

The Kinetics of Hydrogen Atom Recombination

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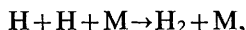
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The rate of recombination of hydrogen atoms at 1072°K has been measured by studying the decay of H-atom concentration in the burnt gases of suitable hydrogen+oxygen+nitrogen flames. The methods of study have included measuring the decay of chemiluminescence when traces of sodium salts are added to the flame gases, and studies of H-atom concentration by means of tracer techniques using their reactions with D₂O and D₂. No significant change in the rates of decay was observed within the range in which it was possible to alter the proportions of N₂, H₂ and H₂O in the burnt gases. This suggests that all these gases give similar third-order recombination constants.

Atom and radical recombination plays an important role as a terminating step in many chemical reactions. This is particularly so in the combustion of hydrogen or hydrocarbons when conditions are such that reaction-vessel wall-effects are small. In flames, where wall effects are absent, such recombinations provide the major terminating steps, and a knowledge of their rates is vital if such systems are to be fully understood kinetically. Furthermore, such information would greatly assist our knowledge of the mechanism of recombination.

When two hydrogen atoms collide, the presence of a third body is necessary to remove some, or all, of the excess energy if association is to occur. The overall reaction may be represented by



where M represents the third body, which may be any other molecule present in the system. Only a few kinetic studies of this reaction have been made. In earlier studies,¹⁻⁵ hydrogen atoms were produced by electrical discharges at low pressures and the rates of recombination studied in a flowing system. Interpretation of these results was complicated by the excessive amount of diffusion of hydrogen atoms and their recombination on the vessel walls. More recently studies have been made by Sugden and collaborators (e.g., ref. (6)-(8)) using hydrogen+oxygen flames as the source of hydrogen atoms. These are well suited for studies of rates of recombination since variations in temperature and composition can readily be made whilst interference from reaction vessel walls is absent. Sugden's studies have been made in the burnt gas of flames having temperatures above about 1400°K. Following the stabilization in this laboratory of slow burning rich hydrogen+oxygen+nitrogen flames having a flame temperature of only 1000-1100°K,⁹ rates of recombination at these lower temperatures have now been studied. Since both hydrogen atoms and hydroxyl radicals are produced in the flames, the decay of hydrogen atoms occurs by the two reactions,



where in the hydrogen-rich flames, M may be either H₂, N₂ or H₂O.

EXPERIMENTAL

In these experiments the recombination reactions are followed by three methods. First, the chemiluminescence when small amounts of sodium salts are added to the flame gases has been shown by Sugden and collaborators to be due to excited sodium atoms formed by reactions (i) and (ii) when M is a sodium atom. Hence the decay of chemiluminescence in the burnt gas may be used as a measure of relative H-atom concentrations. In these low-temperature flames, thermal emission from sodium is negligible. Secondly, the reaction of H atoms with heavy water to form HD by reaction (iii),



has been used to measure their relative concentrations in a few flames. Thirdly, an additional calibration of the H-atom concentration in one flame has been carried out by adding small amounts (about 0.2–0.3 %) of deuterium to the flame gases, and measuring the rate of formation of HD by the exchange reaction.

The flames were burned as large flat horizontal discs on a modified flat-flame burner of the Egerton-Powling type.¹⁰ The burner was 6 cm in diam., and it was surrounded by a twelve-sided chimney consisting of optically flat quartz windows. It was mounted on a vertical slide which could be traversed at a known rate by a synchronous motor. The gases were taken from cylinders (British Oxygen Gases), dried, metered and well mixed before entering the burner. Cylinder deuterium (99.5 %) was supplied by General Dynamics Corporation. Heavy water (99.83 %) or sodium chloride solution (0.005 M) could be added at a known constant rate to the unburnt gas stream by an atomizer. Water vapour could be added by means of a motor driven syringe into a heated vaporizer. Condensation in the apparatus was avoided by heating.

For the photometric measurements, the light from the plane of the flame centre was focused on the sensitive element of a photomultiplier tube. The light actually reaching the photomultiplier was restricted by means of an aperture slit system to that from a narrow horizontal slice of the flame 0.1 mm high at the flame centre and 0.3 mm high at the edges. In early experiments, a monochromator was used to isolate the sodium D lines, but the emission from the flames was so predominantly due to these lines that the monochromator was later found to be unnecessary. The light beam was chopped at 460 c/sec, and the signal was amplified by means of a homodyne system and presented on a chart recorder.

