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The Recombination of Hydrogen Atoms. II. Relative Recombination Rates of Atomic Hydrogen and Atomic Deuterium*

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Many investigations[1] have been made of the mechanism of recombination of hydrogen atoms in attempts to specify the efficiencies of the third bodies necessary in collisions producing molecules. During the past two years the author has made additional measurements on the rate of recombination of hydrogen atoms using a dynamic method. Preliminary analysis of the data indicates that atomic hydrogen recombines almost entirely in the gas phase, hydrogen atoms being at least 10 times more efficient than hydrogen molecules as third bodies.

Since it was possible to obtain from the Ohio Chemical Company D_2O of over 99.9% purity, it was considered advisable to ascertain whether the rate or mechanism of recombination of deuterium atoms was appreciably different from that of hydrogen atoms, especially since comparative rates might be obtained with greater accuracy than absolute values.

Experimental

Deuterium gas, prepared by decomposing D_2O with sodium as described by Lewis and Hanson,[2] was dissociated in a Wood discharge tube and the mixture of atomic and molecular deuterium pumped along a recombination tube whose walls were poisoned with a film of sirupy phosphoric acid from which all excess water had been removed. Atom concentrations were measured by means of a small platinum combination catalyst-calorimeter which could be lowered to various positions inside this recombination tube into which four McLeod gages were tapped for obtaining pressure distributions.

The nature of the circulating system which pumped deuterium through the apparatus, the determination of the rate of flow of deuterium, dn/dt, to the discharge tube and the analysis of the final gas mixture (81% D_2, 18% DH and 1% H_2) have been described in evaluating the viscosity ratio of deuterium and hydrogen.[3]

Results

At a point in the recombination tube 34.1 cm. from the discharge the fraction of atomic deuterium, α, was determined at 30° for four different pumping speeds which were obtained by pumping through capillary by-passes. The value for α is the ratio of the energy brought to the catalyst-calorimeter per second by the atoms which completely recombine on the platinum to the energy required to dissociate completely the moles of gas flowing past the point per second. The energy brought per second was determined by electrically heating the catalyst-calorimeter (with the discharge off) until the temperature as recorded by the internal combination platinum resistance thermometer and heater equaled that obtained from the heating due to recombination of atoms on the catalyst. The energy required for complete dissociation is $dn/dt\Sigma x_i \Delta H_i$ where x_i is the mole fraction of each molecular species and ΔH_i the corresponding heat of dissociation in calories per mole.[4] For the present experiments with deuterium since the rate of flow of gas to the discharge tube was constant this latter energy quantity is equal to $0.700 \times 10^{-5} (0.81 \times 104{,}593 + 0.18 \times 103{,}618 + 0.01 \times 102{,}800) = 0.731$ calorie.

Table I shows the results of runs made with deuterium as well as those previously made with hydrogen at the same point in the recombination tube. P is the pressure at the point of measurement, and P_0 the pressure at the discharge tube for a given run.

P_0 values were obtained by extrapolation of pressure readings along the recombination tube to the discharge tube ($x = 0$). The estimated experimental error in the determination of dn/dt, P, P_0 and α is 0.5–1.0% in each case.

Since the most recent results of Smallwood as well as unpublished data of the present author indicate that the recombination of atomic hydro-

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[1] (a) Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932; (b) Amdur and Robinson, THIS JOURNAL, **55**, 1395 (1933); (c) Robinson and Amdur, *ibid.*, **55**, 2616 (1933); (d) Smallwood, *ibid.*, **56**, 1542 (1934); (e) Farkas and Sachsse, *Z. physik. Chem.*, **B27**, 111 (1934).

[2] Lewis and Hanson, THIS JOURNAL, **56**, 1687 (1934).

[3] Amdur, *ibid.*, **57**, 588 (1935).

[4] Johnston and Long, *J. Chem. Phys.*, **2**, 389 (1934).

TABLE I

INTERNAL DIAMETER OF RECOMBINATION TUBE 0.994 CM.

A. Degree of Dissociation of Deuterium

dn/dt, 10^{-5} mole/sec.	P, mm.	P_0, mm.	100 α
0.700	0.410	0.442	61.9
.700	.635	.659	38.1
.700	.916	.921	21.02
.700	1.167	1.171	13.17

