aqueous solution leads to the view that there is free rotation to much the same degree in both series of compounds. The correlation between dielectric increments, apparent molal volumes and acidity constants is pointed out for these alicyclic amino acids.

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Recombination of Hydrogen Atoms. III

BY I. AMDUR

It is generally conceded that the combination of hydrogen atoms to form molecules proceeds according to a trimolecular mechanism. The presence and extent of first or second order wall reactions, as well as the efficiencies of hydrogen atoms and hydrogen molecules as third bodies, have been the subject of much controversy and speculation. Agreement among various investigators is definitely lacking. Smallwood,[1] for example, contends that it is possible to eliminate any wall reaction and that the essential recombination mechanism involves only triple collisions of hydrogen atoms, whereas Steiner[2] finally concludes that there is a small first order wall reaction, but that hydrogen molecules are the most efficient third bodies. In contradiction to this, Amdur[3] found that the assumption of a homogeneous reaction involving only triple collisions of hydrogen atoms was adequate to account for the experimental data for the relative rate of recombination of atomic hydrogen and atomic deuterium over a narrow range of composition and pressure. And yet, some time previously, Smallwood[4] and Amdur and Robinson[5] had decided that for any extended range of variables it was necessary to include a wall reaction as well as both types of triple collisions. In all the cases cited the investigators used high concentrations of atomic hydrogen (95 to 10%) produced in a discharge tube at total pressures of the order of 1 mm. Other experimenters[6] working at total pressures of the order of 10 mm. with small concentrations of atomic hydrogen (less than 1%) produced by photosensitization of mercury saturated hydrogen, report results as varied as those noted above.

In the opinion of the author, there are several reasons for these discrepancies even after one has taken into account the widely different experimental methods and range of variables. One reason is a tendency, in the treatment of experimental data, to oversimplify the formal rate equation containing the desired velocity constants. To include the proper diffusion terms in the equation involved for the recombination of hydrogen atoms in a dynamic system, for example, involves much laborious calculation and necessitates data of considerable accuracy and consistency. However, the omission of these diffusion terms, whose magnitude is small, is capable of effecting tremendous variations in the rate constants or even of yielding negative values when the constants are simultaneously solved for. The same situation results from the use of values for the fraction or partial pressure of atomic hydrogen which are of low accuracy. Finally, if the range of data is not sufficiently wide, a mechanism may be sponsored which may be quite inadequate to account for experimental results over a larger range of variables. In this connection it should be noted that several mechanisms may fit the experimental data equally well. This point has been overlooked, in some cases, possibly, due to personal prejudice regarding the correct mechanism to be assumed for the reaction.

It is the purpose of this paper to avoid, as much as possible, any arbitrary decisions by treating objectively a very large number of experimental points covering the widest possible range of composition and pressure attainable with the present experimental method. This objective treatment consists, first, of least squaring all the data to fit a family of curves for the various pumping speeds and using least square methods to calculate rate constants taking all experimental points into account; second, of rigorously deriving the rate expressions, taking into account all factors involved

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(1) Smallwood, THIS JOURNAL, **56**, 1542 (1934).

(2) Steiner, *Trans. Faraday Soc.*, **31**, 623 (1935).

(3) Amdur, THIS JOURNAL, **57**, 856 (1935).

(4) Smallwood, *ibid.*, **51**, 1985 (1929).

(5) Amdur and Robinson, *ibid.*, **55**, 1395 (1933).

(6) (a) Senftleben and Riechemeier, *Ann. Physik*, **6**, 105 (1930); (b) Farkas and Sachsse, *Z. physik. Chem.*, **B27**, 111 (1934); (c) Senftleben and Hein, *Ann. Physik*, **22**, 1 (1935).

in a dynamic system as well as all possible mechanisms of recombination, and, finally, of using the calculated rate constants to obtain *calculated* values to compare with the *measured* fraction of atomic hydrogen. Any decision as to mechanism will be based on the agreement between these calculated and measured values.

Experimental

Apparatus.—The essential parts of the apparatus are shown in Fig. 1. Molecular hydrogen from an H-shaped electrolytic generator was expanded through the capillary A into the Wood discharge tube B where the atomic hydrogen was produced by a glow discharge. Mixtures of molecular and atomic hydrogen were pumped along the recombination tube C by means of two parallel four-jet mercury pumps backed by a Langmuir diffusion pump and a Hypervac oil pump. The fraction of atomic hydrogen at any point along the recombination tube was computed from the amount of energy liberated on a catalyst-calorimeter D by the recombination of the atoms. This calorimeter consisted of two concentric platinum tubes $1^{3}/_{4}''$ (4.44 cm.) long with diameters 0.312″ (7.92 mm.) and 0.219″ (5.56 mm.). A platinum ring was gold soldered in one end, producing a double-walled tube having an annular space of 0.046″ (1.17 mm.). A copper tube $1^{1}/_{2}''$ (3.81 cm.) long with diameter and wall thickness to permit a snug fit into the annulus between the platinum tubes was then wound with approximately 20 inches (50.8 cm.) of 0.002″ (0.05 mm.) pure platinum wire which served as a resistance thermometer and heater. Insulation was effected by cutting a double thread into the outside wall of the copper tube and baking a thin layer of enamel glaze into the threads, after which the resistance wire was wound in these grooves and made fast by a top coating of baked enamel. The unit was then inserted into the platinum sheath and the leads led out from the top through small platinum tubes. Lead glass was melted into the top opening of the annulus securing and insulating the platinum tubes. To render the calorimeter less liable to damage, the fine platinum leads were gold soldered to the platinum tubes encasing them, and all electrical connections were made to these tubes. In the recombination tube, the calorimeter was supported by a thin, flexible, four-wire rubber-covered cable connected to the windlass E which permitted movement of the calorimeter in vacuum. The drum of the windlass was calibrated to permit determination of the calorimeter position in the recombination tube by means of a dial attached to the ground joint of the windlass. That greater accuracy might be obtained in estimating the energy liberated on the calorimeter, the recombination tube was surrounded by an oil thermostat at 30.000 ± 0.005°. The McLeod gage arrangement shown in the diagram permitted a simultaneous reading of the pressure at four points along the recombination tube when a steady state had been reached with respect to the calorimeter.

