[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Rate of Recombination of Atomic Hydrogen. II

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The early work on the kinetics of the association of free hydrogen atoms has been ably discussed by Kassel.[1,2,3] All the data so far obtained at pressures less than atmospheric are in agreement with the order of magnitude expected from the predicted triple impact mechanism. The more interesting question of the relative efficiencies of the various third bodies, in effecting combination of two hydrogen atoms, has received a variety of answers.

In order to avoid the difficulties of interpreting the data obtained in a flowing system, it has seemed worth while to measure the rates of combination in a static system. This has been accomplished by noting the rate of change of pressure during the recombination of partially dissociated hydrogen.

Experimental

Outline of Procedure.—The method employed in making the measurements is obvious from Fig. 1, which shows the important features of the apparatus. Atomic hydrogen is allowed to flow through the reaction bulb A until the desired set of conditions is reached. The mercury is then raised in the traps BB by allowing the sinkers CC to drop into the wells connected with the traps. The bulb is thus isolated from the remainder of the apparatus. The course of the reaction is followed by means of the membrane manometer D which measures the difference between the pressure in the bulb and the constant pressure in the chamber surrounding the manometer. From these pressures, recorded at suitable time intervals, together with the pressure in the bulb at the completion of the reaction, the time variation of the partial pressure of atomic hydrogen may readily be calculated.

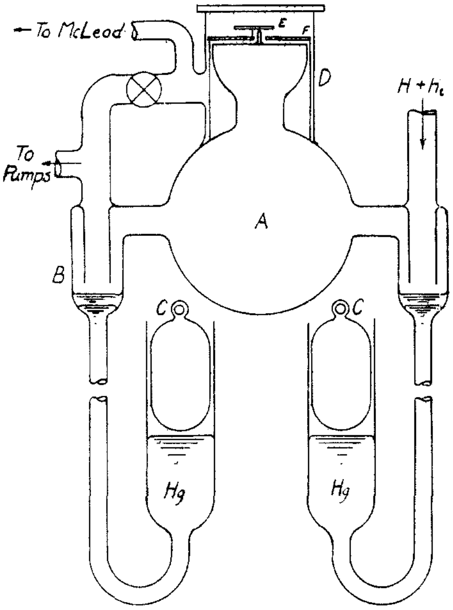

Fig. 1.

Source of Atomic Hydrogen.—The initial dissociation of the hydrogen was produced by means of the familiar Wood tube. Cylinder hydrogen was led through a water bubbler and then expanded through a system of capillaries to pressures of a few tenths of a millimeter of mercury. The pressure in the apparatus was varied by opening or closing the stopcocks leading to the individual capillaries. The discharge tube was of the conventional type, operating at 5–6 kilovolts and 300 milliamperes a. c. The pressure changes recorded by the manometer upon closing the traps corresponded to initial concentrations of the atomic hydrogen of 20–30% of the hydrogen present.

Wall Poisoning.—It was, of course, necessary to prevent contact between the atomic hydrogen and the mercury in the traps. The customary sirupy phosphoric acid could not be used for this purpose since it either was too viscous to cover the moving mercury, or had a vapor pressure sufficiently high to cause ebullition. Concentrated sulfuric acid was found to possess the desired properties. Preliminary experiments showed that, at room temperatures, neither the liquid nor vapor reacts with atomic hydrogen. Presumably the acid absorbed some water vapor from the moist hydrogen when the apparatus was first put in use, but it must soon have come to equilibrium since no pressure changes were ever observed which could be ascribed to clean-up of water vapor by the acid. In addition to protecting the mercury surfaces the sulfuric acid was found to be a very efficient poison for the catalytic effects usually encountered in working with atomic hydrogen. After a few days of exposure to the vapor, in equilibrium with the liquid at room temperature, even scraps of massive platinum are rendered entirely inert. Their activity is, of course, regained on heating in hydrogen.

Manometer.—The type of manometer most suited for the present purpose has been described by Stewardson.[4] The present gage was constructed by blowing a very thin bulb on the end of a tube 2.5 cm. in diameter. This bulb was flattened with a hand torch nearly to its equator, resulting in a membrane 7.5 cm. in diameter. The manometer was then sealed to the bulb of a 2-liter distilling flask as shown in Fig. 1. Membrane manometers of this type are, of course, rather fragile. They can be made suffi-

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(1) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932.

(2) I. Amdur and A. L. Robinson, THIS JOURNAL, **55**, 1395 (1933).

(3) A. L. Robinson and I. Amdur, *ibid.*, **55**, 2616 (1933).

