Summary

Measurements have been made on the velocity of the stoichiometrical reaction $Cr_2O_7^{--} + 6I^- + 14H^+ = 2Cr^{+++} + 7H_2O + 3I_2$ at various concentrations of the reacting ions and in presence and absence of a neutral salt, sodium chloride. All experiments were carried out at 25°.

In dilute solutions the results offer confirmation of the Brönsted activity rate theory of reaction velocity.

In more concentrated solutions in the absence of a neutral salt, the kinetic behavior is incapable of any simple interpretation.

In the presence of 1.5 *M* sodium chloride as neutral salt, the kinetic anomalies disappear. The experimental results clearly indicate that two simultaneous reactions are taking place which may be represented as follows

$$H^+ + I^- + Cr_2O_7^{--} \longrightarrow HI{\cdot}Cr_2O_7^{--} \qquad (1)$$
$$2H^+ + 2I^- + Cr_2O_7^{--} \longrightarrow (HI)_2{\cdot}Cr_2O_7^{--} \qquad (2)$$

The observed velocity constant k is given to within an accuracy of 3% by the expression $k = 14.6\,(H^+)(I^-) + 53{,}000\,(H^+)^2(I^-)^2$.

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[Contribution from the Chemical Laboratory of The Johns Hopkins University]

THE RATE OF RECOMBINATION OF ATOMIC HYDROGEN

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It has been pointed out by a number of investigators[1] that certain exothermic reactions of the type $A + B \longrightarrow AB$ cannot result from simple binary collisions of molecules A and B since, in such a collision, there is no means by which the energy corresponding to the heat of the reaction may be removed from the colliding molecules. In order to react the molecules must collide in the immediate neighborhood of some other object such as another molecule or the wall of the containing vessel. In other words, the reaction can only take place as the result of triplet impacts or three-body collisions.

A few limitations must be made to the foregoing statement. Thus, if there is a possibility of radiation occurring during the collision of molecules A and B, combination may result from a single collision since the energy of combination may be radiated from the system as light. Further, if molecules A and B are relatively complex, the energy of combination may be taken up by their internal degrees of freedom.

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[1] Boltzmann, "Gastheorie. II," Leipzig, **1912**; Herzfeld, *Z. Physik*, **8**, 132 (1922); Born and Franck, *Ann. Physik*, **76**, 225 (1925); *Z. Physik*, **31**, 411 (1925); J. H. Jeans, "The Dynamical Theory of Gases," 4th ed., Cambridge University Press, p. 195.

There are therefore only a few reactions which may be expected to proceed according to the predicted three-body mechanism. One of these, however, is the recombination of atomic hydrogen, represented stoichiometrically by the reaction $H + H \longrightarrow H_2$. The present paper describes a measurement of the rate of this reaction at various pressures. The results obtained are in agreement with the predicted mechanism.

The method used was to allow dissociated hydrogen drawn from an electric discharge to pass along a straight tube.[2] The degree of dissociation of the hydrogen at varying distances along this tube was determined by measuring the heat effect produced upon a piece of platinum foil placed in the flowing gas at the desired distance from the discharge. Wood[2] has shown that metals cause the complete recombination of the atomic hydrogen. Since the heat of this recombination is known and since the rate of flow can be measured, the degree of dissociation is readily calculated.

Experimental

Source of Hydrogen.—Throughout these experiments the hydrogen was taken from a water-cooled electrolytic generator using as electrolyte a 30% solution of potassium hydroxide containing a little barium hydroxide. The hydrogen so obtained contains about 3% of water vapor. Since the presence of this water vapor has been shown to be necessary for the production of the atomic hydrogen, no attempt was made to remove it.

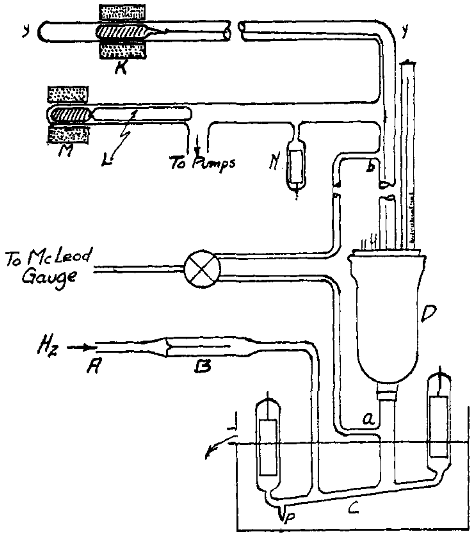

Fig. 1.

