268. *The Kinetics of Some Reactions of Heavy Hydrogen. Part I.*

By H. W. Melville.

A sufficient number of reactions of heavy hydrogen with other molecules has now been investigated to indicate the magnitude of, and in some cases the reason for, the differences in the velocities with which the two isotopes react; *e.g.*, in the combination of hydrogen and chlorine (A. and L. Farkas, *Naturwiss.*, 1934, 218; Rollefson, *J. Chem. Physics*, 1934, **2**, 144) and of hydrogen and bromine (Bonhoeffer, Bach, and Fajans, *Z. physikal. Chem.*, *A*, 1934, **168**, 313), it would appear that the zero-point energy in the rate-determining step, *viz.*, Cl + H_2 and Br + H_2, is the main factor causing the deuterium to react more slowly. Similarly, in catalytic reactions on a nickel surface (Melville, this vol., p. 797), zero-point energy is apparently responsible for the separation. It thus seems possible to apply these ideas to the mechanism of reactions not so well understood in order to facilitate a correct choice from a number of hypotheses.

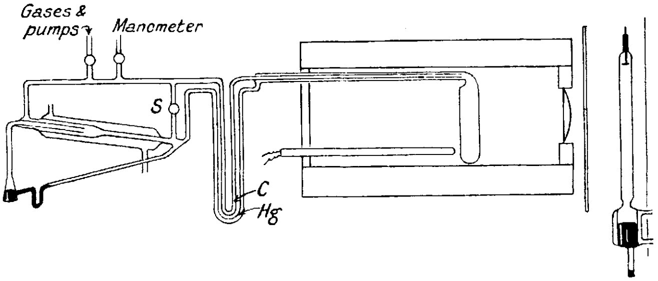
Another problem of considerable interest is the rate at which atomic hydrogen and deuterium react with molecules in the gas phase and also with reducible solid compounds. The atom is now free, and therefore zero-point energy should not contribute to the energy of activation, except that the zero-point energy of the collision complex may slightly favour the reaction of the deuterium atom (Polanyi, *Nature*, 1933, **132**, 819). On the other hand, there is also the possibility of leakage of the hydrogen and deuterium atoms through the potential barrier, in reactions where this exists, causing the former atom to react more quickly. The calculations which have been made by Bell (*Proc. Roy. Soc.*, *A*, 1933, **139**, 466) and by Bawn and Ogden (*Trans. Faraday Soc.*, 1934, **30**, 432) demonstrate that, with reasonable barrier widths and energies of activation, leakage is important; *e.g.*, the last two authors calculated that, for a barrier 2 Å. wide with an energy of activation of 13 kg.-cals., the hydrogen atom reacts 2·7 times more quickly than the deuterium atom at 473° K. The particular form of barrier used in these calculations may, however, tend to yield rather large values for the separation (cf. Topley and Eyring, *J. Chem. Physics*, 1934, **2**, 230).

With the object of gaining some information on these points, the following reactions have been examined : the reduction of oxygen, nitrous oxide, and ethylene with atomic hydrogen, produced photochemically, at room temperature, where the quantum yield is of the order of unity, and at higher temperatures, when chains begin to propagate and the mechanism changes completely.

EXPERIMENTAL.

The arrangement of the reaction system is shown in Fig. 1. Pressures were measured by a glass-spring gauge or by a McLeod gauge. In order to keep the gases saturated with mercury vapour, and in addition, to withdraw the water vapour produced in the hydrogen–nitrous oxide reaction, a small mercury-vapour diffusion pump (vol. 10 c.c.) was attached to the reaction tube of 20 c.c. capacity and 2 cm. in diameter. The water vapour was absorbed with calcium chloride which had been strongly heated in a high vacuum. The rate of pumping was such that the water vapour was so quickly removed from the reaction zone that the manometer really indicated the pressure of the moisture-free gas a few seconds after the light had been cut off. The U-tubes containing the calcium chloride (*C*) and mercury droplets (*Hg*) were kept in an ice-bath during the run. The procedure was simply to admit the gas, note the pressure, then shut the short-circuiting tap (*S*) and expose the bulb to the mercury lamp. After the requisite time the light was cut off, and a few seconds allowed to elapse before the tap was opened prior to the reading of the manometer. To obtain as large an intensity of light as possible, a chromium-plated reflector and a lens were used to concentrate it on the bulb. The reflector alone increased the efficiency many-fold, thus showing that at 2537 Å. well-polished chromium is a reasonably good reflector. A chromel–alumel couple measured the temperature. The gases were prepared as previously described (this vol., p. 797).