(4) E. A. Stewardson, *J. Sci. Inst.*, **7**, 217 (1930).

ciently sensitive, however, and yet capable of withstanding pressure differences of several centimeters of mercury.

Displacements of the membrane were observed by means of an optical lever. A short glass rod was cemented with sealing wax to the center of the membrane. On this rod rested a plane mirror, 2.54 cm. in diameter (*E*, Fig. 1). Vertical displacements of the membrane were thus translated into rotations of the mirror about its axis. The axis was defined by a grooved steel plate cemented to the bottom of the mirror, the groove bearing on the points of two needles set in the brass plate F. This plate was supported by a glass sleeve resting on the reaction bulb, the plate and sleeve being fixed in their respective positions with sealing wax. The whole assembly was encased in a large glass tube, topped with plate glass and sealed to the reaction bulb with sealing wax. It was found necessary to lute the ground joint between the casing tube and the glass plate with beeswax and resin. Elsewhere the German "Weisssiegillack" was employed.

The reaction was sufficiently rapid to necessitate photographic recording of the pressure change. This was most readily effected by using as light source for the optical lever a neon crater lamp of the type used in television. The light beam passed through a suitable lens, was reflected from the manometer mirror, suffered a second reflection from a stationary mirror, and was finally focused on a piece of bromide printing paper affixed to a rotating drum. The length of the light path from the manometer mirror to the recording paper was about 130 cm., corresponding to an approximately thousand fold magnification of the membrane displacement. The image of the crater produced a roughly circular spot on the bromide paper about 1 mm. in diameter. The drum was driven electrically at 1 r. p. m., corresponding to a linear velocity of the bromide paper of 11.4 cm. per minute. In order to obtain a simultaneous time record the neon lamp was not allowed to burn continuously, but was flashed at one second intervals. The flashes were timed by a Telechron clock, their duration being about 0.05 sec. In this way it was possible to record the pressure difference across the manometer membrane at intervals of one second.

The manometer was calibrated against McLeod gages of an accuracy of ±0.001 mm. In the final series of experiments the sensitivities of the manometer were from 0.0220 to 0.0388 mm. pressure difference per cm. displacement of light spot. The positions of the darkenings on the bromide paper produced by the flashes of the neon lamp were measured to within ±0.01 cm. with a cathetometer. Pressures in the reaction bulb were thus determined with an accuracy equal to that of the McLeod gages.

The manometer was found to be reasonably free from vibration and to be capable of following pressure changes much more rapid than those caused by the reaction to be measured. The displacement of the light spot was a linear function of the pressure difference across the membrane over a sufficiently wide range. For any particular setting of the optical lever, the sensitivity was constant within the accuracy of the measurement. The greatest defect of the apparatus was the variability of the zero of the manometer. This was uncertain by several tenths of a millimeter displacement, and constituted the dominant error in the experiments. This lack of stability was presumably due to alterations in the contact between the manometer mirror and the glass rod.

Details of Procedure.—Typical records of experiments are shown in Figs. 2A and 2B. The coördinates of these pressure–time curves are shown on the margins. During the experiment the recording paper is wrapped on a cylindrical drum so that points a and b are coincident with a′ and b′, respectively. The line of spots at the bottom of each record corresponds to the pressure in the reaction bulb during the flow, *i. e.*, while the traps are open. Closing of the traps (point c) results in a sudden increase in the pressure in the bulb since the outlet trap closes a fraction of a second before the inlet trap. The curve d–e shows the pressure drop during the first 43 sec. of the reaction. The subsequent groups of points (f, g, h, etc.) are taken at successive intervals of 65 sec. and serve to determine the pressure at the completion of the reaction. The line m–m is taken at a known, constant pressure difference in order to determine the horizontal axis and the zero point of the manometer during the experiment. Room temperature and the pressure in the chamber surrounding the manometer were read before and after each experiment.