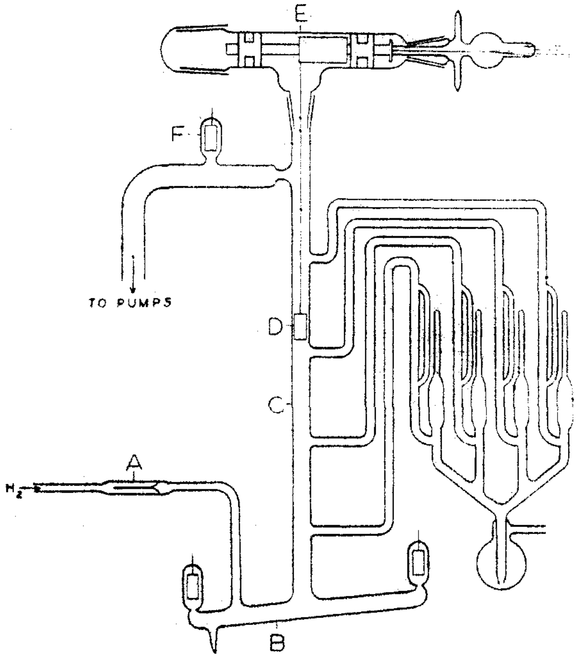

Fig. 1.

Procedure.—All glass parts of the apparatus through which atomic hydrogen flowed were cleaned carefully with cleaning solution and aqua regia, rinsed repeatedly with distilled water and pumped dry. The walls of the recombination and discharge tubes were then coated with sirupy phosphoric acid to minimize wall reaction and the system evacuated until the vapor pressure of water was less than 0.001 mm. The catalyst was then raised and hydrogen pumped through the system to permit a clean-up of the recombination tube by means of the third electrode F. After this treatment, the catalyst was lowered to the bottom of the recombination tube and the discharge turned on and maintained until the catalyst-calorimeter had reached a steady state temperature, as shown by the resistance of the internal platinum wire. The mercury in the McLeod gages was then permitted to rise from a position just below the shutoffs to the height necessary for reading the pressures. The discharge was then shut off, and the proper heating current passed through the catalyst-calorimeter to produce the same resistance change as that previously caused by the recombination of the atoms. From the known current and resistance at this second steady state the energy input to the catalyst-calorimeter was obtained, and since all conditions, with the exception of the presence of hydrogen atoms, were the same in the second part of the run as in the first, this energy input was equal to the energy per second previously produced by the recombination of the atoms. In view of the fact that the heat of dissociation of molecular hydrogen was known (102,800 calories per mole), it was merely necessary to know the number of moles of molecular hydrogen flowing through the apparatus per second in order to determine the fraction of atomic hydrogen. This was obtained directly from the electrolytic current required to produce hydrogen at the same rate at which it was being withdrawn by pumping as shown by equal heights of the electrolytic liquid (30% potassium hydroxide containing a small amount of barium hydroxide) in the limbs of the H-shaped generator. For a given position of the catalyst-calorimeter runs were made at seven different pumping speeds by using different combinations of diffusion pumps and by pumping with the Hypervac through 2-cm. tubing as well as through capillary by-passes. Runs were made in this manner for all pumping speeds at 10-cm. intervals along the recombination tube.

All electrical quantities were measured with a Type K potentiometer using precision standard resistances to determine currents. The McLeod gages were read with a cathetometer. It was possible to return the catalyst to a given position and check within 0.5% a previous determination made several weeks earlier under the same conditions of flow and pumping speed.

Preliminary Treatment of Data.—Since there were but four pressure taps along the recombination tube, there were a great many positions of the catalyst-calorimeter between any two of these taps for which the appropriate pressures were obtained by interpolation. To secure these interpolated values, for a given pumping speed, the drop in pressure, ΔP_{a-b}, between taps a and b was determined for all runs in which the calorimeter was at tap b or above, and, similarly, the pressure drop, ΔP_{b-c}, between taps b and c was obtained in all runs where the catalyst was at or above tap c. This was repeated for all pumping speeds. It was found that for all pump combinations, except the first two at low pressures, the pressure distribution along the recombination tube was a linear function of distance. Deviations from linearity were less than 0.5%, the approximate error in the measurement of pressures at the taps. In the case of pump combinations I and II, ΔP_{c-c} was greater than ΔP_{a-b} by 0.009 and 0.008 mm., respectively. For these combinations, it was assumed that ΔP_{c-d} exceeded ΔP_{b-c} by like amounts. Since the distance between taps was known, it was possible to obtain $\Delta P/\Delta x$ values for all pump combinations and, in the case of combinations I and II, for different positions along the recombination tube. Using these $\Delta P/\Delta x$ values the pressure existing at the calorimeter when it was *between* any two taps was found by interpolation. Examination of the pressure data showed that the pressure distribution below the calorimeter was independent of the position of the calorimeter in the recombination tube. For this reason it is felt that the accuracy of the interpolated pressures is not less than that of the pressures recorded at the four taps.