For the deuterium and heavy-water experiments, samples of the gases at various positions in and after the flame were removed by means of a quartz microprobe made from 1 mm ext. diam. tubing drawn down to produce a 25 μ orifice. The position of the probe in this non-luminous flame was obtained by measuring the distance of its tip from the schlieren maximum. The samples withdrawn were analyzed mass spectrometrically in order to determine the [HD]/[H₂] ratios.

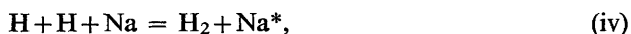
ANALYSIS OF EXPERIMENTAL RESULTS

DETERMINATION OF APPARENT SECOND-ORDER RECOMBINATION RATE CONSTANTS

In a flowing reaction system containing H-atoms, the H-atom concentration is related to distance by means of eqn. (1):

$$f[d[\text{H}]/dt]_{\text{chem}} dy = S[\text{H}] - D_{\text{H}} d[\text{H}]/dy. \quad (1)$$

$[d[\text{H}]/dt]_{\text{chem}}$ is the chemical rate of formation of hydrogen atoms, y represents the distance co-ordinate from some arbitrary plane, S is the linear flow velocity and D_{H} is the diffusion coefficient of H atoms in the mixture. If it is assumed that in the burnt gas of the flame, H and OH are effectively equilibrated and that the chemiluminescence is due to formation of excited Na* by reactions (iv) and (v),



then the result is obtained that $I_{\text{Na}} = Ak_a[\text{H}]^2$, where k_a is an apparent second-order velocity constant for a given gas composition, and A is a proportionality constant for the mixture. In the chemiluminescence experiments, eqn. (1) may therefore be replaced after some rearrangement by eqn. (2):

$$\sqrt{\frac{k_a}{A}} \int I_{\text{Na}} dy = S_b \sqrt{I_{\text{Na}}} - D_{\text{HD}} d(\sqrt{I_{\text{Na}}})/dy. \quad (2)$$

The quantity k_a/A may therefore be found for each flame by means of a straight line plot.

In the flames where D_2 or D_2O were added to the flame gases, the chemical rates of formation of HD were found by application of a diffusion equation similar to eqn. (1). A kinetic analysis¹¹⁻¹³ of the reactions leading to the formation and removal of HD then leads to eqn. (3) and (4):

$$\text{for } \text{D}_2, \quad [d[\text{HD}]/dt]_{\text{chem}} = k_6[\text{H}][\text{D}_2] - \frac{[\text{HD}]}{2[\text{D}_2]} [d[\text{H}_2\text{O}]/dt]_{\text{chem}}; \quad (3)$$

$$\text{for } \text{D}_2\text{O}, \quad [d[\text{HD}]/dt]_{\text{chem}} = k_3[\text{H}][\text{H}_2]_0 \left\{ \frac{[\text{D}_2\text{O}]_0}{[\text{H}_2]_0} - \frac{[\text{HD}]}{2[\text{H}_2]} \right\} - \frac{[\text{HD}]}{2[\text{H}_2]} [d[\text{H}_2\text{O}]/dt]_{\text{chem}}, \quad (4)$$

where k_6 is the velocity constant of $\text{H} + \text{D}_2$ exchange reaction. In order to convert the experimental values of $[\text{HD}]/[\text{H}_2]$ into H-atom concentrations it is, of course, necessary to know both the hydrogen and water concentration profiles. These also are measured by analysis of samples withdrawn from the flames.