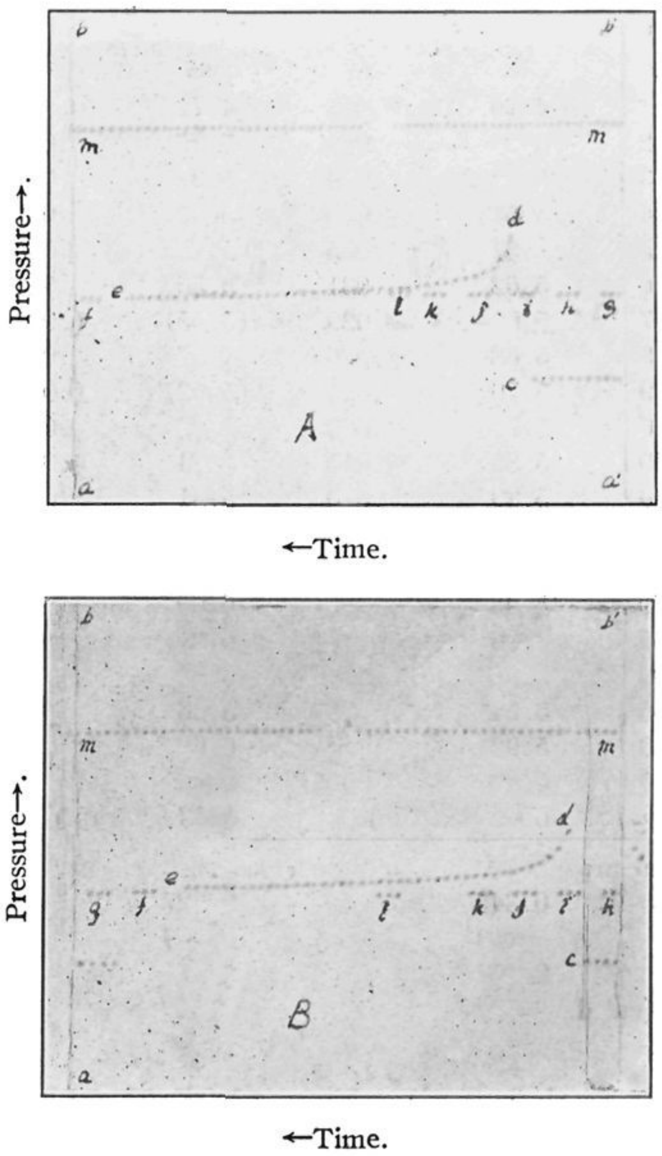

Fig. 2.

Most of the measurements were made at room temperature (25 ± 1.5°). In order to obtain information on the temperature coefficient of the reactions, the bulb was, in one series of runs, cooled by a rapid spray of tap water.

Although this method of temperature control was rather crude, it resulted in cooling the bulk of the reacting gas by about 15°.

Results

Method of Calculation.—In Table I are listed all the data relevant to the records of Figs. 2A and 2B, together with the calculated partial pressures of atomic hydrogen. All pressures are recorded in mm.

TABLE I

	A		B	
Room temp.	24.5°		26.2°	
P_1	0.113		0.116	
t	s, cm.	P_H	s, cm.	P_H
1	4.79	0.098	4.72	0.104
2	5.25	.060	5.09	.073
3	5.43	.046	5.27	.059
4	5.53	.038	5.39	.050
5	5.57	.035	5.45	.045
6	5.62	.031	5.50	.041
7	5.65	.029	(5.55)	(.037)
8	5.68	.026	5.57	.036
9	5.70	.025	(5.62)	(.032)
10	5.73	.023	5.62	.032
20	5.83	.015	5.74	.023
30	5.89	.010	5.81	.017
40	5.92	.008	5.86	.013
105	5.97		5.95	
170	5.98		6.00	
235	5.96		6.01	
300	5.95		6.01	
365	5.94		6.00	
430	5.92		6.00	
495	5.89		6.03	
∞	6.02 (extrap.)		6.03 (extrap.)	
Line m–m:				
P_2	0.345		0.327	
P_1	.113		.116	
s	2.46		2.67	
s_0 (calcd.)	8.70		8.84	

$m = 0.0388$

The symbols in this table have the following meanings. P_1 represents the pressure in the chamber surrounding the manometer, P_2 the pressure in the reaction bulb. The s's represent the heights of the various spots on the records, measured from an arbitrary zero. The pressures in the bulb are related to these by the equation

$$P_2 - P_1 = m\,(s_0 - s)$$

The partial pressures of atomic hydrogen are calculated from the equation

$$P_H = 2\,m(s_f - s)$$

where s_f is the s corresponding to $t = \infty$.

Blank experiments showed that the closing of the traps caused a slight compression of the gas in the bulb. This was noticeable for the first few points of the run and was corrected for in calculating the partial pressures of atomic hydrogen at these points. In the runs tabulated this amounted to the addition of 0.03 cm. to the first $(s_f - s)$.

