyst is perfectly efficient. That such is actually the case was proved by Smallwood, who showed, in addition, that heat conduction from the discharge or transfer of energy by metastable molecules was negligibly small.

Discussion

The calorimetric method of measuring atomic hydrogen concentrations has been criticized by von Wartenberg and Schulze⁷ and Steiner and Wicke⁴

(12) Steiner and Wicke (Ref. 4) seem to feel that the calorimetric method yields low results.

on the ground that the abrupt recombination of atoms on the catalyst produces a pressure drop which in turn causes a sudden diffusion of the gas mixture at the catalyst. Although these authors claimed that the effects of diffusion are sufficient to vitiate results obtained by the calorimetric method, they made no attempt to calculate or determine the magnitude of the effect. It might be pointed out, in addition, that due to a slight lag in the transfer of heat to the calorimeter the catalyst is somewhat warmer than the gas stream below it. This would tend to warm the gas and cause additional diffusion. In order to determine definitely the contribution of these diffusion effects, pressure measurements were made at various points along the recombination tube with the discharge on, first with the catalyst present and then with the catalyst removed. It was found that the large linear velocities of the gas stream (9 to 12 meters per second) seem to overcome the pressure drops due to diffusion since pressures measured at various points along the tube were independent of the position of the catalyst in the tube and did not change when the catalyst was removed.

The presence of a wall reaction as a factor in the recombination of hydrogen atoms is still subject to question. Smallwood, using an apparatus whose walls were poisoned by water vapor introduced with the hydrogen, found that it was possible for the entire reaction to take place within 10^{-7} cm. of the wall if the reaction were represented as second order with respect to hydrogen atoms, the wall itself being the third body. He decided against a first order wall reaction since this would require an adsorbed layer of atomic hydrogen on the tube walls in spite of the fact that the tubing had not been baked out previously and was constantly covered with a water layer. Von Wartenberg and Schulze found that atomic hydrogen is reflected from aqueous films, not adsorbed. Moreover, a monomolecular reaction would give a wall process with a rate 10^5 times as great as the actual measured recombination rate.

Senftleben and Riechemeier, on the other hand, found a first order wall reaction whose magnitude varied from experiment to experiment but was always quite small. Steiner and Wicke do not regard these results as conclusive since, due to extremely low percentages of atomic hydrogen (less than 0.1%), only the very end portion of the reaction was being investigated. The statement of Steiner and Wicke that the wall reaction is negligible is based on the constancy of their trimolecular rate constants with respect to time and pressure. They present evidence to the effect that a wall reaction, if it existed, should be monomolecular, making impossible the obtaining of good trimolecular constants for the gas phase reaction if an existing wall effect is neglected. An additional argument given by these authors is the reproducibility of results with a tube coated with either water vapor or sirupy phosphoric acid.

In the case of our experiments, it was found that water vapor was not effective in producing a catalytically inert tube. The catalytic activity in this case was thought to be due to traces of metal rubbed off the brass chain supporting the catalyst. Coating the tube with sirupy phosphoric acid and replacing the brass chain by a less corrosive German silver chain produced an apparatus in which reproducible results could be obtained when runs were not taken at too widely separated intervals. That a wall reaction is present nevertheless in this investigation is indicated by the drift of the constants. The contribution to the total rate, however, is probably small, inasmuch as the values of our constants do not differ materially from those of Steiner and Wicke, who used a recombination tube of much larger diameter. Furthermore, the values of our constants obtained from experiments in a tube coated with sirupy phosphoric acid are in good agreement with those of Smallwood obtained in a tube coated with water vapor.

In regard to the gas phase reaction, the nature of the apparent rate constants in the present investigation indicates a more complicated mechanism than that proposed by Steiner and Wicke, who claim that only hydrogen molecules are significantly effective as third bodies in the reaction. Their statement is based on the fact that the rate constants for the reaction between two atoms and a molecule have values in all experiments of $9 \pm 2 \times 10^{15}$ cc.² mole⁻² sec.⁻¹, while the rate constants for the reaction in which molecules and atoms are regarded as equally efficient third bodies vary considerably and show definite drifts. However, an inspection of the data of Steiner and Wicke indicates that their accuracy cannot be high, certain experimental points deviating by 70% from the smoothed curves drawn. Further uncertainty is introduced by the calibration of the intensity of the H_α line, so that the calculated rate constants depend to some degree upon what seems to be an arbitrary selection of experimental values and the constancy found must be partly fortuitous. In a recent theoretical article¹³ Steiner considers the homopolar valence binding forces acting between two hydrogen atoms and the probability of resonance interchange between this atom pair and a hydrogen molecule, and concludes that this process could be mainly responsible for the combination of hydrogen atoms, in agreement with the experimental results of Steiner and Wicke. Kimball¹⁴ has pointed out that there is an equally probable way in which this triple collision could take place, first a collision between a hydrogen atom and a hydrogen molecule followed by a collision with the second hydrogen atom. A kinetic study cannot distinguish between these two mechanisms since both are expressed formally by $d(\text{H})/dt = -k(\text{H})^2(\text{H}_2)$; only the calculation of kinetic theory diameters is affected.