Apparatus.—Figure 1 shows the essential parts of the apparatus finally adopted. Hydrogen from the generator (not shown) was admitted at A and expanded through the capillary B to a pressure of a few tenths of a millimeter. It was then led to the discharge tube C, which was immersed in a water-bath. While in the discharge tube the hydrogen was almost completely dissociated, so that recombination took place along the vertical tube, ab. The pressure at each end of this tube could be measured on a McLeod gage by means of the connections shown in the sketch. D is a calorimeter (shown in detail in Fig. 2) which could be slid up or down the tube ab. The calorimeter was made in the shape of a small Dewar flask with a hole in the bottom, the joint between the calorimeter and the central tube ab being made water tight by means of a short piece of gum tubing, E. The calorimeter was flared slightly at the top to permit the insertion of a rubber stopper

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[2] R. W. Wood, *Proc. Roy. Soc. London,* **97A**, 455 (1920); **102A**, 1 (1925); *Phil. Mag.*, **42**, 729 (1921); **44**, 538 (1922); Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

carrying a stirrer, F, a Beckmann thermometer, G, and a platinum heating unit, H, used to determine the heat capacity of the calorimeter. J was the catalytic surface causing the recombination of the atoms of hydrogen. It consisted of a cylinder of platinum foil fitting snugly inside the central tube and suspended from a fine nickel wire. The other end of this wire was fastened to a glass tube containing soft iron which could be moved along the tube yy by means of the electromagnet K (Fig. 1). In this way the platinum could be moved along the central tube with the calorimeter. The pressure in the apparatus was regulated by sliding the core L into or out of the gas stream by means of the electromagnet M. N is an auxiliary electrode whose use will be described below.

The tube ab was approximately one meter long and 0.8 cm. in internal diameter. The discharge tube was made of thin-walled 0.6-cm. tubing to facilitate cooling, the distance between the inlet and outlet taps being about 10 cm. The distance between the discharge and tap a was 8 cm. The electrodes were the usual cylinders of aluminum foil fastened to tungsten wires which were sealed through the pyrex. Rapid streams of water played over the exposed ends of the electrodes, thus preventing the conduction of heat from the discharge to the calorimeter. The volume of the calorimeter was slightly greater than 100 cc. The calorimeter stirrer was rotated by a small electric fan motor.

Procedure.—The primary consideration for experiments with atomic hydrogen is that the regions where it is to be produced and studied must be absolutely free from substances which may catalyze the recombination. Apparently all metals are active catalysts, together with porous or adsorbent surfaces. With this in mind the apparatus was designed to permit washing *in situ*. Each apparatus was made from new pyrex glass. After complete assembly aqua regia was forced through the arm P up to the top of the tube ab and then allowed to drain back. Of course, during the washing the platinum catalyst J was lifted out of range of the acid. The apparatus was then rinsed repeatedly with distilled water, after which the arm P was sealed off and the pump started. Before making any runs a discharge was passed from the auxiliary electrode N to the discharge tube. Bonhoeffer[2] has previously shown that this is useful in preparing a catalytically inert tube.

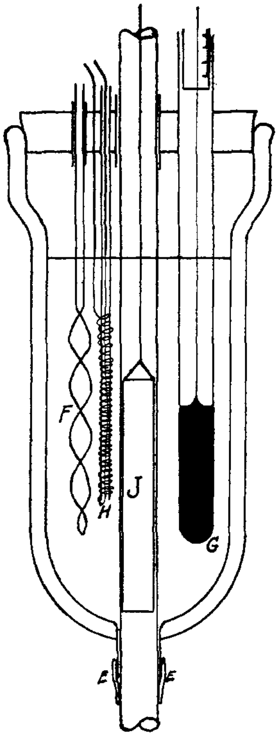

Fig. 2.

The foregoing procedure has been found in practically every instance to give apparatus in which reproducible results can be obtained. Presumably the aqua regia removes any metallic dust from the tube wall, the water fills up the pores in the wall and the discharge melts into the glass any active spots not removed by the acid. The discharge tubes show a pronounced fatigue effect after twenty to thirty hours of running. This fatigue is gradual and coincident with the appearance of appreciable quantities of sputtered material from the electrode. No successful method has so far been found for rejuvenating a spent tube.

The actual measurements were carried out as follows. The calorimeter and catalyst were set at the desired distance from the discharge and the pressure was allowed to reach the desired value; 100 cc. of distilled water, one or two degrees below room temperature, was pipetted into the calorimeter and the stirrer started. After the warming of the calorimeter had reached a steady rate the Beckmann thermometer was read at one-minute intervals (timed by an electric clock) for a period of five minutes, in order to obtain the rate of warming at the start of the run. At the end of this period the discharge was turned on and the temperature readings were continued until the temperature rise was great enough to ensure the desired accuracy. This required ten minutes or less. The temperature measurements were continued for five minutes after the discharge was turned off to determine the final cooling curve. Fig. 3 shows several typical temperature–time curves. The pressure in the apparatus was measured at points a and b twice each during each run. The room temperature was maintained constant within 0.5° throughout each run.

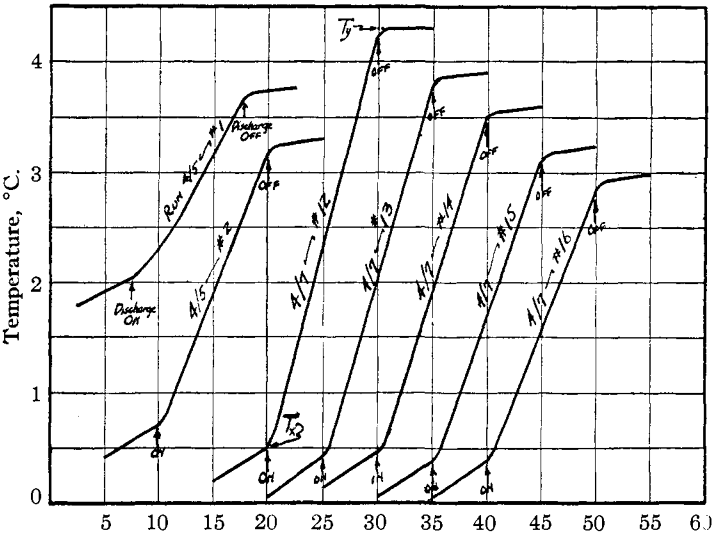

Fig. 3.