It will be noticed that the last six measured points of run A show a gradual *increase* in the reaction bulb pressure. This indication is due to a slow drift of the manometer zero, caused by small temperature differences in the apparatus, and was of fairly frequent occurrence. It was measured in a series of blank experiments made under conditions identical with those of the actual experiments, except for the absence of the atomic hydrogen, and was corrected for in the extrapolation of s to infinite time.

The seventh and ninth readings in run B are enclosed in parentheses. Inspection of Fig. 2B shows that these points are blurred and definitely off the smooth curve defined by the remaining points. Such irregularities were occasionally noticeable; they were caused by transitory vibrations of the manometer assembly. When definitely pronounced, as in run B, such points were omitted from the subsequent calculations.

The velocity constants are calculated from the experimental data in the following manner. The differential equation of the combination of hydrogen atoms by triple collisions with the wall, hydrogen atoms, and hydrogen molecules is

$$-\mathrm{d}[\mathrm{H}]/\mathrm{d}t = K_1[\mathrm{H}]^2 + K_2[\mathrm{H}]^3 + K_3[\mathrm{H}]^2[\mathrm{H}_2] \quad (1)$$

which may be rewritten in the more convenient form

$$-\frac{\mathrm{d}P_H}{\mathrm{d}t} = \left\{\frac{K_1}{RT} + \frac{K_3}{(RT)^2}P_f\right\}P_H{}^2 + \frac{1}{(RT)^2}\left(K_2 - \frac{1}{2}\underline{K_3}\right)P_H{}^3 = aP_H{}^2 + bP_H{}^3 \quad (2)$$

The integrated form of this equation is not well adapted for the determination of the constants a and b. It is altogether more satisfactory from the points of view of both convenience and accuracy to obtain them graphically This can be done by writing equation (2) as

$$\mathrm{d}(1/P_H)/\mathrm{d}t = a + bP_H \quad (3)$$

If the difference quotients, $\Delta(1/P_H)/\Delta t$, are plotted against the average values of P_H during the intervals Δt, one should obtain a straight line whose intercept at $P_H = 0$ gives the bimolecular constant a, and whose slope gives the trimolecular constant b. Figure 3 shows a number of such lines, the figures on the left end of each line giving the values of a and b found from the plot.

Since the partial pressure of atomic hydrogen is proportional to $s_f - s$, the relative experimental error in the measure of P_H increases rapidly as the reaction proceeds. For this reason only the data obtained in the first ten seconds of each experiment were included in the calculations of the rate constants, and greater weight was given to the points corresponding to high P_H in drawing the straight lines of Fig. 3.

A large number of experiments were made according to the above procedure. In the following paragraphs are summarized all of the data obtained with the final design of manometer mirror mounting, with the exception of two in which manometer vibration obscured the records. The data obtained prior to this were less accurate than those to be reported and are, therefore, omitted. To within the limit of their accuracy, however, they were in accord with the final results.

The Bimolecular Reaction.—The bimolecular part of the recombination of hydrogen atoms (constant a, equation (2)) has been found to depend on the pretreatment of the wall of the reaction bulb. At the start of a series of measurements, prior to which the reaction bulb was filled with air at atmospheric pressure for an appreciable time, a was found to have a relatively large value. This decreased with the time during which atomic hydrogen flowed through the bulb until it became negligibly small. Molecular hydrogen flowing through the bulb at a few tenths of a millimeter of mercury also tended to lessen the bimolecular reaction, but was not as efficient in so doing as was atomic hydrogen. After the constant a had become zero, further treatment of the bulb wall with atomic hydrogen caused no change in the rate constants deduced from the measurements. This behavior is shown in more detail by the data of Table II, in which are summarized two series of consecutive runs.

TABLE II

P_f	T, °C.	a	b	Pretreatment of wall
				Series 1
0.208	24.5	1.5 (A)	60	Air, 1 atm., 40 hrs.
.178	24.8	1.2 (B)	45	H, 0.1 mm. Hg, 1/2 hr.
.181	25.2	0.7	50	H_2, 0.1 mm. Hg, 2 hrs.
.196	26.3	0 (C)	49	H, 0.1 mm. Hg, 1 1/4 hrs.
.461	25.5	0	41	H, 0.3 mm. Hg, 2 hrs.
				Series 2
				Air, 1 atm., 40 hrs.
0.227	24.3	1.7	49	H, 0.1 mm. Hg, 1/2 hr.
.178	25.3	1.0	50	H_2, 0.1 mm. Hg, 3 1/2 hrs.
.194	26.7	0	50	H, 0.1 mm. Hg, 1 hr.