A feature of the use of both D_2 and D_2O as indicators is that the forward exchange reaction (vi),



has an activation energy of only about 7 kcal mole⁻¹, whereas the D_2O reaction (iii) has an activation energy of about 25 kcal mole⁻¹. Consequently, reaction (vi) reaches equilibrium in the flame much sooner than reaction (iii), and in fact reaction (vi) is not suitable for studying the burnt gases. On the other hand, the velocity constant k_3 has not, so far as we are aware, previously been measured experimentally, though Fenimore and Jones¹² quote a value based on an extrapolation to higher temperatures of the rate constant measured by Avromenko and Lorentso¹⁴ for the reaction (vii),



Accordingly, in this work, values of $k_3[\text{H}]$ were first determined from the D_2O experiments. The use of these values in conjunction with eqn. (1) leads to values of the ratio k_a/k_3 . Next, for one particular flame, D_2 was added and the maximum H-atom concentration from the D_2 experiments was assumed to coincide with the maximum chemiluminescent intensity. Thirdly, the position on the chemiluminescence profile for this flame was found where, with suitable scaling, the curve of $[k_3[\text{H}]]^2$ against distance could be superimposed upon it. Hence the values of $[\text{H}]$ and k_3 corresponding to the D_2O experiments were found and k_9 , the apparent second-order H-atom recombination rate constants, were obtained. The method depends on the equilibration of H and OH by reaction (vii) throughout the chemiluminescent region. This will not be strictly true and will tend to lead to low apparent values of the H-atom concentration in the D_2O experiments, thus giving an upper limit to the value of k_3 and the values for the recombination rate constants k_a .

CALCULATION OF THIRD-ORDER VELOCITY CONSTANTS

The rate of decay of H and OH in the burnt gases from a hydrogen-oxygen flame is given by

$$-d\{[H] + [OH]\}/dt = k_1^{N_2}[H]^2[N_2] + k_1^{H_2}[H]^2[H_2] + k_1^{H_2O}[H]^2[H_2O] + k_2^{N_2}[H][OH][N_2] + k_2^{H_2}[H][OH][H_2] + k_2^{H_2O}[H][OH][H_2O], \quad (5)$$

here $k_1^{N_2}$, etc., are the appropriate third-order rate constants.

If H and OH may be regarded as equilibrated in the hot gases, eqn. (5) may be written :

$$-d\{[H] + [OH]\}/dt = [H]^2\{k_1^{N_2}[N_2] + k_1^{H_2}[H_2] + k_1^{H_2O}[H_2O] + k_7 \frac{[H_2O]}{[H_2]}\{k_2^{N_2}[N_2] + k_2^{H_2}[H_2] + k_2^{H_2O}[H_2O]\} = k_a[H]^2, \quad (6)$$

where K_7 is the known equilibrium constant of reaction (vii), and k_a is the measured apparent second-order velocity constant.

If a series of rich hydrogen+oxygen+nitrogen flames is studied such that the water vapour concentration in the burnt gas is constant, then $[N_2] + [H_2] = B$, a constant, and k_a may be expressed as a function of the concentrations by eqn. (7).

$$k_a = [H_2]\{k_1^{H_2} - k_1^{N_2}\} + C/[H_2] + D,$$

where

$$C = K_7[H_2O]\{k_2^{N_2}B + k_2^{H_2O}[H_2O]\}$$

and

$$D = k_1^{N_2}B + k_1^{H_2O}[H_2O] + K_7[H_2O]\{k_2^{H_2} - k_2^{N_2}\}. \quad (7)$$

Alteration of the water concentration may be effected without altering the flame temperature by incorporating steam in the gases entering the flame and adjusting the proportions of the other gases accordingly. By studying the variation of C and D with the water-vapour concentration in the burnt gas, values of all the third-order velocity constants may, therefore, be found.

RESULTS

CHEMILUMINESCENCE

Fig. 1 shows the variation in intensity of chemiluminescence with distance in the burnt gas for a few typical flames studied. The measured intensities were corrected to intensities for a standard flame diameter by using constant total gas flows for all the flames and adjusting numerically for the known changes in diameter caused by changes in linear burning velocity. Perhaps the most striking feature of the curves is their near identity within the range of compositions studied. It must be concluded that such variations in overall recombination rate constant as do occur are largely balanced by the changes in flow velocity and diffusion coefficient associated with the changes in composition.

The flame temperature used in this lower temperature study was 1072°K. Using this flame temperature, stable flames could be obtained with burnt gas compositions in the approximate range: H_2 , 2.5-17.5 %; N_2 , 70-87.5 %; H_2O , 10-20 %. The burning velocities, determined by photographing stroboscopically illuminated fine MgO particles entrained in the flame gases, varied between 7.5 and 10.5 cm sec⁻¹ (linear velocities at 18°C/760 mm). These correspond to flow velocities S_b in the burnt gas of between about 28 and 35 cm sec⁻¹. The diffusion coefficient of H-atoms, present as a trace component in a mixture of hydrogen, nitrogen and steam, was calculated to be consistent with some of the recent high-temperature diffusion data of Walker and Westenberg¹⁵ and with the data of Wise¹⁶ for H-atoms in hydrogen.