FIG. 1.

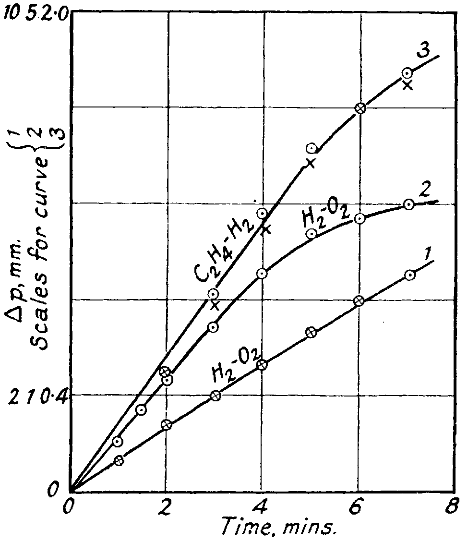


Photochemical Results.

Low Temperatures.—In these experiments the circulating pump was dispensed with, and a small quantity of thoroughly dehydrated calcium chloride placed in the bottom of the silica insolation tube. Blank experiments were made to ensure that no complications intruded by this method of removing water vapour. To stabilise the discharge in the lamp, an inductance of about 1 Henry was placed in series with the regulating resistance. Two runs were made with ordinary hydrogen to check the constancy of the lamp, the third run with heavy hydrogen, and a fourth run again with ordinary hydrogen. As has been shown (*loc. cit.*), the hydrogen–nitrous oxide reaction goes at very nearly (within 10%) the same speed with light and with heavy hydrogen. Similar experiments with oxygen and with ethylene, employing excess hydrogen (4 : 1), also showed that there was no appreciable difference in velocity. A number of typical pressure–time curves are given in Fig. 2. These curves are nearly straight, *i.e.*, the reactions are of zero order. Curve 2 illustrates a run with ordinary hydrogen carried almost to completion; it only bends round when the oxygen pressure has fallen to 0·3 mm.

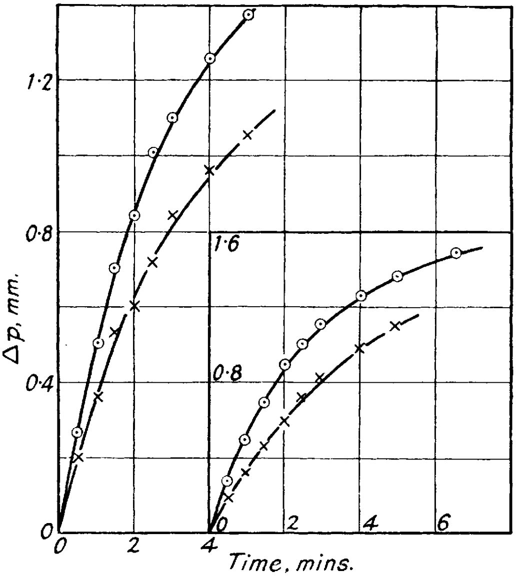
Quite different results are obtained when oxygen is in excess, $O_2 : H_2 = 4 : 1$ (Fig. 3). The two series of experiments show that deuterium reacts much more slowly. The ratios of the initial slopes of the curves are 1·39 and 1·50 for a 66% deuterium mixture. Moreover, the reaction is no longer of zero order, but is nearly unimolecular (with respect to the hydrogen, since the oxygen is in large excess). Experiments at a total pressure of 12 mm. with different compositions show that when hydrogen is in excess, the rate is independent of composition, whereas with excess oxygen, it is approximately proportional to the oxygen content, as noted by Marshall (*J. Physical Chem.*, 1926, **30**, 34). These observations consequently indicate that when the excited mercury atom is deactivated by oxygen there is no formation of water.* Even if oxygen atoms are produced in this process, which is probably true in a small fraction of the collisions, they are more likely to react with oxygen to form ozone (Kistiakowski, *J. Amer. Chem. Soc.*, 1930, **52**, 1868). With excess hydrogen, the quantum yield of water formation is of the order of unity (Frankenburger and Klinkhardt, *Z. physikal. Chem.*, 1932, **15**, *B*, 421) and, furthermore, the temperature coefficient of the reaction is very small; it is important to note that in the radiochemical reaction the number of water molecules produced per ion pair remains constant down to as low a temperature as — 180° (Schiflett and Lind, *J. Physical Chem.*, 1934, **38**, 327). These observations strongly suggest that, whatever be the mechanism by which water is formed, every hydrogen atom produced ultimately combines with oxygen and is not removed in any competing reaction which might seriously retard water formation. In other words, the rate at which water is formed is governed essentially by the rate of hydrogen-atom production. Thus, it would be expected that hydrogen and deuterium would react at apparently the same speed. But the data do not show whether, apart from a collision-frequency factor, the rate of $H + O_2$ is identical with that of $D + O_2$. A similar argument applies to the hydrogenation of nitrous oxide and of ethylene. To determine whether these reactions actually do proceed at the same speed, it would be necessary to compare them with some competing reaction, the velocity of which could be accurately calculated.