The heat capacity of the calorimeter was determined by noting the temperature rise caused by passing a current through the heating unit, H, the power input being measured by means of a milliammeter and millivoltmeter. The rate of flow of hydrogen was measured by disconnecting the hydrogen generator and allowing the hydrogen to be drawn instead from a gas buret.

Results

A series of preliminary experiments showed the qualitative conditions that must be fulfilled for the best production of atomic hydrogen. Aside from the necessity of the absence of catalysts, all the other variables affect the degree of dissociation of the hydrogen at a point some distance from the discharge. Thus the degree of dissociation is increased by high current density in the discharge and by water cooling the discharge. These two factors are, however, of secondary importance compared to the pressure and the quantity of hydrogen flowing. If the pumping capacity is approximately constant, these last two quantities are roughly proportional, the pressure increasing if the quantity of hydrogen admitted to the apparatus is increased. Since the degree of dissociation at a point removed from the discharge decreases rapidly as the pressure increases, there will be some set of conditions for each apparatus at which the greatest *amount* of atomic hydrogen is obtained at a point outside the discharge. The pressure and the rate of flow at which the greatest amount of atomic hydrogen is obtained are determined by the efficiency of the pumps and the dimensions of the apparatus.

The best series of measurements of the rate of recombination are summarized in Table I and plotted in Fig. 4. The degree of dissociation is expressed by α, the fraction of the total amount of hydrogen which is present in the atomic form x cm. from the point of measurement of the initial pressure (P_0).

TABLE I

RESULTS OF MEASUREMENTS

Rate of flow of H_2 = n_0 = 1.03×10^{-5} moles/second. Primary current to transformer = 25 amps. Internal diameter of tube ab = 0.848 cm. Length ab = 108.3 cm. Heat capacity of calorimeter = C = 121.5 Cal./deg.

		Dist. from a to calorim.	Press. (mm. Hg) meas. at		Temp. rise in calorim. °C.		Dissociation,
Date	No.	x (cm.)	a, P_0	b, P_1	$T_{\text{obs.}}$	$T_{\text{corr.}}$	100 α, %
4/5	1*	86.2	0.524	0.150	2.53	1.62	31.6
	2*	86.2	.514	.142	2.51	2.14	41.8
	3	86.2	.584	.290	2.23	1.79	35.0
	4	86.2	.632	.356	2.04	1.48	29.0
	5	86.2	.714	.494	1.75	1.03	20.2
	6	86.2	.798	.584	1.23	0.77	15.1
	7	86.2	.508	.138	3.10	2.43	47.5
	8	65.9	.508	.140	3.43	2.73	53.4
	9	65.9	.642	.360	2.66	1.94	38.0
	10	65.9	.716	.484	2.36	1.44	28.2
	11	65.9	.788	.583	2.00	1.11	21.7
	12	65.9	.874	.684	1.44	0.87	17.0
	13	65.9	.508	.142	3.48	2.69	52.7
4/7	1*	65.9	.498	.134	3.27	2.57	50.3
	2	47.6	.488	.132	3.59	2.94	57.5
	3	47.6	.622	.360	2.98	2.25	44.0
	4	47.6	.696	.468	2.59	1.83	35.8
	5	47.6	.766	.568	2.33	1.45	28.4
	6	47.6	.850	.666	2.11	1.16	22.7
	7	31.6	.476	.136	3.25	3.23	63.2
	8	31.6	.616	.366	3.35	2.53	49.5
	9	31.6	.688	.474	2.73	2.25	44.0
	10	31.6	.762	.568	2.49	1.93	37.8
	11	31.6	.874	.666	2.08	1.53	29.9
	12	18.8	.488	.132	3.77	3.43	67.1
	13	18.8	.622	.364	3.43	3.01	58.9
	14	18.8	.694	.474	3.10	2.74	53.6
	15	18.8	.780	.570	2.79	2.39	46.8
	16	18.8	.834	.672	2.13	2.08	40.7

TABLE I (*Concluded*)

Date	No.	Dist. from a to calorim. x (cm.)	Press. (mm. Hg) meas. at a, P_0	b, P_1	Temp. rise in calorim. °C. $T_{\text{obs.}}$	$T_{\text{corr.}}$	Dissociation, 100 α, %
4/10	1	18.8	.502	.148	3.62	3.52	68.8
	2	8.3	.504	.148	3.93	3.89	76.1
	3	8.3	.642	.374	3.56	3.62	70.8
	4*	8.3	.708	.500	2.58	2.50	49.1
	5	8.3	.784	.578	3.06	2.96	57.9
	6	8.3	.864	.678	2.99	2.86	56.0
	7	8.3	.710	.490	3.35	3.38	66.2
	8	1.4	.496	.142	3.71	4.10	80.2
	9	1.4	.638	.394	3.39	3.91	76.5
	10	1.4	.710	.490	3.51	3.76	73.6

The pressures recorded are each the average of two readings taken during the particular run. During each of the runs the discharge was on for ten minutes except Run 4/7 No. 7, the time of which was eight minutes. The temperature–time readings were plotted on a large scale as soon as obtained.