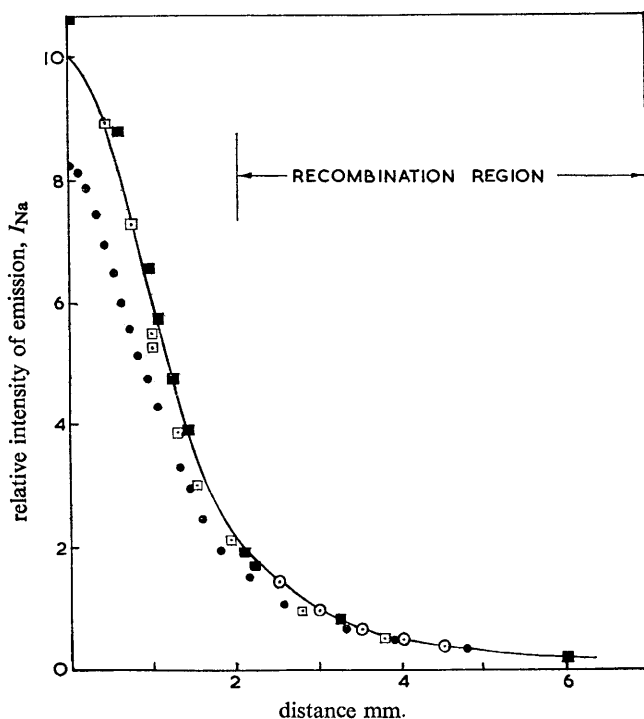


FIG. 1.—Intensity of chemiluminescence in the burnt gas of some slow burning hydrogen+oxygen+nitrogen flames

Open circles represent scaled D_2O results; line is intensity curve for same flame.

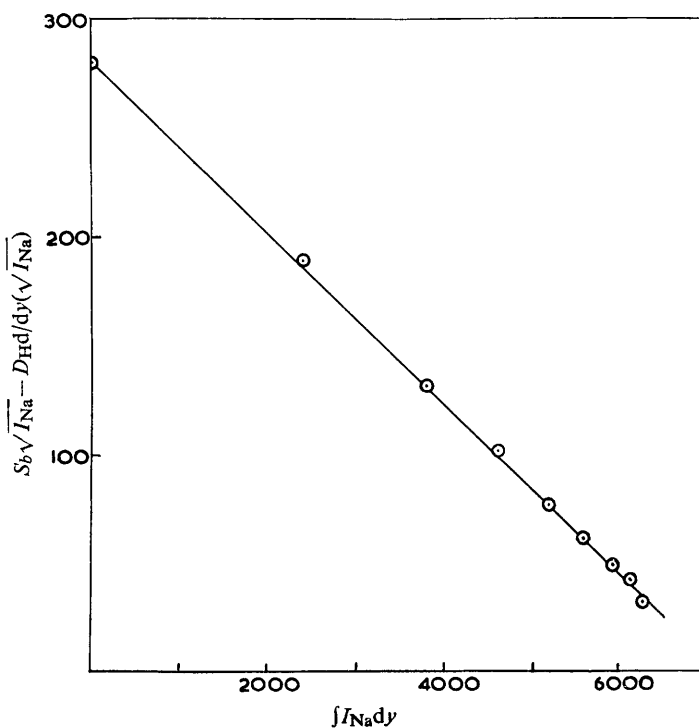


FIG. 2.—A plot of $S_b\sqrt{I_{Na}} - D_{HD}\sqrt{I_{Na}}/dy$ against $\int I_{Na} dy$ for flame 5.

For the experimental burnt gas mixtures, the calculated diffusion coefficient for H-atoms varied between 11.1 and 11.9 cm² sec⁻¹ at 1072°K.