FIG. 2.



Curve 1 : p_{H_2} 10·40 *mm.*, p_{O_2} 2·05 *mm.*, Δpa 6·15.
Curve 2 : p_{H_2} 6·02 *mm.*, p_{O_2} 1·22 *mm.*, Δpa 3·66.
Curve 3 : p_{H_2} 10·0 *mm.*, $p_{C_2H_4}$ 2·00 *mm.*, Δpa 2·00.
Temp. 20°; X ≡ 66 % *deuterium*, ⊙ ≡ *ordinary hydrogen.*

FIG. 3.



5·0 *mm.* O_2, 1·25 *mm.* H_2. *Temp.* 20°.
X ≡ 66 % *deuterium.*

When oxygen is in excess, several of the excited atoms are deactivated by it, and hence there is a competition between H_2 (HD,D_2) and oxygen, with the result that the rate at which

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* As flow experiments have shown, the first product is hydrogen peroxide, which in a static system is photochemically decomposed to water and oxygen (cf. especially Bates, *J. Amer. Chem. Soc.*, 1933, **53**, 110).

hydrogen and deuterium atoms are produced will be different for a given composition. The rate of hydrogen-atom formation is proportional to

$$\frac{\sigma_{H_2}{}^2(1/M_{H_2} + 1/M_{Hg})^{\frac{1}{2}}[H_2]}{\sigma_{H_2}{}^2(1/M_{H_2} + 1/M_{Hg})^{\frac{1}{2}}[H_2] + \sigma_{O_2}{}^2(1/M_{O_2} + 1/M_{Hg})^{\frac{1}{2}}[O_2]}$$

where σ is the sum of the effective collision radii and M is the mass of the partners in the collision. With excess hydrogen, the expression for hydrogen and for deuterium reduces to unity, and so no difference in this respect is to be anticipated for the two isotopes. Employing excess oxygen, however, the expressions for hydrogen and deuterium will be

$$\frac{\sigma_{H_2}{}^2(1/M_{H_2})^{\frac{1}{2}}[H_2]}{\sigma_{O_2}{}^2(1/M_{O_2})^{\frac{1}{2}}[O_2]} \quad \text{and} \quad \frac{\sigma_{D_2}{}^2(1/M_{D_2})^{\frac{1}{2}}[D_2]}{\sigma_{O_2}{}^2(1/M_{O_2})^{\frac{1}{2}}[O_2]}$$

the ratio being very nearly $(M_{D_2}/M_{H_2})^{\frac{1}{2}} = 1{\cdot}41 : 1$, for it is probable that $\sigma_{H_2}{}^2$ and $\sigma_{D_2}{}^2$ are identical. In a 66% deuterium mixture there are H_2, HD, and D_2 molecules, and since the gas was prepared by decomposition of water on a tungsten filament, equilibrium is established, and the composition of the mixture is 11% H_2, 45% HD and 44% D_2 (the equilibrium constant for the reaction $2HD \rightleftharpoons H_2 + D_2$ is taken as 4). The separation should therefore be $1/[0{\cdot}11 + 0{\cdot}45(M_{H_2}/M_{HD})^{\frac{1}{2}} + 0{\cdot}44(M_{H_2}/M_{D_2})^{\frac{1}{2}}] = 1{\cdot}28$, while the observed value is about 10% higher than this. It is probable that the ethylene and nitrous oxide reactions would behave in the same way, save that complications would occur with the former on account of polymerisation.