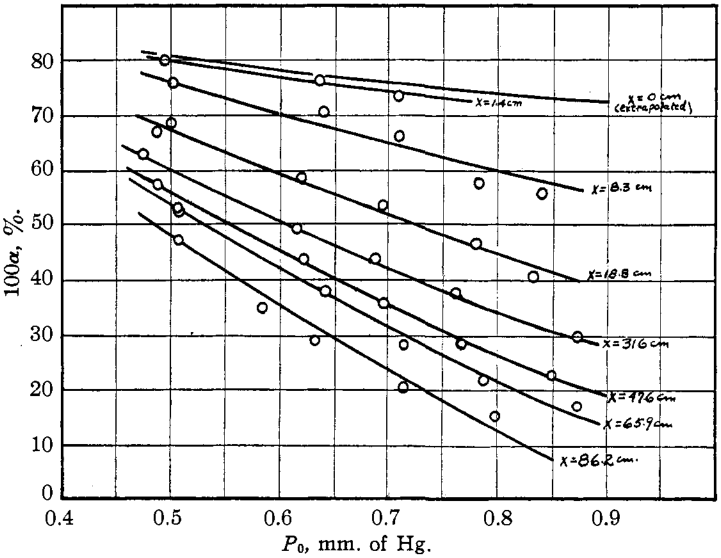

Fig. 4.

The observed temperature rise was obtained by subtracting the temperature at the start of the period when the discharge was on from the temperature obtained by extrapolation of the final cooling curve back to the time at which the discharge was turned off ($T_{\text{obs.}} = T_y - T_x$, Fig. 3). The correction for radiation and conduction of heat to or from the surroundings and for the heat of stirring was obtained by averaging the rate of cooling at the start and at the end, multiplying this average rate by the time during which the discharge was on and adding or subtracting, as the case might be, to the observed temperature rise. The figures so obtained are tabulated under the heading "$T_{\text{corr.}}$"

The fraction dissociated was calculated from the relation

$$\alpha = \frac{CT_{\text{corr.}}}{60\, n_0 t\, \Delta H} \tag{1}$$

where ΔH is the heat of formation of one mole of molecular hydrogen from the atoms. This quantity was taken to be 100,400 Cal., which is an average of the values reported by Dieke and Hopfield,[3] and Witmer[4] from studies of the molecular spectrum of hydrogen. The "t" of Equation 1 stands for the time in minutes during which the discharge was on. The other symbols have the meanings assigned in Table I.

It will be noticed that the starred (*) runs of Table I are omitted from the plot of Fig. 4, since it was apparent from the varying slopes of the respective temperature–time curves that conditions changed during these runs. This discrepancy is of common occurrence and is undoubtedly due to a temporary catalytic effect. For example, if the apparatus is filled with air and left overnight, it requires from fifteen to twenty minutes' running before the degree of dissociation of the hydrogen outside the discharge builds up to a reproducible value, possibly due to a slow clean-up of oxygen adsorbed on the glass. This effect accounts for the first three inconsistent runs of Table I. It is readily recognized on the temperature–time curve, as may be seen by comparing the first two curves of Fig. 3. It is not evident in the first experiment of the third day since the discharge was run for thirty minutes before the runs were started. The other inconsistent run may have been caused by a catalytic particle working into the discharge and then being rendered inactive. It must be emphasized that, once active catalysts have been removed, the results do not depend on the apparatus. Duplicate runs which checked well within the experimental error have been made in different apparatus and at intervals of several weeks.

As will be pointed out below, an interpretation of the results requires a knowledge of the manner in which the pressure varied along the tube ab. An attempt was made to measure this, at the conclusion of the experiments, by sealing a number of taps into the tube and connecting these taps through stopcocks to the McLeod gage. The results so obtained are shown in Fig. 5, the dotted portions of the curves corresponding to the pressure drop caused by the presence of the platinum foil. Unfortunately some catalytic substance must have been present during these runs because the curves corresponding to the dissociated gas have the same slope as those for the molecular hydrogen. This would mean that the mixture of atomic and molecular hydrogen has the same viscosity as pure molecular

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[3] Dieke and Hopfield, *Z. Physik,* **40,** 299 (1926).

[4] Witmer, *Phys. Rev.,* **28,** 1223 (1926).

hydrogen. That this is not the case has been shown by Harteck.[5] It is much more probable that very little atomic hydrogen reached the Tube ab due to the presence of an active catalyst. There was no way of checking this point since the calorimeter was necessarily removed during the remodeling of the apparatus.