Fig. 2 shows a typical graph of $S_b\sqrt{I_{Na}} - D_{HD}/dy(\sqrt{I_{Na}})$ against $\int I_{Na} dy$ (cf. eqn. (2)). Due to small uncertainties about the position of the base line in the intensity curves, these plots were not always perfectly linear, but deviated from the linear law at the larger distances from the flame. In such cases a small baseline adjustment was made to give the best straight line in that distance range. The slope of the resulting line gives the appropriate value of k_a/A . In these slow burning flames the diffusion term $-D_{HD}(\sqrt{I_{Na}}/dy)$ is of the same order of magnitude as the convection term $S_b\sqrt{I_{Na}}$ even far out from the flame where the concentration gradients are comparatively small. Nearer the flame itself the diffusion flow of H-atoms may be two or more times greater than the convection flow.

Table 1 summarizes those results which are regarded as reliable. Other compositions gave lower values of k_a/A , and this may well have been due to slight non-flatness of the flame. Such low values were observed particularly for the flames containing added water, and the quality of some of these was visibly not quite as high as for the flames without water addition.

TABLE 1.—RELATIVE APPARENT SECOND ORDER RECOMBINATION VELOCITY
CONSTANTS IN THE BURNT GAS AT 1072°K

| flame | mole fractions | | | expt. | | calc. |
|-------|----------------|-----------|------------|---------|----------|----------|
| | X_{H_2} | X_{N_2} | X_{H_2O} | k_a/A | k_a/A' | k_a/A' |
| 1 | 0.0274 | 0.8776 | 0.095 | 0.1421 | 0.1348 | 0.1329 |
| 2 | 0.0523 | 0.8527 | 0.095 | 0.1341 | 0.1292 | 0.1277 |
| 3 | 0.1011 | 0.8039 | 0.095 | 0.1310 | 0.1277 | 0.1278 |
| 4 | 0.1432 | 0.7618 | 0.095 | 0.1267 | 0.1255 | 0.1299 |
| 5 | 0.1748 | 0.7302 | 0.095 | 0.1347 | 0.1347 | 0.1319 |
| 6 | 0.1060 | 0.698 | 0.196 | 0.1325 | 0.1272 | |

The fifth column in table 1 gives values of k_a/A derived directly from the experimental data. The sixth column shows the relative values k_a/A' when corrected by means of a Stern-Volmer factor for differences in the quenching properties of the burnt gas mixtures. It is not easy to estimate values for this factor, and the correction applied here is slightly arbitrary in that it is assumed that the proportion of excited Na* which radiates is small compared with the proportion which is quenched by collision. It follows that the intensity of radiation bears a simple inverse ratio to the number of collisions suffered by Na* in any constant time interval. The magnitude of the correction is not large.

In order to obtain information on the third-order velocity constants the values of k_a/A' in table 1 were fitted to eqn. (7) by the method of least squares. The fit obtained using

$$(k_1^{H_2} - k_1^{N_2})_{rel} = 0.777, \quad D_{rel} = 0.116 \quad \text{and} \quad C_{rel} = 3.97 \times 10^{-4}.$$

is shown by the values given in the last column of table 1.

D₂O AND D₂ RESULTS

The experiments in which D₂O was added to the flame gases lead, by means of eqn. (4) to values of $k_3(H)$ at 1072°K, and then by further analysis to values of k_a/k_3 . If k_3 is known, this provides an independent method of measuring k_a . Satisfactory measurements by this method have so far only been carried out on a single flame

(flame 3) and have allowed k_3 to be estimated by comparison with the D_2 results described below. Since the chemiluminescent intensity is directly proportional to $\{k_3[H]\}^2$ it should be possible to fit values of the latter quantity on to the I_{Na} curves. This is done in fig. 1.

When D_2 gas was the trace additive to flame 3, the method of analysis of the results outlined earlier leads to a maximum value of $k_6[H]$ of $1.0 \times 10^4 \text{ sec}^{-1}$ at 900°K . Using the recent value of $k_6 = 6.1 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ at 1000°K obtained by Boato *et al.*,¹⁷ together with an activation energy of $6.65 \text{ kcal mole}^{-1}$, a maximum H-atom concentration in the flame of $2.5 \times 10^{-8} \text{ mole cm}^{-3}$ at 900°K is obtained. In order to calibrate the chemiluminescence curves and in order to evaluate k_3 , this value was assumed to correspond with the maximum of the intensity curve. This leads in turn to values at 1072°K of $k_3 = 5.0 \times 10^9 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$, together with

$$k_a = 4.7 \times 10^{10} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \text{ for flame 3,}$$

and

$$A' = 3.7 \times 10^{11},$$

$$(k_1^{H_2} - k_1^{N_2}) = 2.5 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$$

$$= 7 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1};$$

$$D = 4.3 \times 10^{10} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1},$$

and

$$C = 1.7 \times 10^3 \text{ sec}^{-1} \text{ for the flames without added water.}$$