The records of the runs marked (A) and (C) are shown as Figs. 2A and 2B. Complete data for these runs are given in Table I. The plots of $\Delta(1/P_H)/\Delta t$ vs. P_H for runs (A), (B), (C) of Table II are shown in Figs. 3A, 3B, 3C.

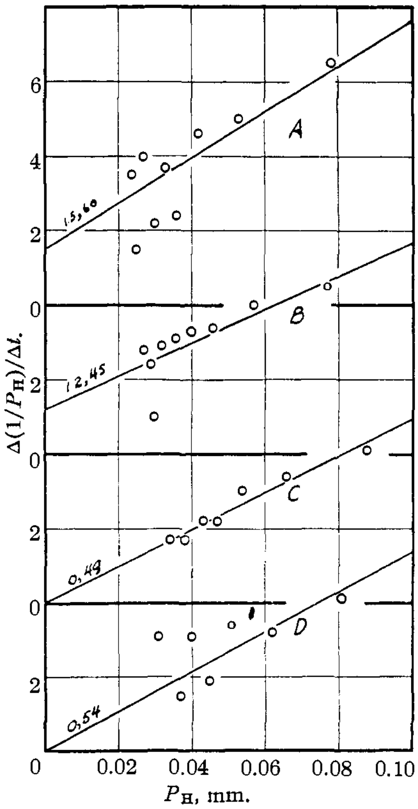

Fig. 3.

Elimination of the bimolecular reaction was effected much more readily when the apparatus was in use every day. The amount of rinsing with atomic hydrogen which was needed to bring a to zero was roughly proportional to the time during which the apparatus had been filled with air, up to four or five days. Disuse for longer periods produced no noticeable additional effect.

The Trimolecular Reaction.—The trimolecular constant, b, is most accurately determined from those runs in which the bimolecular reaction was eliminated, since, when this was the case, the observed pressure drops were larger. All of the runs in which a was essentially zero are tabulated in Table III.

The graphical determination of the constant was sufficiently accurate for the quality of the initial data. The points of Fig. 3 show the extent of definition of the lines drawn. In Fig. 3C the points lie more nearly on the line than

TABLE III

TRIMOLECULAR RATE CONSTANTS

P_f	t, °C.	b
0.194	26.7	50
.196	26.3	49
.223	24.7	60
.272	23.3	57
.279	25.9	57
.323	26.2	50
.345	26.0	54
.348	26.9	46
.402	25.1	40
.459	23.9	48
.461	25.5	41
.480	25.2	45
	Average	50

usual; Fig. 3D shows the worst set of points obtained in the runs of Table III.

The individual points of the runs are well represented by the integral of (2) with $b = 50$ and the appropriate value of a. The greatest deviation of the points from these curves is 0.004 mm.; in general the agreement is within ±0.001 mm.

The Temperature Coefficient.—Three runs were made during which the reaction bulb was immersed in a stream of tap water at 8.5°. Prior to these a run at room temperature showed the bimolecular reaction to have been eliminated in the usual manner. In spite of this the first run at the low temperature gave a value of $a = 2$ and $b = 55$. This was the only instance in which a bimolecular reaction reappeared after its elimination, without an intermediate filling with air. The two other low temperature runs showed $a = 0$ and $b = 60$ and 67.

Although the average of these three values of the trimolecular rate constant (61) is greater than the average of the values obtained at room temperature (50), the difference is barely outside the probable error of the determinations.

Afterglow.—Throughout these experiments it was necessary to mask the light from the discharge in order to avoid fogging the bromide paper. It was, therefore, possible to observe the afterglow accompanying the recombination. This glow has been reported by Kaplan.[5] It is too feeble to be seen when the light from the discharge is not screened off, but, when this is done, it appears as a faint yellow glow extending through the apparatus, diffusing into dead ends to distances of a meter or more from the main stream. When the bimolecular reaction had been suppressed, it extended through a carbon dioxide trap, terminating in the characteristic blue luminescence of atomic hydrogen and mercury vapor, the latter coming from the diffusion pump.

Under the conditions of the runs reported above, the afterglow was visible in the reaction bulb for about one minute after closing the traps. Variations of pressure and temperature did not noticeably affect this duration, but, when the amount of water vapor carried by the incoming hydrogen was increased, the afterglow lasted as much as ten minutes after the traps were closed. This is strong indication that the luminescence is produced in a side reaction between atomic hydrogen and water or its decomposition products.