It was hoped at first that the method could be used to measure the rates of the gaseous reactions of atomic hydrogen. This could not be done, however, because these reactions take place along such a short interval of the tube (5–20 cm.) that accurate results could not be expected. In the course of the preliminary experiments it was found, however, that if atomic hydrogen is led along a tube lined with a thin coating of sulfur, from $^1/_6$ to $^1/_5$ of the atomic hydrogen reacts to form hydrogen sulfide. This is to be expected since the first hydrogen sulfide formed rapidly catalyzes the recombination of the remainder of the hydrogen atoms.[6]

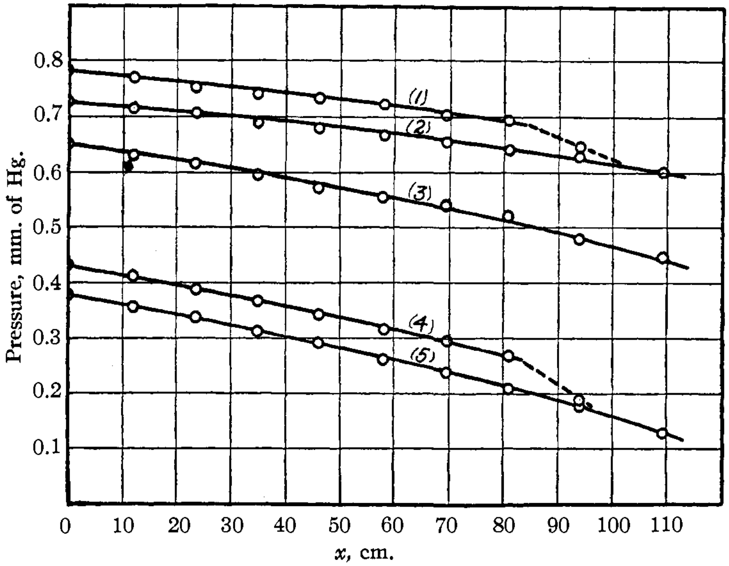

Fig. 5.—Curves 2, 3 and 5 obtained with discharge off and platinum out of outlet tube. Curves 1 and 4 obtained with discharge on and platinum at x = 83 cm.

It was also found that nitric oxide catalyzes the recombination without itself being reduced. Analysis of the gases leaving the mixing chamber showed that over 99% of the nitric oxide was unchanged. However, a very minute amount of ammonia was formed in each case. Thus in one experiment 2.8×10^{-5} mole of ammonia was found while there were available 0.01 mole of atomic hydrogen and 0.0088 mole of nitric oxide.

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[5] P. Harteck, *Z. physik. Chem.*, **139A**, 98 (1928).

[6] Boehm and Bonhoeffer, *ibid.*, **119**, 385 (1926).

This ammonia may have been due to the presence of nitrogen oxide as an impurity in the nitric oxide. Blank experiments showed that it was not present in the original hydrogen or nitric oxide and that it did not come from the combination in the discharge of the hydrogen with a small contamination of nitrogen. It is difficult to explain the catalysis of nitric oxide by means of a chain mechanism such as has been used by Bonhoeffer for the similar effect of hydrogen sulfide, hydrochloric acid, etc., since if the nitric oxide molecule is ever broken up it is extremely unlikely to form again under the conditions of the experiment. Possibly an unstable molecule of the type H—NO is formed, in which case the mechanism would be

$$\mathrm{H} + \mathrm{NO} \longrightarrow \mathrm{H{-}NO}$$
$$\mathrm{H{-}NO} + \mathrm{H} \longrightarrow \mathrm{H_2} + \mathrm{NO}$$

The H—NO molecule might be quite short-lived and yet account for the effect.

The errors incident to this method of determining atomic hydrogen may be classified under four headings. In the first place the method is liable to the usual errors of calorimetry. These probably predominate in the present experiments, limiting the accuracy to 2–3%. Second, the method depends upon a knowledge of the heat of recombination of atomic hydrogen. This quantity, however, is now known with an accuracy within the above limits. Third, the heat effect registered in the calorimeter may be too small either because the recombination is not completely catalyzed by the platinum or because some of the heat is conducted away by the hydrogen stream. The first effect is extremely improbable since the rate of diffusion of atomic hydrogen under the conditions of the experiment is so high that a minute speck of metal in front of the calorimeter completely stops the heat effect. Further, in some of the preliminary experiments a thermometer with a silvered bulb was hung in the gas leaving the calorimeter and showed no temperature rise. Since the quantity of hydrogen flowing was small it would have had to be heated to an unreasonably high temperature to remove an appreciable amount of heat from the system. Finally, heat may be brought to the calorimeter in other ways than by the recombination of the atoms. Thus heat may be conducted from the discharge along the glass walls. This, however, was too small to affect the results since, when the whole discharge tube was water cooled, numerous runs in catalytically active apparatus showed no heat effect. This fact also removes the possibility of metastable molecules bringing energy to the calorimeter. It might also be supposed that, since the atomic hydrogen is recombining along the tube between the calorimeter and the discharge tube, sufficient heat could be liberated to affect the results. This is unlikely since in some of the preliminary experiments this tube was water cooled without affecting the results.

The accuracy of the method, therefore, is limited by the errors involved in the calorimetry of quantities of heat which, in this case, varied from 5 to 40 Cal. per minute.

The Three-Body Mechanism

It will now be shown that the results summarized in Table I are in accord with the predicted mechanism of recombination by triple impacts. The fundamental assumption is that at constant pressure

$$\frac{-\mathrm{d}N_{\mathrm{H}}}{\mathrm{d}t} = 2\Sigma\nu_3 \tag{2}$$

where N_{H} is the number of hydrogen atoms per cc. at the time t and $\Sigma\nu_3$ is the number of triple impacts per second per cc. in which at least two of the colliding bodies are hydrogen atoms.