B. Degree of Dissociation of Hydrogen

dn/dt, 10^{-5} mole/sec.	P, mm.	P_0, mm.	100 α
1.100	0.441	0.479	68.8
1.125	.455	.493	66.9
1.110	.474	.511	64.1
1.100	.477	.514	63.6
1.115	.639	.671	45.4
1.145	.704	.733	37.6
1.161	.746	.773	34.8
1.140	.866	.889	27.24
1.110	1.044	1.060	19.97
1.161	1.120	1.134	17.54

gen proceeds homogeneously as the result of triple collisions involving atoms (rather than molecules) as third bodies the rate equation may be written as

$$-\mathrm{d}[\mathrm{H}]/\mathrm{d}t = k[\mathrm{H}]^3 \qquad (1)$$

Equation (1) does not include a term for the diffusion of atoms due to a non-linear concentration gradient along the recombination tube. Under the most unfavorable conditions this term does not exceed 10% of the total recombination rate so that for the calculation of the *comparative* recombination rates of atomic hydrogen and atomic deuterium, it is advisable to use equation (1) and its analog for deuterium. This greatly simplifies calculations since the inclusion of the diffusion term changes equation (1) into a second order differential equation which is both inhomogeneous and non-linear. In addition, the result obtained below for the absolute value of k agrees so well with that obtained by Smallwood using a static system which eliminated diffusion that the possible 10% effect of diffusion may be considered as a very liberal estimate.

As shown in a previous derivation for a given pumping speed equation (1) reduces to

$$-\mathrm{d}(V_{\mathrm{x}}[\mathrm{H}])/\mathrm{d}x = k[\mathrm{H}]^3 \qquad (2)^{1c}$$

where V_{x} is the linear velocity of the gas in the recombination tube at the point x

$$V_{\mathrm{x}} = \frac{\mathrm{d}n/\mathrm{d}t}{\pi r^2([\mathrm{H}_2] + 0.5\ [\mathrm{H}])} \qquad (3)$$

The concentrations of atoms and molecules in moles per cc. are given by

$$[\mathrm{H}] = \frac{P}{RT}\frac{2\alpha}{1+\alpha}$$

$$[\mathrm{H}_2] = \frac{P}{RT}\frac{1-\alpha}{1+\alpha}$$

Substituting $T = 303.16°\mathrm{K}.$ and $R = 6.241 \times 10^4$ cc. mm./moles °K. equation (2) takes the form

$$-2.186 \times 10^{16}\ \mathrm{d}n/\mathrm{d}t\ \frac{(1+\alpha)^3}{\alpha^3}\,\mathrm{d}\alpha = kP^3\,\mathrm{d}x \qquad (4)$$

In order to integrate equation (4) P must be expressed as a function of x. In the interval $x = 0$ to $x = 34.1$, P varies linearly with the distance, but since Table I shows that P_0 is in no case more than 8% greater than P, P may be replaced by the mean pressure, $\overline{P}$ (that corresponding to $x = 17.05$), which is given by $(P_0 + P)/2$. The error introduced in this way is never as large as 0.5%. The integral of equation (4) is then

$$\frac{2.186 \times 10^{16}\ \mathrm{d}n/\mathrm{d}t}{\overline{P}^3}\left(\frac{1}{2\alpha^2} + \frac{3}{\alpha} - 3\ln\alpha - \alpha\right) = 34.1\,k + \frac{2.186 \times 10^{16}\ \mathrm{d}n/\mathrm{d}t}{\overline{P}^3}\,C \qquad (5)$$

where C is an integration constant whose value depends upon the fraction of atomic hydrogen (or deuterium) at the discharge tube and for a given hydrogen isotope is therefore independent of pumping speed. Setting

$$\frac{1}{2\alpha^2} + \frac{3}{\alpha} - 3\ln\alpha - \alpha = \Phi$$

equation (5) becomes

$$\frac{6.41 \times 10^{14}\ \mathrm{d}n/\mathrm{d}t}{\overline{P}^3}\,\Phi = k + \frac{6.41 \times 10^{14}\ \mathrm{d}n/\mathrm{d}t}{\overline{P}^3}\,C \qquad (6)$$

which should give straight lines for the deuterium and hydrogen data of Table I when $[(\mathrm{d}n/\mathrm{d}t)/\overline{P}^3]\Phi$ is plotted against $(\mathrm{d}n/\mathrm{d}t)/\overline{P}^3$. For each of these curves the intercept (multiplied by 6.41×10^{14}) is the specific reaction rate constant for the recombination of atomic deuterium (90% D, 10% H) and hydrogen, respectively, in accordance with the mechanism specified by equation (1).

Figure 1 shows the curves drawn by the method of least squares from the experimental data of Table I. Since the absolute error was independent of the value of α, the values of Φ were weighted with this in view. As seen from equations (4) and (5) $\mathrm{d}\Phi/\mathrm{d}\alpha = (1+\alpha)^3/\alpha^3$ so that the weighting factor for Φ is $\alpha^3/(1+\alpha)^3$. Weighting the Φ values in this manner prevents the least accurate low valued points from unduly influencing the fit of the curve. The specific rate constants as calculated from the intercepts of the curves are 1.56×10^{16} and 2.05×10^{16} cc.^{2} mole^{-2} sec.$^{-1}$ for the deuterium mixture and hydrogen, respectively. The deuterium mixture, however, produced only 90% D atoms upon complete dissociation so that for pure deuterium the decrease in rate constant would be (2.05 − 1.56) × 10^{16}/0.90 or 0.54 × 10^{16} giving 1.51 × 10^{16} as the rate constant for the recombination of atomic deuterium.