Discussion

Critique of the Method.—The foregoing calculations of the experimental data have been based on the assumptions that, during the recombination, the temperature and concentration of atomic hydrogen are constant throughout the reaction bulb. If, at the start of the reaction, there were appreciable heating of the gas, errors might be introduced in either of two ways. First, the rate of recombination might be altered as a result of the temperature change. Second, the observed pressure drop, which has been ascribed wholly to the combination, might in part be due to the cooling of the gas. Although the total quantity of heat liberated in the reaction is small, the ratio of this heat to the heat capacity of the gas is large, so that it is necessary to investigate the rate at which heat is conducted through the gas.

The wall of the reaction bulb may be assumed to be at room temperature prior to the start of an experiment. Because of its large heat capacity its temperature cannot be raised appreciably during the reaction. For the sake of simplicity in calculation, the reaction bulb will be regarded as a sphere. The appropriate equation of heat conduction is then

$$\frac{1}{r}\frac{\mathrm{d}^2(rT)}{\mathrm{d}r^2} - \frac{1}{\lambda}\frac{\Delta H}{2N_A}\frac{\mathrm{d}N_H}{\mathrm{d}t} = 0$$

where λ is the thermal conductivity of the gas, ΔH the heat evolved in the formation of one mole of H_2 (102 k. cal.) and N_H the number of hydrogen atoms per cc. If, as a first approximation, it be assumed that $\mathrm{d}N_H/\mathrm{d}t$ is independent of T, the integral of the equation becomes

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(5) J. Kaplan, *Phys. Rev.*, **30**, 639 (1927).

$$T - T_{\mathrm{R}} = -\frac{\Delta H}{12\lambda N_{\mathrm{A}}}\frac{\mathrm{d}N_{\mathrm{H}}}{\mathrm{d}t}(R^2 - r^2)$$

where T_{R} is the temperature of the bulb wall and R its radius. Substituting for λ the thermal conductivity of molecular hydrogen, 3.3×10^{-4}, and for $\mathrm{d}N_{\mathrm{H}}/\mathrm{d}t$ the greatest observed rate of recombination, it is found that under these conditions the temperature at the center of the bulb is only 3° greater than the temperature of the wall, and that the average temperature of the gas is about 1° greater than that of the wall. These temperature differences are too small to affect the results in either of the ways mentioned above. Analogous calculations show that, even if the entire reaction be assumed to take place on the bulb wall, diffusion is sufficiently rapid, compared to the observed reaction rate, to maintain the concentration of atomic hydrogen constant throughout the bulb to within 0.1%. The assumptions noted at the beginning of this section are, therefore, fully justified.

As has been previously mentioned, the controlling error in the measurements occurs in the estimation of the final pressure in the reaction bulb. The extrapolation for s_f was uncertain by 0.3–0.4 mm. Since displacements of the light spot as small as 2–3 mm. were included in the calculations, it seems conservative to set the probable error of the trimolecular rate constant at ±20%.

The Heterogeneous Reaction.—A variable wall reaction in the combination of hydrogen atoms has been observed in an earlier series of experiments,[6] in which the walls were poisoned with water vapor. All of the properties of this bimolecular reaction are consistent with the supposition that it is due to reaction of atomic hydrogen with a layer of adsorbed, or more probably dissolved, oxygen.

The Homogeneous Reaction.—From the average value of the trimolecular rate constant, K_2 (equation (1)) is found to equal $1.7(\pm 0.3) \times 10^{16}$ cc.^{2} mole^{-2} sec^{-1}. This value is close to that previously reported[6] and may be accounted for in terms of Tolman's definition of a triple collision, if the maximum distance between the three colliding atoms is 10^{-9} cm. More recently Steiner[7] has given a detailed calculation of the number of triple collisions between hydrogen atoms, taking into account the lessening of the lifetime of an atom pair due to the mutual attractive forces. From his treatment it follows that energy transfer must take place across internuclear distances as great as 5.8×10^{-8} cm. or 11.0×10^{-8} cm., depending on the type of potential function assumed for the attractive force. These distances seem unduly large. This is perhaps due to the fact that Steiner's discussion is based on calculations of the chance of a pair of adjacent atoms being hit by a third atom, the exchange of energy being assumed to take place only from the pair to the relatively distant third atom. As Steiner points out, the three atoms should be treated symmetrically in attacking the problem.

According to equation (2) and the expression for the number of triple collisions, the constant b should be proportional to $T^{-3/2}$. Assuming an average temperature lowering of 15° in the low temperature experiments, an increase of b of 7% is to be anticipated. This is less than the experimental error. The only statement that can be made from these measurements, concerning the activation energy of the reaction, is that this energy is small. It is probably equal to zero.