There is considerable uncertainty as to the quantitative definition of a three-body collision. Whatever be the definition, however, $\Sigma\nu_3$ may be set equal to

$$\Sigma\nu_3 = K_1N_{\mathrm{H}}^2 + K_2N_{\mathrm{H}}^3 + K_3N_{\mathrm{H}}^2N_{\mathrm{H}_2} \tag{3}$$

where K_1, K_2 and K_3 are proportionality constants and N_{H_2} is the number of hydrogen molecules per cc. The first term on the right of Equation 3 takes account of triple impacts in which the wall is the third body. In the second term the third body is a hydrogen atom and in the third a hydrogen molecule.

To express the present results it will be necessary to take account of the fact that the atomic hydrogen is recombining at variable pressure while flowing along the tube. This may be accomplished by writing the equation of continuity of the hydrogen atoms

$$\frac{\partial N_{\mathrm{H}}}{\partial t} - \frac{\partial(N_{\mathrm{H}}u)}{\partial x} = 0 \tag{4}$$

where u is the linear velocity of the gas at the point x

$$u = \frac{n}{\pi r^2\left(N_{\mathrm{H}_2} + \frac{1}{2}\,N_{\mathrm{H}}\right)} \tag{5}$$

Here n is the number of hydrogen molecules admitted to the apparatus per second ($n = n_0N_A$). Since

$$N_{\mathrm{H}} + N_{\mathrm{H}_2} = \frac{P}{kT} \tag{6}$$

and

$$\alpha = \frac{N_{\mathrm{H}}}{2N_{\mathrm{H}_2} + N_{\mathrm{H}}} \tag{7}$$

$$N_{\mathrm{H}} = \frac{P}{kT} \times \frac{2\alpha}{1+\alpha} \tag{8}$$

$$N_{\mathrm{H}_2} = \frac{P}{kT} \times \frac{1-\alpha}{1+\alpha} \tag{9}$$

Substituting Equations 2, 3, 5, 8 and 9 in Equation 4, there is obtained

$$\frac{-\partial\alpha}{\partial x} = \frac{\pi r^2}{n} \times K_1 \frac{4\alpha^2\,P^2}{(1+\alpha)^2\,k^2T^2} + K_2 \frac{8\alpha^3\,P^3}{(1+\alpha)^3\,k^3T^3} + K_3 \frac{4\alpha^2(1-\alpha)P^3}{(1+\alpha)^3\,k^3T^3} \tag{10}$$

Equation 10 cannot be integrated except by means of a series development. It is possible, however, that any one of the three terms may predominate. To integrate these three simplified equations it will be necessary to know P as a function of x. This pressure gradient could be calculated from the data of Harteck[5] but this would make the computations quite complicated. Since Harteck found that the viscosity of mixtures of atomic and molecular hydrogen does not differ greatly from the value for molecular hydrogen alone, it is believed that an empirical method will be sufficiently accurate for the present purposes. It will therefore be assumed that

$$P = \sqrt{P_0^2 - \beta x} \tag{11}$$

where β is a constant to be evaluated from the data of each experiment. This equation is equivalent to the assumption that the viscosity of the gas is constant along the tube. In order to calculate the constant β it may reasonably be assumed that, since all of the hydrogen is molecular after leaving the calorimeter, the curves of Fig. 5 give the true pressure gradient for this part of the flow. If this is the case it is possible to determine the pressure P at the calorimeter from the measured value of P_1, by interpolation. Since P, P_0 and x are known, β may be calculated for each run. Although this method of calculation is approximate, the results seem fairly certain for large values of x. Thus in the first five of the runs calculated in Table II β varies irregularly between 3520 and 4440 (pressure expressed in dynes/cm.^{2}). In the last five runs β decreases fairly regularly from 4160 to 3190. The calculated value of β for molecular hydrogen is 3570.

Using the assumption of Equation 11 and setting alternately K_2 and K_3, K_1 and K_3, K_1 and K_2 equal to zero, the following equations are obtained

$$K_1 = \frac{nk^2T^2\left[\frac{1}{\alpha} - \frac{1}{\alpha_0} + 2\ln\frac{\alpha_0}{\alpha} + \alpha_0 - \alpha\right]}{4\pi r^2\left(P_0^2x - \frac{\beta x^2}{2}\right)} \tag{12}$$

$$K_2 = \frac{5\beta nk^3T^3\left[\frac{1}{2}\left(\frac{1}{\alpha^2} - \frac{1}{\alpha_0^2}\right) + 3\left(\frac{1}{\alpha} - \frac{1}{\alpha_0}\right) + 3\ln\frac{\alpha_0}{\alpha} + \alpha_0 - \alpha\right]}{16\pi r^2[P_0^5 - (P_0^2 - \beta x)^{5/2}]} \tag{13}$$

$$K_3 = \frac{5\beta nk^3T^3\left[4\ln\frac{\alpha_0}{\alpha} + 8\ln\frac{1-\alpha}{1-\alpha_0} + \frac{1}{\alpha} - \frac{1}{\alpha_0} - (\alpha_0 - \alpha)\right]}{8\pi r^2[P_0^5 - (P_0^2 - \beta x)^{5/2}]} \tag{14}$$

Equation 12 embodies the assumption that the recombination of hydrogen atoms is largely heterogeneous; Equation 13 that it is homogeneous, but that only the hydrogen atoms can act as the third body; and the last equation that only the hydrogen molecule can act as the third body. Table II summarizes the values of these constants calculated from some of the experiments of Table I. The values of α_0 used in the calculations were taken from the extrapolated curve of Fig. 4.