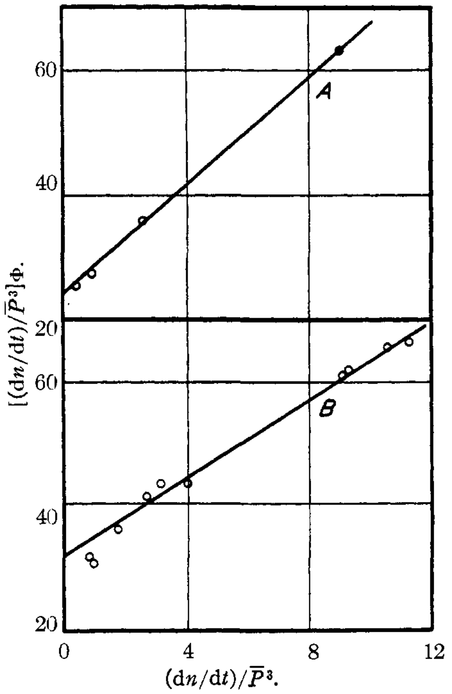

Fig. 1.—A, atomic deuterium; B, atomic hydrogen.

Discussion

Although equation (1) was felt to be justifiable for comparative determinations of rate constants, the excellent agreement of the absolute value in the case of hydrogen with that obtained by Smallwood indicates that the mechanism of recombination is essentially triple collisions involving only atoms. For hydrogen, the present value of k, allowing for experimental error, is (2.05 ± 0.07) × 10^{16} as compared with (1.7 ± 0.3) × 10^{16} obtained by Smallwood. The present value for deuterium is (1.51 ± 0.05) × 10^{16}. Atomic hydrogen, therefore, combines at a faster rate than atomic deuterium in the ratio

$$(2.05 \pm 0.07)/(1.51 \pm 0.05) = 1.36 \pm 0.06$$

According to Tolman,[5] the number of triple collisions involving only hydrogen atoms is given by

$$Z = 32\ N^3\ [\mathrm{H}]^3 \pi^{3/2} \sigma_{\mathrm{H}}^4\, \delta_{\mathrm{H}} \sqrt{RT/M}$$

where σ_{H} is the diameter, N, Avogadro's number and M, the mass (grams per mole) of the hydrogen atom. δ_{H} is the distance to which the third atom must approach relative to the first two atoms in order for a triple collision to occur. For the case of atomic hydrogen, therefore, the specific rate constant is given by

$$k_{\mathrm{H}} = 32\ N^2\ \pi^{3/2}\ \sigma_{\mathrm{H}}^4\, \delta_{\mathrm{H}} \sqrt{RT}$$

and for atomic deuterium

$$k_{\mathrm{D}} = 32\ N^2\ \pi^{3/2} \sigma_{\mathrm{D}}^4\, \delta_{\mathrm{D}} \sqrt{RT/2}$$

The experimental value, 1.36 ± 0.06, for the ratio $k_{\mathrm{H}}/k_{\mathrm{D}}$ indicates that the diameters and forces are equal for hydrogen and deuterium atoms ($\sigma_{\mathrm{H}} = \sigma_{\mathrm{D}}$ and $\delta_{\mathrm{H}} = \delta_{\mathrm{D}}$) since under these conditions the theoretical ratio for $k_{\mathrm{H}}/k_{\mathrm{D}}$ is $\sqrt{2/1}$ or 1.41. It is interesting to observe that the determination of the viscosity ratio indicates a similar equality of *molecular* diameters and forces for hydrogen and deuterium.

Summary

1. Using a dynamic method, the rates of recombination of atomic hydrogen and atomic deuterium have been measured under analogous conditions.

2. The reaction velocity constant for the recombination of atomic hydrogen, k_{H}, is (2.05 ± 0.07) × 10^{16} and that for atomic deuterium, k_{D}, (1.51 ± 0.05) × 10^{16} $\mathrm{cc.}^2\,\mathrm{mole}^{-2}\,\mathrm{sec.}^{-1}$.

3. The ratio of these rates, $k_{\mathrm{H}}/k_{\mathrm{D}}$, is 1.36 ± 0.06 indicating that the atomic diameters and interatomic forces are equal for hydrogen and deuterium atoms.

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