The fact that the bimolecular reaction could be suppressed to an unobservably small amount shows that the hydrogen atom is more efficient than the molecule in effecting the combination. Allowing for the maximum error in the extrapolation for the constant a (see Fig. 3D), it follows that $a < 0.5$. From equation (2), assuming $K_1 = 0$ and $P_f = 0.480$

$$K_3/K_2 > 50$$

the atom efficiency is more than 50 times that of the molecule. Steiner[7] has given a number of reasons for supposing the molecule to be more efficient than the atom, but his arguments are qualitative and a number of objections may be raised against them. There seems to be no obvious reason for expecting much difference between the efficiencies of atom and of molecules, but a detailed calculation would be necessary in order to account for the experimental result.

Comparison with Previous Results.—Working in a static system, but with very small concentrations of atomic hydrogen, Senftleben and Riechemeier[8] found a variable wall reaction (which they express as first order) and that the atom efficiency is 2×10^3 greater than the molecule efficiency. This is not inconsistent

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(6) H. M. Smallwood, THIS JOURNAL, **51**, 1985 (1929).

(7) W. Steiner, *Z. physik. Chem.*, **15B**, 249 (1932).

(8) H. Senftleben and O. Riechemeier, *Ann. Physik*, **6**, 105 (1930).

with the present results, but their rate constant for the atom reaction (K_2, equation (1)) is 20 times greater than the present value. The reason for this discrepancy is not apparent.

From data obtained in a flowing system, Steiner and Wicke[9] conclude that the atom reaction is negligibly small compared to the molecule reaction. The criticisms of this work, raised by Amdur,[10] seem to invalidate their conclusion.

There remain the data referred to in Ref. 6 and those of Amdur and Robinson.[2] These two sets of measurements are in close agreement with each other. They were made by the same method, according to which the atom concentration of a stream of partially dissociated hydrogen, flowing through a tube, is determined by noting the heat developed on a platinum catalyst suspended at various points in the flowing gas. The measurements were, for the most part, concerned with higher concentrations of atomic hydrogen than those of the present paper. The results of the two methods should, however, be identical.

It is not possible to integrate the rate equation for the flowing system without making some assumptions regarding the rate constants to be determined. If, as the present results show, the atom reaction is dominant, the equation for the flowing system can be integrated (Ref. 6, equation (13)). Provided the differential equation for the flowing system is correct, this integrated equation should give the same value for K_2 as was obtained from the present measurements, *i. e.*, 1.7×10^{16}. My previous measurements gave constants varying from 1.0 to 1.8×10^{16}. Amdur and Robinson, covering a slightly wider range of independent variables, obtain values from 0.6 to 2.7×10^{16}. The agreement between the two methods is excellent, as far as order of magnitude is concerned, but the constants obtained from the flowing systems show regular drifts, so that it has been concluded that the underlying assumption is not valid.

The explanation of this discrepancy is to be sought by considering the effects of diffusion in the flowing system, first emphasized by von Wartenburg and Schultze.[11] Amdur and Robinson conclude that diffusion may safely be neglected because the presence of the catalyst in the gas stream does not alter the pressure gradient, and because the term $D\ d^2[H]/dx^2$ in the equation of flow is small compared to $d(v[H])/dx$. The first of these reasons is not very convincing since, because the viscosities of mixtures of atomic and molecular hydrogen do not change greatly with changes in the degree of dissociation, the pressure gradient is a most insensitive means for detecting alterations in concentration gradient. The second reason is beside the point, since alteration in the concentration gradient by diffusion is of necessity less important than the transport of atomic hydrogen by diffusion to the catalyst, the latter process being proportional to the first, instead of the second, derivative of [H] with respect to x.

It is very difficult to calculate the extent of this process with any accuracy, but a rough estimate may be made in the following manner. Consider a stream of $H + H_2$ flowing through a tube 1 cm. in diameter. Assume that at a point 100 cm. from the discharge the linear velocity of the gas is 10^4 cm./sec., its pressure 0.5 mm. and the dissociation is 50%. Then, neglecting diffusion, the flow of the gas brings to the catalyst (if placed at the point in question) $\pi r^2 v[H] = 1.4 \times 10^{-4}$ moles of H per second. Assume now that there is no flow of the gas as a whole, but that the discharge maintains 100% dissociation at $x = 0$. The catalyst ensures zero dissociation at $x = 100$. Under these conditions the concentration gradient is linear and the flow to the catalyst, due to diffusion, is $\pi r^2 D d[H]/dx = 1.2 \times 10^{-6}$ mols H per sec. ($D = 2.95 \times 10^3$ cm.^{2} sec.$^{-1}$ at 0.5 mm. and 23°). Thus, in these extreme cases the diffusive flow is nearly 1% of the mass flow. In the actual case of combined diffusion and mass flow the contribution of the former will be considerably increased, since the flow alters the concentration gradient, decreasing it at small values of x and increasing it immediately in front of the catalyst.