Higher Temperatures.—At higher temperatures a number of changes take place, each reaction behaving differently. The nitrous oxide reaction may be considered first. At about 250°, chains begin to appear, and analysis of the kinetics of the reaction (Melville, *Proc. Roy. Soc.*, *A*, 1933, **144**, 524; *Trans. Faraday Soc.*, 1933, **29**, 1255) leads to the conclusion that the steps are

$$\begin{aligned}&H + N_2O \longrightarrow N_2 + OH \text{ (energy of activation 15—20 kg.-cals.)}\\ &OH + H_2 \longrightarrow H_2O + H\end{aligned}$$

the first step being the slower, and that at the low pressures employed in these experiments, termination takes place by combination of hydrogen atoms on the walls. If deuterium is substituted for hydrogen, a number of consequences may cause the velocity of water formation to decrease. By employing excess hydrogen, the rate at which chains are started is the same for both isotopes. Hydrogen atoms will collide more frequently with nitrous oxide molecules in the ratio $\sqrt{2} : 1$, but on the other hand, they will reach the wall of the reaction vessel $\sqrt{2}$ times more quickly. These effects therefore cancel out. Secondly, the hydrogen atom is free, and zero-point energy does not contribute to the energy of activation (except that of the collision complex); any greater reactivity of hydrogen compared with deuterium may reasonably be attributed to "leakage." But as Fig. 4 shows, at 333°, the rates of reaction are identical within a few units %, the chain length being about 3, and therefore it is concluded that at this temperature, at least, quantum-mechanical leakage of hydrogen atoms is very small.

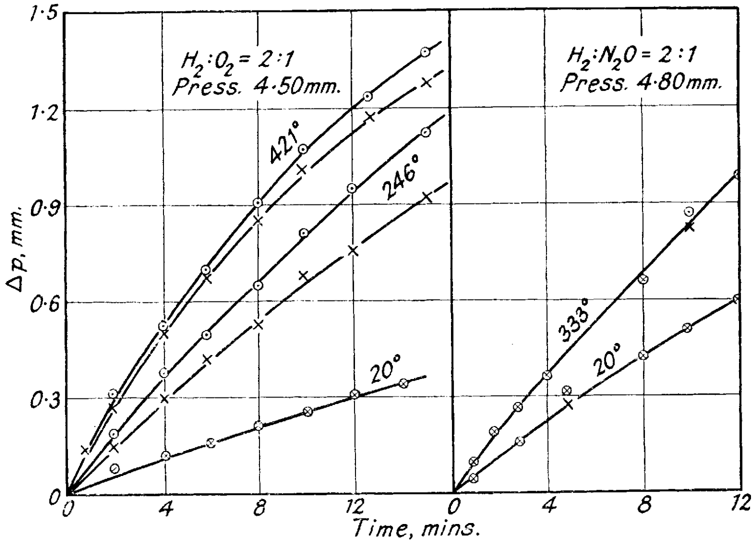
This result may now be applied to the question of the mechanism of chain propagation in the hydrogen–oxygen reaction. A close comparison of this reaction with that of nitrous oxide under exactly the same conditions (Melville, *Proc. Roy. Soc.*, in the press) has shown that the chain length is a little longer (about 10 at 300°), and again the chain step involving the disappearance of the hydrogen atom accompanied by the production of a hydroxyl radical is slower than $OH + H_2 \longrightarrow H_2O + H$. Moreover, the kinetic analysis has also revealed that reaction at the ternary collision $H + O_2 + H_2 = H_2O + OH$ does not occur. It is more probable that HO_2 is formed first, and then reacts with hydrogen to yield water and hydroxyl, the latter reaction likewise requiring 15 kg.-cals. of activation. The important point is that a hydrogen molecule is now concerned in the rate-determining step. It is to be expected that zero-point energy will again contribute its quota to the energy of activation, with the consequence that deuterium should react more slowly than hydrogen. The diffusion and the collision factor cancel out if the chains end by the combination of hydrogen atoms on the walls. These anticipations are realised, for it is only when chains are propagated that separation appears. The data are given in detail in Table I, and additional experiments in Fig. 4, and it is seen that at 246° and 339° there is a measurable separation which decreases as the temperature is raised to 421°. The results quoted in the table for ordinary hydrogen are the mean of three runs, *viz.*, the two control experiments and the final check run.