That a triple collision of three hydrogen atoms leading to the forma-

(13) Steiner, *Z. physik. Chem.*, **B15**, 249 (1932).

(14) Kimball, *THIS JOURNAL*, **54**, 2396 (1932).

tion of a hydrogen molecule does not involve an energy of activation is indicated by Eyring's¹⁵ potential energy diagram for this system. Our results indicate that both types of triple collisions contribute to the formation of hydrogen molecules. The constants for the reaction involving two atoms and a molecule, k_2 , tend to reach a constant value only in regions of high molecular (low atomic) hydrogen percentages, while the constants involving three atoms, k_3 , drift in the opposite direction. This is particularly noticeable in the runs where the atomic hydrogen percentage varied four- and six-fold (see Sets Nos. 3 and 4, Tables I and II), indicating the presence of two reactions, namely, collisions of two atoms and a molecule and collisions of three atoms, the former predominating at low atomic hydrogen percentages and the latter at high atomic hydrogen percentages. The fact that the variation of k_1 , which involves equally efficient collisions of two atoms with either a third atom or a molecule, is less than that of k_2 or k_3 tends to confirm the presence of two reactions. These one to one efficiencies may be considerably varied (ratio of atom efficiency to molecule efficiency may be as small as one to four) without appreciably changing the values of k_1 . One may conclude, therefore, that the results of this investigation cannot be represented by Steiner's mechanism alone since the best trimolecular constants are obtained only when the effects of both hydrogen atoms and molecules as third bodies are taken into account, an efficiency for molecules four times that for atoms being permissible.

Some measurements of the reaction velocity have been made in the temperature range 194 to 372°K. We hope to discuss these measurements in an article now in preparation.

We wish to extend our sincere thanks to Professor A. E. Ruark of the Department of Physics, University of Pittsburgh, for his generous aid and advice offered throughout the course of this investigation.

Summary

1. Objections raised against the calorimetric method for determining percentages of atomic hydrogen in an atomic-molecular hydrogen gas mixture have been discussed. Diffusion due to the large pressure drop caused by recombination of atoms on the catalyst and by the heating of the gas stream by the warm catalyst seems to be minimized by the large linear velocities of the gas stream, since pressure measurements cannot detect the effects of such a diffusion.

2. There is a possibility of the existence of a wall reaction in the recombination of hydrogen atoms, but the facts that the rate constants for the reaction between three hydrogen atoms at high atomic hydrogen percentages do not vary greatly with pressure and that consistent results are ob-

(15) Eyring, *THIS JOURNAL.*, **53**, 2537 (1931); *Chem. Rev.*, **10**, 103 (1932).

tained in different apparatus under different conditions of the wall surface indicate that the contribution of the wall reaction to the total rate is small.

3. Both atoms and molecules can act as third bodies with an allowable greater efficiency for molecules.

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Azeotropic Hydrobromic Acid Solutions at Pressures of 100 Mm. to 1200 Mm.

BY WALTER D. BONNER, LYMAN G. BONNER AND FRANCIS J. GURNEY

Some years ago we undertook as a part of the research program of this Laboratory a careful study of the boiling points, compositions, and densities of the azeotropic or "constant-boiling" acid solutions. The present paper represents the second acid thus far studied, the data on hydrochloric acid having been already published.¹

Preparation of Hydrobromic Acid.—Two different methods were used in preparing the hydrobromic acid. The simpler was that of reduction of bromine by sulfur dioxide in the presence of sufficient water to give a solution of approximately constant boiling composition. This solution when freed of excess sulfur dioxide contained, of course, the equivalent amount of sulfuric acid, but the more volatile hydrobromic acid was readily removed from this by distillation. After this first distillation the HBr solution was treated with an excess of solid barium bromide and again distilled. The sulfate-free acid was then repeatedly redistilled, rejecting the first and the last portions, until a solution was obtained which was constant boiling at atmospheric pressure, and which also was free from any analytically significant impurity. In some cases we used bromine which we had carefully purified by the method of Baxter² while in other cases we used bromine of "reagent" quality, without further purification. The final acid solutions could not be distinguished.

The second method of preparation of hydrogen bromide solutions was that of direct synthesis from the elements. The hydrogen bromide solutions prepared by this method were indistinguishable from those prepared by the simpler method. Most of our acid was consequently made by the first method.

Preparation of Azeotropic Solutions.—The methods were much the same as those used previously for preparing constant boiling hydrochloric acid.¹ Due, however, to the particularly corrosive character of

(1) Bonner and Branting, *THIS JOURNAL*, **48**, 2093 (1926); Bonner and Titus, *ibid.*, **52**, 633 (1930); Bonner and Wallace, *ibid.*, **52**, 1747 (1930).

(2) Baxter, *ibid.*, **28**, 1325 (1906).