Considerable evidence for the importance of diffusion may be obtained from the constants listed by Amdur and Robinson (last column, Table II, Ref. 2). The effect of diffusion is to increase the heat developed on the catalyst, resulting in too high values of α and too low values of K_2. With two exceptions all of their twenty values of K_2 are less than that deduced from the present measurements; the exceptions

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[9] W. Steiner and F. W. Wicke, *Z. physik. Chem.*, Bodenstein-Festband, 817 (1931).

[10] I. Amdur, *Phys. Rev.*, **43**, 208 (1933).

[11] H. v. Wartenburg and F. Schultze, *Z. physik. Chem.*, **2B**, 1 (1929).

occur for low values of α and $d\alpha/dx$ where experimental errors are magnified. All of the earlier data gave constants below the upper limit set for K_2 in the present paper. The K_2's obtained from the flowing systems decrease with decreasing x, presumably because the concentration gradient is thereby increased, resulting in more diffusion and consequently greater depression of K_2 from the true value. For the same reason K_2 would be expected to decrease with the total pressure. This is not observed: it may be masked by variation in the amount of atomic hydrogen combining along the tube. It may be concluded from the foregoing discussion that measurements made in flowing systems cannot lead to information on the relative efficiencies of third bodies in effecting combination of hydrogen atoms, unless the processes of diffusion are taken into account, or unless linear rates of flow are used which are much greater than those previously reported.

Summary

1. An apparatus for measuring the rate of recombination of atomic hydrogen in a static system is described.

2. The results obtained show that, after elimination of the wall reaction, the rate of the reaction is proportional to the third power of the concentration of atomic hydrogen, and that the temperature coefficient is small.

3. A lower limit has been set for the ratio

$$\frac{\text{efficiency of atom}}{\text{efficiency of molecule}}$$

in causing combination of a pair of atoms.

4. Some properties of the afterglow accompanying the reaction have been observed and recorded.

5. The results have been discussed in relation to the triple impact mechanism, and have been compared with those of other authors.

CAMBRIDGE, MASS. RECEIVED MAY 25, 1934

NOTES

Thin Films of Mercury on Glass

BY H. E. BENT

The familiar phenomenon of capillary depression of mercury in a glass tube and the convex surface of the liquid have led to the general conception that mercury does not adhere to glass. It is common knowledge, however, that manometers which have been carefully baked out to remove adsorbed gases exhibit a concave meniscus and that the mercury will "stick" to the top of the tube, as is frequently observed with a McLeod gage when a high vacuum has been obtained.

In order to demonstrate these phenomena before a class in physical chemistry and the accompanying negative pressures which exist in the mercury when the liquid has stuck to the top of the tube, two "U" tubes were prepared and carefully boiled out. Each tube was about seven centimeters high and had an inside diameter of about nine millimeters. The mercury was found to stick so tightly to the top of the tube that frequently a very sharp blow on the desk was necessary to cause the mercury to drop. Sometimes, however, the column would break, leaving a thin film of mercury completely covering the inside surface of the glass. The film would usually last from two to twelve seconds and then disappear with about the suddenness of a bursting soap bubble. By means of a cathetometer the height of the mercury in the other arm of the "U" was measured before and after the film broke. If this change in level is attributed entirely to liquid which has run down from the side of the tube the thickness can be calculated to be 0.008 ± 0.01 mm. After the film has broken the contact angle of the mercury and glass is about 90°. Before the film has broken the contact angle is 0°. Hence the capillary rise of the mercury before the film breaks will be 1.32 mm. Half of this, or 0.66, should be the change in height in one arm of the "U" tube. The observed change varied from 0.45 to 0.79 mm. From these data one may conclude that the film is very thin, probably less than 0.01 mm. There are too many uncontrollable variables such as minute drops remaining on the surface of the glass to permit an accurate determination of the thickness of the film by observations on the position of the meniscus.

These tubes were prepared first in October, 1932, and have retained this property for more than a year and a half. The films are much less stable