DISCUSSION

FURTHER ANALYSIS AND COMPARISON WITH OTHER DATA

Although with the results at present available it is impossible to derive values for all six of the velocity constants involved in the two recombination reactions (i) and (ii), it is nevertheless possible to assess the order of magnitude of the various terms in the expressions for C and D of eqn. (7). First, the single result with water added initially suggests that the third-body effect of H_2O is similar in magnitude to that for N_2 (in the composition region of this result reaction (iii) accounts for only 3.4 % of k_a). If it is assumed that the two effects are equal in both reactions (i) and (ii), i.e., that $k_1^{N_2} = k_1^{H_2O}$ and $k_2^{N_2} = k_2^{H_2O}$, then the value for C leads to the result that $k_2^{N_2} = k_2^{H_2O} = 9 \times 10^{16} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$. Secondly, for the group of flames without initial added water $C/\rho \ll D$, where ρ is the molar density at 1072°K ; and if it is again assumed that the relative third-body effects in reactions (i) and (ii) are similar then it can be shown that the third term in the expression for D is negligible compared with the other two. The values $k_1^{N_2} = k_1^{H_2O} = 3.8 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1} = 1 \times 10^{-32} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$ then result, together with $k_1^{H_2} = 6.3 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1} = 1.7 \times 10^{-32} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$.

The earlier work on the recombination of H-atoms was carried out at room temperature using a discharge tube as the source and molecular hydrogen as the third body. Values obtained¹⁻⁵ for the third order velocity constant in the region of 300°K varied between 8×10^{15} and $2 \times 10^{16} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. More recently, Sugden and co-workers have made a number of studies of the recombination of atoms and radicals in flame gases at temperatures of 1400°K upwards to the region of 2100°K . At 1650°K , the results of Bulewicz and Sugden⁷ would give an apparent second-order velocity constant of about $4 \times 10^{10} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ for the H-atom recombination, and if all the species present were assumed to have equal efficiencies as third bodies, this would correspond with a third-order constant of $5.4 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$. Despite the higher temperature, this result is somewhat higher than that obtained in the present work.

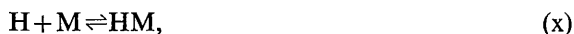
MECHANISM OF RECOMBINATION

Two mechanisms of atom recombination have been postulated. The first, which has recently been discussed by Pritchard¹⁸ and others, assumes that the two atoms come together to form a molecule in the highest vibrational level. On collision with a third body, a molecule in a lower vibrational level is formed which does not dissociate. This may be represented by the pair of equations, (viii) and (ix):



From this theory it is predicted that the efficiencies of the third bodies are given simply by the number of collisions of the $\text{H} \cdots \text{H}$ complex with M. For hydrogen atom recombination the rate constants should then be in the approximate ratio, $k_1^{\text{H}_2} : k_1^{\text{N}_2} : k_1^{\text{H}_2\text{O}} = 1 : 1 : 0.7$.

The alternative approach is to use the type of scheme first suggested by Rabinowitch,¹⁹ and recently thoroughly investigated by Porter and Smith²⁰ for iodine-atom recombination. Here the third body acts as a chaperon, forming (in H-atom recombination) a complex HM which then either decomposes or reacts with a second H-atom:



By means of this mechanism it is possible to account for differences in the negative temperature coefficient of the reaction for different chaperons, and for widely different efficiencies of these chaperons, as occurs in the iodine-atom recombination.

In the H-atom recombination the probable error in the results is such that hydrogen may be between one and two times as efficient a third body as nitrogen. Within the limitations of the experiments the recombination constants for H_2 , N_2 and H_2O otherwise appear not to be vastly different from each other and they could be consistent with either theory.

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