The values of the pressure, P, thus obtained were valid only for the particular rate of flow of molecular hydrogen (as recorded by the ammeter of the electrolytic circuit) existing during the particular run. In order to simplify treatment of the data, all pressures were corrected to a single average rate of flow. If I is the electrolytic current giving the number of moles of hydrogen flowing per second in a given run, and I', the corresponding current for the desired average rate of flow, $(I' - I)/I'$ is the fractional deviation of the actual rate of flow from the mean. The nature of the ΔP values showed that there was viscous or Poiseuille flow in the recombination tube. The end of the recombination tube near the pumps being at essentially zero pressure, the pressure in the section of the tube containing the pressure taps should vary as the square root of the number of moles of hydrogen flowing per second, or the fractional pressure change should be $^1/_2(I' - I)/I'$. In this manner all pressures were corrected to a single rate of flow. To obtain new α values consistent with the new P values, a curve of α against P for each pumping speed was drawn from the original data. Values of $\mathrm{d}\alpha/\mathrm{d}P$ were obtained graphically from these curves. The correction applied to α, therefore, was $\mathrm{d}\alpha/\mathrm{d}P\delta P$ where δP was the correction to the original pressure. On the average, δP was about 1% of the original pressure, and $\delta\alpha$, about 1% of the original α value.

As measurements of α were made at a single calorimeter position for all pumping combinations before proceeding to a new position, it was necessary to take into account possible changes in pumping speed with time. In some cases, for example, some α determinations with the same pump combination were made two months apart. Inasmuch as it had been ascertained that the ΔP values between taps for all the pump combinations did not vary with time, the correction of pressures to constant pumping speed for each pump combination was simply made by passing a curve with the proper slope through the P values (corrected to a single rate of flow) existing at the catalyst. In the case of pump combinations I and II this meant graphically fitting the P values (at the corresponding values of x) to a curve whose first and second derivatives were fixed. For all other combinations a single $\Delta P/\Delta x$ value for the entire length of the recombination tube was used, corresponding to a constant first derivative. After making the proper constant pumping speed corrections to the pressure, it was again necessary to calculate the corresponding corrections to α. These were determined as explained in connection

TABLE I

Internal diameter of recombination tube = 0.994 cm. Common rate of flow of H_2 = n_0 = 1.117 × 10^{-6} mole/sec.

	I		II		III		IV		V		VI		VII	
x	P	α	P	α	P	α	P	α	P	α	P	α	P	α
34.1	0.438	0.693	0.477	0.638	0.612	0.482	0.703	0.376	0.739	0.353	0.856	0.278	1.044	0.200
44.1	.425	.601	.465	.550	.602	.423	.694	.314	.731	.300	.849	.213	1.039	.142
54.1	.411	.609	.452	.522	.592	.335	.684	.241	.723	.222	.842	.172	1.035	.1132
64.1	.397	.566	.439	.478	.582	.280	.675	.202	.715	.178	.835	.139	1.030	.091
74.1	.381	.485	.424	.417	.572	.232	.666	.176	.707	.151	.828	.114	1.025	.0719
84.1	.364	.471	...	...	.562	.194	.657	.148	.699	.135	.821	.0948	1.020	.0617
94.1	.348	.461	.394	.389	.552	.196	.648	.146	.691	.128	.814	.0891	1.016	.0573
104.1	.332	.455	.379	.388	.542	.198	.639	.141	.683	.125	.807	.0858	1.011	.0529
114.1	.313	.442	.362	.360	.532	.170	.630	.121	.675	.110	.800	.0753	1.006	.0472
124.1	.295	.442	.345	.364	.522	.176	.620	.112	.667	.108	.793	.0736	1.002	.0456
134.1	.276	.454	.328	.368	.512	.162	.611	.112	.659	.104	.786	.0659	0.997	.0410

with the reduction to a single rate of flow. The constant pumping speed pressure corrections averaged slightly over 1% showing that the pumps retained their speed characteristics remarkably well. The corresponding average change in α was less than 1%.

The application of the above-mentioned corrections for each of the seven pump combinations yielded a set of α, x and P values applicable to a single rate of flow and constant pumping speed. It should be emphasized that the *average total correction to the original data was only about 2%* and in only three runs out of 83 did the total correction reach 5%. Since the individual corrections were known to at least 5%, the final values of α and P, in addition to being self-consistent, are as accurate as the original measured values.

Results

Analytical Representation of Data.—The experimental results, corrected to constant rate of flow and constant pumping speed, are given in Table I. The Roman numerals represent pump combinations; x, the distance in cm. from the bottom of the calorimeter to the discharge tube; P, the pressure in mm. existing at x, and α, the fraction of atomic hydrogen. All measurements were taken at 30.000 ± 0.005°.