TABLE II

SUMMARIZED VALUES OF CONSTANTS

P_0	x	α_0	α	$K_1 \times 10^{16}$	$K_2 \times 10^{32}$	$K_3 \times 10^{32}$
0.508	86.2	0.810	0.475	4.20	4.20	12.40
.584	86.2	.790	.350	4.24	3.60	9.04
.632	86.2	.778	.290	4.68	4.16	8.24
.714	86.2	.758	.202	5.04	4.72	6.32
.798	86.2	.740	.151	5.20	4.96	4.84
.508	65.9	.810	.534	3.84	3.48	14.44
.642	65.9	.775	.380	3.76	2.84	7.44
.716	65.9	.758	.282	4.24	3.24	6.04
.788	65.9	.743	.217	4.44	3.48	4.88
.874	65.9	.728	.170	5.12	3.60	3.88

Each of the three constants shows a well-defined drift so that it may be concluded that none of the three equations expresses the actual mechanism of recombination. The variation of the constants, however, is such as to make it seem probable that the differential Equation 10 does express the correct mechanism. Thus as the pressure is increased the apparent value of K_1 increases, K_2 first decreases and then increases and K_3 decreases. The increase in K_1 indicates that there is relatively less recombination taking place on the wall at the high pressures. Similarly, the decrease of K_3 shows that there are relatively more effective collisions involving two hydrogen atoms and one hydrogen molecule at the higher pressures. These two effects combined can account for the changes in K_2. Thus increasing the pressure lessens the relative amount of wall reaction, which would cause K_2 to decrease, and increases the relative amount of recombination caused by the molecules, which would cause K_2 to increase. Since the wall reaction varies as the square of the pressure and the "molecule reaction" as the pressure cubed, the first effect predominates at the low pressures and the second at the higher pressures. K_2, therefore, passes through a minimum.

An attempt was made to calculate the constants directly from the differential equation, by obtaining the slope graphically. This is a very unfavorable way of calculating the data since the determinants of the various sets of equations nearly vanish. Thus a change of 2% in the slope changes the constants by a factor of 100 or more.

A series of approximate calculations, however, indicated that the data would be satisfied if K_1, K_2 and K_3 are of the orders of magnitude 10^{-16}, 10^{-32} and 10^{-32}, respectively.

The approximate values of the constants so obtained may render possible a more quantitative definition of a three-body collision. Thus a three-body collision in which the wall is the third body may be defined as a collision between two hydrogen atoms occurring less than a short distance, δ, from the wall. In other words, the number of such collisions per second per cc. equals the number of collisions between hydrogen atoms per sec. per cc. times the volume of a cylindrical shell of radius r, thickness δ and length such that the volume inclosed by the shell shall be 1 cc. That is

$$\nu_{3(\text{wall})} = 2N_{\text{H}}^2\sigma_{\text{H}}^2\sqrt{\frac{\pi kT}{m_{\text{H}}}} \times \frac{2\delta}{r} \tag{15}$$

where σ_{H} is the diameter and m_{H} the mass of the hydrogen atom. Therefore

$$K_1 = \frac{4\sigma_{\text{H}}^2\delta}{r}\sqrt{\frac{\pi kT}{m_{\text{H}}}} \tag{16}$$

In arriving at this relation it is assumed that the tube wall is perfectly smooth. Although this cannot be the case, the actual area of the wall is probably not greatly different from the assumed value since the small adsorbing pores of the wall are filled with water. Substitution of numerical values in Equation 16 shows that δ is of the order of magnitude of 10^{-7} cm. Irregularities in the wall would decrease this figure. In the calculation the diameter of the hydrogen atom has been assumed to be 2×10^{-8} cm.

A three-body collision involving three molecules may be defined in a number of different ways. For example, Tolman[7] defines it as one in which the distances between Molecule I and Molecule II and between Molecule II and Molecule III are equal to or less than some short distance, δ. From the relation obtained by him it follows that

$$K_2 = 32\pi^2\sigma_{\text{H}}^4\delta\sqrt{\frac{kT}{\pi m_{\text{H}}}} \tag{17}$$

and

$$K_3 = 16\pi^2\sigma_{\text{H}}^2\left(\frac{\sigma_{\text{H}} + \sigma_{\text{H}_2}}{2}\right)^2\delta\sqrt{\frac{kT}{\pi m_{\text{H}}}}\left(1 + \sqrt{\frac{m_{\text{H}} + m_{\text{H}_2}}{m_{\text{H}_2}}}\right) \tag{18}$$

where σ_{H_2} and m_{H_2} are, respectively, the diameter and mass of the hydrogen molecule. From either equation it is found that δ is of the order of magnitude 10^{-9} cm.