In order to use all the experimental data in solving for reaction velocity constants it is necessary to have extremely self-consistent values for $d\alpha/dx$ as a function of x. To obtain these, the x, α values of Table I were fitted to an empirical family of seven curves by the method of least squares. An examination of the α values of Table I shows several slightly erratic variations. Since all values were reproducible, such variations were probably due to slight gradual changes in the catalytic activity of the recombination tube. The effect of fitting the data to a family of curves is to smooth out such fluctuations in the same manner for all pump combinations.

As a result of many attempts, the type equation best representing all x, α values was found to be

$$x = a(-\log_{10} \alpha) + b(-\log_{10}\alpha)^c \qquad (1)$$

Although much calculation is involved, it is possible to solve for a, b and c in equation (1) using the method of least squares. The process involves successive approximations and can be used to calculate a, b and c to any desired accuracy. Table II summarizes the results of Table I in terms of the values of a, b and c necessary to represent the α and x values for each pump combination. The percentage deviation column gives the magnitude of the average absolute percentage deviation of the α values as given by equation (1) from the experimental values of Table I. Since equation (1) is not explicit in α, calculated α-values were obtained from the curves which resulted from plotting x's calculated from given α's using equation (1). Figure 2 shows how the points of Table I scatter with respect to the smooth curves derived from the constants of Table II.

TABLE II

ANALYTICAL REPRESENTATION OF EXPERIMENTAL α,x VALUES

	a	b	c	Deviation, %
I	226.2851	78.6940 × 10^5	11.67250	3.0
II	175.1821	201.1848 × 10^2	7.40127	2.5
III	112.3282	434.3611	9.61006	3.9
IV	81.1155	69.4310	5.78891	3.1
V	79.3988	62.1211	8.73140	5.1
VI	63.1952	21.6183	6.28395	2.9
VII	49.3034	8.1251	6.46043	2.7

The variation of pressure with distance for each pump combination was also expressed in analytical form by quadratic equations for pump combinations I and II and by linear equations for all other pump combinations. The general equation in this case is

$$P = P_0 - Ax - Bx^2 \qquad (2)$$

where P_0 is the pressure at the discharge tube and where B is zero for all pump combinations except I and II. Table III summarizes the representation of pressure as a function of distance. The values of P_0, A and B are such as to give the pressure, P, in dynes/sq. cm.

TABLE III

ANALYTICAL REPRESENTATION OF EXPERIMENTAL P,x VALUES

	P_0	A	B
I	639.9	1.492	0.00802
II	688.0	1.396	.00702
III	860.6	1.332	.0
IV	977.8	1.221	.0
V	1020.7	1.066	.0
VI	1170.8	0.932	.0
VII	1412.1	.628	.0

The maximum deviation of P values calculated from equation (2) using the above constants, from the experimental values of Table I is less than 0.5%.

Derivation of Rate Expressions.—In order to derive rigorous rate expressions applicable to a dynamic system, it is necessary to take into account loss of atoms (a) by both heterogeneous and homogeneous recombination, (b) by the streaming of gas along the recombination tube and (c) by diffusion resulting from concentration gradients.

If it is assumed that recombination at the wall may result from collision of atoms in the gas phase with atoms adsorbed on the wall and also from the collision of two atoms from the gas phase at the wall, the rate of removal of atoms by recombination at a point x along the recombination tube is

$$-\left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}\right)_{x(\mathrm{a})} = k_1[\mathrm{H}] + k_2[\mathrm{H}]^2 + k_3[\mathrm{H}]^2[\mathrm{H}_2] + k_4[\mathrm{H}]^3 \qquad (3)$$

where k_1 and k_2 are the wall reaction rate constants, k_3, the rate constant for the recombination of hydrogen atoms by triple collisions with molecules and k_4, the corresponding rate constant for the case of hydrogen atoms as third bodies. [H] and [H_2] are the concentrations of atoms and molecules in moles per cc.

The removal of atoms by the streaming of gas is given by the equation of continuity

$$-\left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}\right)_{x(\mathrm{b})} = \frac{\mathrm{d}(V_x[\mathrm{H}])}{\mathrm{d}x} \qquad (4)$$

where V_x is the linear velocity of the gas stream in centimeters per second at x. For a rigorous derivation it is necessary to take account of the fact that V_x is affected by diffusion which, in addition to the pumps, causes a transport of mass along the recombination tube. The considerations are as follows.

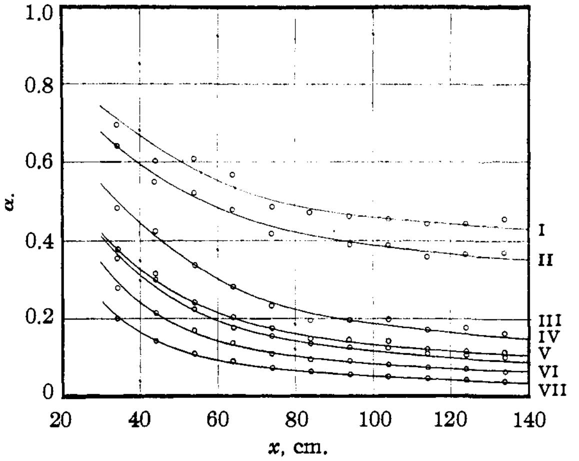

Fig. 2.

The mass of gas per cm.^{2} transferred per second by flow is

$$V_x\rho = V_x(M[\mathrm{H}] + 2M[\mathrm{H}_2]) \qquad (5)$$

where ρ is the density of the gas mixture and M the atomic weight of hydrogen. The mass of gas per cm.^{2} transferred per second by diffusion is

$$-D_{12}\frac{\mathrm{d}\rho}{\mathrm{d}x} = -D_{12}\left(M\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}x} + 2M\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}x}\right) \qquad (6)$$

where D_{12} is the diffusion coefficient for the mixture of atoms and molecules at the conditions existing at x. Since the mass of gas per cm.^{2} admitted per second to the apparatus is $2Mn_0/\pi r^2$

$$V_x(M[\mathrm{H}] + 2M[\mathrm{H}_2]) - D_{12}\left(M\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}x} + 2M\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}x}\right) = \frac{2Mn_0}{\pi r^2} \qquad (7)$$

so that

$$V_x = \frac{2n_0/\pi r^2 + D_{12}\left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}x} + 2\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}x}\right)}{([\mathrm{H}] + 2[\mathrm{H}_2])} \qquad (8)$$

Equation (4) thus becomes

$$-\left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}\right)_{x(\mathrm{b})} = \frac{\mathrm{d}}{\mathrm{d}x}\left\{\frac{\frac{2n_0}{\pi r_2} + D_{12}\left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}x} + 2\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}x}\right)}{([\mathrm{H}] + 2[\mathrm{H}_2])}[\mathrm{H}]\right\} \qquad (9)$$

In addition to diffusion of atoms and molecules altering the linear velocity, atoms are removed from the point x by diffusion according to the equation

$$-\left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}\right)_{x(\mathrm{c})} = -D_{12} \text{ div. grad. } [\mathrm{H}] \qquad (10)$$

Since the construction of the calorimeter was such as to give the average value of α across the cross section of the recombination tube at x, the concentration of atomic hydrogen at x in a plane perpendicular to the axis of the recombination tube may be considered constant. Equation (10), therefore, reduces to

$$-\left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}\right)_{x(\mathrm{c})} = -D_{12}\frac{\mathrm{d}^2[\mathrm{H}]}{\mathrm{d}x^2} \qquad (11)$$

At the steady state

$$\left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}\right)_{x(\mathrm{a})} + \left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}\right)_{x(\mathrm{b})} + \left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}\right)_{x(\mathrm{c})} = \left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t}\right)_{x} = 0$$

so that the rigorous general rate expression obtained by adding equations (3), (9) and (11) is

$$D_{12}\frac{\mathrm{d}^2[\mathrm{H}]}{\mathrm{d}x^2} - \frac{\mathrm{d}}{\mathrm{d}x}\left\{\frac{2n_0/\pi r^2 + D_{12}\left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}x} + 2\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}x}\right)}{([\mathrm{H}] + 2[\mathrm{H}_2])}[\mathrm{H}]\right\} - k_1[\mathrm{H}] - k_2[\mathrm{H}]^2 - k_3[\mathrm{H}]^2[\mathrm{H}_2] - k_4[\mathrm{H}]^3 = 0 \qquad (12)$$

There are numerous special cases which are of interest in connection with equation (12). For example, if the wall reaction is assumed to be second order $k_1 = 0$, while if it is assumed to be first order $k_2 = 0$. In the present case, all such mechanisms which include a third order rate constant (k_3, k_4) will be considered and appropriate rate constants calculated. Decisions regarding the suitability of any mechanism will depend upon how well such rate constants reproduce the α-values calculated with the constants of Table II.

Evaluation of Rate Constants.—Before solving for combinations of k_1, k_2, k_3 and k_4, it is necessary to express the various terms as functions of the measured variables α, x and P and the calculated derivatives $\mathrm{d}\alpha/\mathrm{d}x$, $\mathrm{d}^2\alpha/\mathrm{d}x^2$, $\mathrm{d}P/\mathrm{d}x$, $\mathrm{d}^2P/\mathrm{d}x^2$. From considerations involving viscosity data it was found[7] that the diffusion coefficient for mixtures of atomic and molecular hydrogen could be represented by the relation

$$D_{12} = \frac{374.9T^{3/2}(1.0364 - 0.0303\,\alpha)}{P(1 + 31.9/T)} \qquad (13)$$

Starting with

$$[\mathrm{H}] = \frac{P}{RT}\frac{2\alpha}{1 + \alpha} \qquad (14)$$

and considering both α and P functions of x, the first and second derivatives of [H] are found to be

$$\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}x} = \frac{2}{RT}\frac{P}{(1 + \alpha)^2}\frac{\mathrm{d}\alpha}{\mathrm{d}x} + \frac{2}{RT}\frac{\alpha}{1 + \alpha}\frac{\mathrm{d}P}{\mathrm{d}x} \qquad (15)$$

and

$$\frac{\mathrm{d}^2[\mathrm{H}]}{\mathrm{d}x^2} = \frac{2}{RT(1 + \alpha)}\left[\frac{2}{(1 + \alpha)}\frac{\mathrm{d}\alpha}{\mathrm{d}x}\frac{\mathrm{d}P}{\mathrm{d}x} - \frac{2P}{(1 + \alpha)^2}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}x}\right)^2 + \frac{P}{(1 + \alpha)}\frac{\mathrm{d}^2\alpha}{\mathrm{d}x^2} + \alpha\frac{\mathrm{d}^2P}{\mathrm{d}x^2}\right] \qquad (16)$$