The definition suggested by Herzfeld[1] and used by Bodenstein[8] in his calculations of the rate of the reaction between NO and O_2 is identical with the above except that δ is identified as the diameter of the colliding molecules. The expressions obtained from the two definitions for the number of triple collisions differ only by a numerical factor of the order ten.

[7] Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," The Chemical Catalog Co., New York, **1927**, p. 247.

[8] Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

Syrkin[9] has calculated the number of multiple collisions between point molecules by defining a multiple collision as one in which the colliding molecules are within a small sphere of radius r. Applying his general equation to the present case, there are obtained the equations

$$K_2 = \frac{\left(\frac{4}{3}\pi r^3\right)^2}{3!r} \times \frac{2}{3}\sqrt{\frac{2\pi kT}{m_{\mathrm{H}}}} \tag{19}$$

$$K_3 = \frac{\left(\frac{4}{3}\pi r^3\right)^2}{2!r} \times \frac{2}{3}\sqrt{2\pi kT}\sqrt{\frac{\frac{2}{m_{\mathrm{H}}} + \frac{1}{m_{\mathrm{H_2}}}}{3}} \tag{20}$$

From either equation r is found to be of the order 10^{-8} cm.

It may therefore be concluded that the recombination of hydrogen atoms proceeds according to the predicted three-body mechanism. The experimental proof, however, is not as definite as might be desired since no integral of Equation 10 was obtained. For this reason the experimental method was not considered suitable for an investigation of the effect of mixing other gases with the dissociated hydrogen.

There are a number of other possible mechanisms for the recombination of atomic hydrogen. Thus it might be supposed that even under the best circumstances the walls of the containing vessel still exert a specific catalytic power at relatively isolated points. If, however, this were the principal means of recombination, K_1 calculated from Equation 12 should be constant. It might further be supposed that the water vapor present in the gas might enter into the mechanism. The fact that Bonhoeffer[10] and Mohler[11] have shown that the OH bands are excited by atomic hydrogen might be cited as evidence in favor of this statement. Since, however, the reaction

$$\mathrm{H} + \mathrm{H_2O} \longrightarrow \mathrm{H_2} + \mathrm{OH} - 12\ \mathrm{Cal.}$$

is endothermic, it may be ruled out. It seems more probable that unexcited OH molecules are produced in the discharge tube and that the bands result from triple impacts between these and two hydrogen atoms. Under the conditions of the present measurements such an effect would be too small to influence the results.

No account has been taken of the possibility of recombination taking place in the adsorbed phase. Langmuir[12] has shown that atomic hydrogen is appreciably adsorbed by glass surfaces at room temperature but in his experiments the glass was thoroughly baked out prior to the adsorption while in the present case the tube wall was covered with a film of water. Furthermore, if the wall were covered with a reactive adsorbed film the

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[9] Syrkin, *Physik. Z.*, **24**, 236 (1923).

[10] Bonhoeffer, *Z. physik. Chem.*, **116**, 391 (1925).

[11] Mohler, *Phys. Rev.*, **29**, 419 (1927).

[12] I. Langmuir, This Journal, **34**, 1310 (1912); **36**, 1711 (1914); **37**, 417 (1915); **38**, 2270 (1916).

recombination would be at least 10^5 times more rapid. In the light of these facts it seems extremely improbable that the wall as a whole adsorbs atomic hydrogen. There remains the possibility that isolated points on the wall are absorbent and hence catalytic. Such a possibility is unlikely since if this were the case duplicate results could not be obtained in different apparatus.

In conclusion the author wishes to express his indebtedness to Dr. H. C. Urey and to Professor K. F. Herzfeld for their advice during the course of this work.

Summary

1. A calorimetric method for the estimation of the amount of atomic hydrogen obtained from a Wood tube is described, together with the application of this method to the measurement of the rate of recombination of the hydrogen atoms.
2. This rate has been measured through the pressure range 0.5–0.9 mm. of mercury.
3. It was found that, under the conditions of the experiment, one-fifth to one-sixth of the atomic hydrogen present reacted with solid sulfur and that nitric oxide catalyzes the recombination of the atomic hydrogen.
4. The data obtained for the rate of recombination are discussed and it is concluded that they are in accordance with the predicted three-body mechanism.

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THE REACTIVITY OF IODINE CYANIDE IN DIFFERENT ORGANIC SOLVENTS

BY ERWIN CHARGAFF[1]

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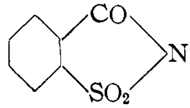
F. Feigl and the author have stated[2] that the reactivity of iodine toward the silver salt of saccharin depends upon the solvent used. In the so-called active solvents, which give brown solutions of iodine (*viz.*, ethyl ether, ethyl alcohol, etc.), almost only AgI is formed. In the inactive solvents (*viz.*, carbon disulfide, carbon tetrachloride, etc.), in which iodine dissolves with a violet color, there apparently is formed an addition compound  NAg...I_2, which, being unstable, easily decomposes into

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[1] Milton Campbell Research Fellow in Chemistry, 1928–1929.

[2] F. Feigl and E. Chargaff, *Monatsh.*, **49**, 417 (1928). (In. *C. A.*, **22**, 3816 (1928), and **22**, 4083 (1928), both times the second author's name is incorrectly reported.)