Since

$$[\mathrm{H}_2] = \frac{P}{RT}\frac{1 - \alpha}{1 + \alpha} \qquad (17)$$

the total concentration of atoms and molecules is

$$[\mathrm{H}] + [\mathrm{H}_2] = P/RT \qquad (18)$$

from which it follows that

$$\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}x} = \frac{1}{RT}\frac{\mathrm{d}P}{\mathrm{d}x} - \frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}x} \qquad (19)$$

By using the above relations the following identity is obtained

$$\frac{\mathrm{d}}{\mathrm{d}x}\left\{\frac{2n_0/\pi r^2 + D_{12}\left(\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}x} + 2\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}x}\right)}{([\mathrm{H}] + 2[\mathrm{H}_2])}[\mathrm{H}]\right\} = \frac{2n_0}{\pi r^2}\frac{\mathrm{d}\alpha}{\mathrm{d}x} + \frac{2}{RT(1 + \alpha)}\frac{374.9T^{3/2}(1.0364 - 0.0303\,\alpha)}{P(1 + 31.9/T)}\left[\frac{1}{1 + \alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}x}\frac{\mathrm{d}P}{\mathrm{d}x} - \frac{(1 - \alpha)P}{(1 + \alpha)^2}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}x}\right)^2 + \alpha\frac{\mathrm{d}^2P}{\mathrm{d}x^2} - \frac{\alpha}{P}\left(\frac{\mathrm{d}P}{\mathrm{d}x}\right)^2 - \frac{\alpha}{1 + \alpha}\frac{P\mathrm{d}^2\alpha}{\mathrm{d}x^2}\right] \qquad (20)$$

The remaining terms of the rate equations are obtained directly from equations (14) and (17).

The substitution of numerical values into the rate expressions was carried out in the following manner. At each pump combination a series of α-values at increments of 0.025 were taken, starting near the highest measured value and ending near the lowest measured value. The corresponding x's were then calculated from equation (1) using the appropriate constants from Table II, and the desired values of P computed from equation (2) using Table III. General expressions for $\mathrm{d}\alpha/\mathrm{d}x$ and $\mathrm{d}^2\alpha/\mathrm{d}x^2$ were obtained by direct differentiation of equation (1) resulting in

$$\frac{\mathrm{d}\alpha}{\mathrm{d}x} = \frac{2.3026\,\alpha}{-a - bc\,(-\log_{10}\alpha)}^{c-1} \qquad (21)$$

and

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}x^2} = \frac{1}{\alpha}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}x}\right)^2\left[1 - \frac{1}{\alpha}\frac{bc\,(c - 1)(-\log_{10}\alpha)^{c-2}}{2.3026}\frac{\mathrm{d}\alpha}{\mathrm{d}x}\right] \qquad (22)$$

The required numerical values for these derivatives were obtained by using the constants of Table II. In like manner $\mathrm{d}P/\mathrm{d}x$ and $\mathrm{d}^2P/\mathrm{d}x^2$ values were obtained by differentiation of equation (2) and the use of Table III.

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[7] Amdur, *J. Chem. Phys.*, **4**, 339 (1936).

After substitution of numerical values it is possible to solve simultaneously for all the reaction velocity constants in any one rate equation.[8] In the present case, using the method of least squares, all experimental data (represented by 83 measured α-values) were used to solve for the reaction velocity constants in each rate equation. This corresponded to the use of 71 rounded α-values in solving for each set of constants. The results of these solutions are summarized in Table IV, where the rate constants are in the following units: k_1, sec.$^{-1}$; k_2, cc.^{1} mole^{-1} sec.$^{-1}$; k_3 and k_4, cc.^{2} mole^{-2} sec.$^{-1}$. The nature of the mechanism is deduced from the constants regarded as having zero value.

TABLE IV

REACTION VELOCITY CONSTANTS FOR POSTULATED MECHANISMS

Mechanism	k_1	$k_2 \times 10^{-8}$	$k_3 \times 10^{-16}$	$k_4 \times 10^{-16}$
A	0.69	2.33	1.00	1.70
B	0	3.234	1.004	1.419
C	1.956	0	1.038	2.578
D	0	0	1.212	3.063
E	0	6.028	0	0.745
F	0	5.810	0.925	0
G	4.231	0	0	2.770
H	8.425	0	1.233	0
I	0	0	0	4.160
J	0	0	3.634	0

The method of calculating α-values using the above constants can be illustrated by considering a specific mechanism, A. Using the numerical values of the constants for each of the 71 rounded experimental points (7 pump combinations) the quantities $k_1[\mathrm{H}]$, $k_2[\mathrm{H}]^2$, $k_3[\mathrm{H}]^2[\mathrm{H}_2]$ and $k_4[\mathrm{H}]^3$ are evaluated. From the sum of these terms the quantity $D_{12}\dfrac{\mathrm{d}^2[\mathrm{H}]}{\mathrm{d}x^2}$ is subtracted leaving a numerical quantity Z, where

$$Z = -\frac{2n_0}{\pi r^2}\frac{\mathrm{d}\alpha}{\mathrm{d}x} - \Phi$$

Φ is identified from equations (12) and (20) as

$$\frac{2}{RT(1+\alpha)}\,\frac{374.9T^{3/2}\,(1.0364 - 0.0303\,\alpha)}{(1 + 31.9/T)}\left[\frac{1}{1+\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}x}\frac{\mathrm{d}P}{\mathrm{d}x} - \frac{(1-\alpha)P}{(1+\alpha)^2}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}x}\right)^2 + \alpha\frac{\mathrm{d}^2P}{\mathrm{d}x^2} - \frac{\alpha}{P}\left(\frac{\mathrm{d}P}{\mathrm{d}x}\right)^2 - \frac{\alpha}{1+\alpha}\frac{P\mathrm{d}^2\alpha}{\mathrm{d}x^2}\right]$$

If the appropriate Φ values are now added to each of the 71 Z values and the resulting sums $(Z + \Phi)$ multiplied by $-\pi r^2/2n_0$, the result is 71 calculated $\mathrm{d}\alpha/\mathrm{d}x$ points. A number of $\mathrm{d}\alpha/\mathrm{d}x$ points are derived from smoothed experimental points using equation (21) and plots made of $\alpha_{\text{exptl.}}$ *vs* $\mathrm{d}\alpha/\mathrm{d}x_{\text{exptl.}}$ for each pump combination. From these plots the 71 α's corresponding to the 71 calculated $\mathrm{d}\alpha/\mathrm{d}x$'s are read.

The results of the above procedure for the ten mechanisms of Table IV are summarized in Table V for all pump combinations. The numbers are the average absolute percentage deviations of the α's calculated from numerical rate constants from the corresponding smoothed experimental points. For all mechanisms, the individual deviations in each pump combination scattered well between positive and negative values.

TABLE V

PERCENTAGE DEVIATION OF α-VALUES

Mechanism	I	II	III	IV	V	VI	VII
A	3.2	3.4	6.2	3.2	5.9	4.0	5.6
B	3.2	3.4	6.2	3.2	5.9	4.0	5.6
C	3.2	3.4	7.1	3.6	6.7	5.2	7.2
D	3.6	2.6	8.6	3.6	7.2	4.6	5.6
E	10.3	9.6	6.8	4.4	8.9	8.0	12.0
F	3.2	4.6	5.5	5.2	6.3	4.6	8.0
G	9.8	9.4	8.0	5.2	8.9	9.2	13.6
H	7.3	9.4	13.2	13.2	12.2	15.4	21.6
I	8.2	8.0	12.9	9.6	11.8	15.4	24.8
J	16.4	17.6	21.5	10.8	8.4	21.4	46.3

Discussion

In interpreting Table V it should be noted that the average experimental value of α for pump combination VII is almost five times smaller than that for pump combination I, so that equal percentage deviations correspond to different actual deviations. This is apparent from the curves of Fig. 2. Thus a 1% average absolute deviation is equivalent to the following changes in the rounded α-values:

I	II	III	IV	V	VI	VII
0.0056	0.0050	0.0032	0.0025	0.0024	0.0018	0.0012

An inspection of Table V reveals that five of the mechanisms (E, G, H, I and J) fail to reproduce the experimental data over the entire range. Thus recombination does not take place homogeneously as the result of triple collisions involving only atoms (mechanism I) as suggested by Smallwood,[1] nor as the result of triple collisions involving only molecules as third bodies (mechanism J). The proposal of Steiner[2] that

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[8] In the case of equation (12) it was found that the smoothed experimental data and derivatives lacked the necessary self-consistency to permit simultaneous solution for k_1, k_2, k_3 and k_4. A change of but 0.05% in the constant terms of the final least square equations was sufficient to produce four positive constants instead of the usual three positive and one negative. The values given in Table IV for this particular mechanism, therefore, were obtained by trial and error substitution in the four final least square simultaneous equations and reproduce these equations to better than 0.2%.

recombination occurs as the result of a first order wall reaction and a homogeneous reaction involving only molecules as third bodies (mechanism H) is ruled out. Similarly, the assumption of a first order wall reaction with a three atom homogeneous reaction (mechanism G) or a second order wall reaction with a three atom homogeneous reaction (mechanism E) fails to provide the proper mechanism.

The other five mechanisms (A, B, C, D and F) show percentage deviations not much larger than those of the experimental and analytically smoothed α's (Table II), and are therefore all regarded as possible mechanisms. On the basis of the deviations in Table V, it is not possible to advocate one of these mechanisms in preference to the others. Thus the elimination of a first order wall reaction (mechanism B) produces α-values which are identical with those derived assuming both types of heterogeneous and homogeneous reaction (mechanism A). The elimination of a second order wall reaction (mechanism C) or the assumption of completely homogeneous reaction involving both types of third bodies (mechanism D) also reproduces the data almost as well as the other postulated mechanisms. Only one of the five mechanisms (mechanism F) does not require both atoms and molecules as third bodies. Although there is no reason to exclude the possibility of a mechanism involving a second order wall reaction and only molecules as third bodies, it should be pointed out that the difference in k_3 values for mechanisms D and F is but 31% so that the second order wall reaction of mechanism F is numerically equivalent, within a factor of 1.31, to the three atom homogeneous reaction of mechanism D.

A final decision as to which of the five mechanisms is correct can be made only when independent evidence eliminates four of the mechanisms as being incorrect. For example, if it could be shown experimentally that there is no wall reaction, mechanism D would be the correct solution; or if it could be shown that the wall reaction must be *only* first order, mechanism C would be correct. Independent accurate evaluations of k_4 might also be used as a means of choosing the one correct mechanism.

The author wishes to emphasize that the correct mechanism in all probability will not be some average mechanism derived from mechanisms A, B, C, D and F but a specific one of these five with the numerical rate constants as given in Table IV.

Objection has been raised to the present experimental method on the basis that the sudden recombination of atoms at the catalyst causes diffusion of atoms toward the catalyst and consequent high values of α. In order to determine the magnitude of this effect accurately, it is necessary to integrate equation (12). Since this cannot be done readily it is only possible to present evidence showing that the effect is negligible.

The diffusion produced by the catalyst is equivalent to increasing suddenly the linear velocity of the gas stream and thus shortening the time of recombination. This acceleration is greatest at the catalyst and dies off very rapidly for high linear velocities. The disturbance produced by the catalyst will be most marked when the catalyst is near the discharge for two reasons. First, the high concentration of atomic hydrogen will result in a greater diffusion when the concentration is suddenly reduced to zero at the catalyst. Second, the rate of recombination near the discharge tube is very rapid (as shown by the curves of Fig. 2) so that a given effective increase in velocity results in less recombination than that resulting from the same increase in velocity occurring far up in the recombination tube. Catalyst measurements such as those made in pump combinations IV, V, VI and VII at α-values from 0.125 to 0.05 should, therefore, be correct to a high degree of accuracy with respect to disturbance produced by the catalyst. If, now, the catalyst measurements at higher values of α produced high numerical results, rate constants calculated using all α-values should be smaller than those obtained from only low α-values. Consequently, rate constants which reproduced high values of α measured near the discharge tube should fail to reproduce low values of α measured far up in the recombination tube. That this is not the case is observed from the percentage deviation of the α-values in Table II for the possible mechanisms A, B, C, D and F. Pump combinations I, II and III contain many high values of α as compared with combinations IV, V, VI and VII where low α-values predominate. Actually, an examination of the individual percentage deviations from which the averages of Table V were computed shows that for very low values of α at high values of x, the α's computed from rate constants are slightly *higher* than the experimental values instead of lower. In fact, it is these wrong direction deviations which cause the average absolute percentage deviations of Table V for the five possible mechanisms to be slightly greater than the smoothing deviations of Table II.

Summary

Using a dynamic system, the fraction of atomic hydrogen has been measured as a function of distance along the recombination tube for seven pumping speeds at pressures ranging from 0.276 to 1.044 mm. The measured fraction of atomic hydrogen varied from 0.0410 to 0.693.

The experimental data have been fitted to a family of empirical curves by the method of least squares. The resulting smoothed variables as well as calculated derivatives have been used to solve for rate constants in rigorous equations applicable to a dynamic system.

Ten mechanisms involving recombination by triple collisions have been postulated and appropriate rate constants calculated using all the smoothed experimental data to obtain unique numerical values for the rate constants in each mechanism.

On the basis of the ability of the calculated rate constants to reproduce the smoothed experimental values for the fraction of atomic hydrogen, five of the postulated mechanisms have been eliminated.

It has been pointed out that, on the basis of reproducibility, it is not possible to advocate any specific one of the remaining five acceptable mechanisms but that future definite information regarding the presence and nature of a wall reaction could determine which one of the five possible sets of rate constants should be used to describe the recombination of hydrogen atoms.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FRESNO STATE COLLEGE]

Electrical Factors in the Adsorption of Polar Molecules at the Surface of Solutions

BY ROBERT DUBOIS AND ERIC E. TODD

In an earlier paper McBain and DuBois[1] reported extensive measurements of adsorption at the air–solution interface which were made as experimental tests of the Gibbs adsorption equation

$$\Gamma_{2(1)} = -\frac{d\sigma}{RT\,d\ln a_2} = -\frac{d\sigma}{RT\,d\ln c_2} \qquad (1)$$

where $\Gamma_{2(1)}$ is the absolute excess of solute (component 2) adsorbed in 1 sq. cm. of the surface of a binary solution, σ is the surface tension of the solution, and a_2, c_2 are, respectively, the activity and the molar concentration of the solute in the bulk solution. ($\Gamma_{2(1)}$ is defined in the Gibbs manner[2] so that $\Gamma_1 = 0$.) The adsorption of various solutes on the surfaces of moving bubbles was measured and found to be much larger than the values calculated by means of the above equation. These results confirmed the earlier measurements of McBain and Davies[3] made with similar apparatus and are in line with the excessive adsorption found by other workers using dynamic methods of measurement.

As a result of this apparent failure of the Gibbs equation to account for the experimental values, it has been suggested by several writers that an electrical term should be added to the equation to take account of the known electrification of the bubbles and drops upon which the adsorption takes place. The validity of such suggestions will be discussed later; their implication is that the excess of the observed adsorption over the calculated value is of electrical origin. As part of a general investigation of the factors responsible for the excessive adsorption on moving bubbles, the present authors have undertaken to test the electrical explanation by measuring the effect of enhanced electrification of the bubbles on the observed adsorption.

Meaning of the Term "Electrification."—The term "electrification of bubbles and drops" may refer to any of the following:

(1) *Electrokinetic double layer*, the electrical double layer which always exists at the surface of any bubble or drop in contact with water or an aqueous solution and whose parts may be tangentially displaced under the influence of an external electric field. The charge which is thus made evident by cataphoretic migration originates in the dissociation of a surface layer, either a part of the

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[1] McBain and DuBois, THIS JOURNAL, **51**, 3534 (1929).

[2] Gibbs, "Collected Works," Longmans, Green and Co., New York, N. Y., 1928, Vol. I, p. 234.

[3] McBain and Davies, THIS JOURNAL, **49**, 2230 (1927).