From the results at 246° and 339°, the ratio of the rates has been calculated by taking the average value of the ratio of the times required for the pressure to fall to a given series of values. At 246°, the ratio is 1·26, at 339° 1·30, and at 421° 1·12. With a 66% mixture, it being assumed that the chains are long and that the zero-point energy is wholly responsible for separation, the ratio of rates should be

$$[H_2]/\left([H_2] + [HD]e^{\frac{-800}{RT}} + [D_2]e^{\frac{-1800}{RT}}\right)$$

which, at 339°, is equal to 2·17. The discrepancy may partly be due to the shortness of the chains at the low pressures employed. In this circumstance, the initial step in the reaction, where separation does not occur, is comparable with the propagating step, and thus the difference in the latter is to a large extent obscured. Another small contributory cause may be the exchange reaction $D + H_2O \longrightarrow H + DHO$, by which the deuterium content of the original mixture is decreased in contrast to the normal increase brought about in the course of the reaction. The magnitude of this effect is difficult to calculate, for the value of the equilibrium constant is not yet known accurately.

Fig. 4.



These groups of results were obtained with different intensities and are arranged in the diagram to show only approximately the increase in reaction velocity with temperature. X = 66% *deuterium.*

Table I.

Hydrogen–oxygen reaction at high temperatures; 2 : 1 mixture. Pressure 4·60 mm.

	246°.		339°.		421°.	
t.	Δp_{H_2}.	Δp (66% D).	Δp_{H_2}.	Δp (66% D).	Δp_{H_2}.	Δp (66% D).
2	0·18	0·17	0·23	0·16	0·31	0·30
4	0·36	0·29	0·43	0·31	0·54	0·50
6	0·54	0·43	0·62	0·46	0·76	0·71
8	0·70	0·56	0·77	0·60	0·93	0·90
10	0·84	0·70	0·93	0·76	1·10	1·04
12	0·98	0·79	1·08	0·90	1·24	1·16
15	1·16	0·95	1·32	1·08	1·42	1·32
20	1·46	1·21	—	—	1·66	1·49

The water vapour was not removed in these experiments.

These results agree with the experiments on the thermal reaction above the upper limit (Hinshelwood, Williamson, and Wolfenden, *Nature*, 1934, **133**, 836) where the chains also terminate on the walls. In this case, however, the nature of the initiating reaction is not known, and it may well be that separation occurs at this stage, so that the total observed value is rather larger than in the present experiments. The separation in the heterogeneous reaction on a silica surface is also in good agreement with that obtained on a nickel surface at much lower temperatures (Melville, this vol., p. 797).

Experiments at Low Pressures with a Palladium-coated Tube.

An attempt has been made to determine whether in their reactions with oxygen, nitrous oxide, and ethylene, hydrogen reacts at the same speed as deuterium. The reaction with which these have been compared is the combination of atomic hydrogen on a surface of palladium-black, the assumption being made that hydrogen atoms combine at the same speed as deuterium atoms on such a catalyst. The palladium was deposited on copper-foil by immersion of the latter in a solution of palladium nitrate. The foil was then rolled into a cylinder so that, when introduced into a silica tube of 1 cm. diameter, a slit about 4 mm. wide was exposed to the lamp.

As in the other cases, the diffusion and collision factors cancel out if excess hydrogen is employed. Clearly, it is necessary to work at such a pressure that the wall reaction removes an appreciable fraction of the atomic hydrogen generated. In all three cases the reactions, at high enough pressures, are of zero order and do not show any signs of becoming of higher order until the pressure decreases to a few mm.; *e.g.*, with hydrogen–oxygen (2 : 1 mixture), the rate at 15·38 mm. was the same as that at 2·31 mm., *viz.*, 0·118 mm./min. When the pressure was reduced to 0·229, the rate fell to 0·026 mm./min. Only a small fraction of this decrease is due to radiation of resonance radiation, and from the results of Zemanski (*Physical Rev.*, 1930, **36**, 919) on the quenching radius of molecular hydrogen, the value of 0·026 mm./min. requires to be increased by 25%. Even with this correction, the decrease is very marked. To avoid any change in the mean life of the excited atom with the pressure of hydrogen and oxygen, owing to reabsorption of resonance radiation, the mercury-vapour pressure was maintained at 10^{-4} mm. (*cf.* Garrett, *Physical Rev.*, 1932, **40**, 779). The behaviour of hydrogen and deuterium was therefore compared at a pressure of about 0·15 mm., and the results in Table II show practically no difference except that the deuterium curve is a little below that for ordinary hydrogen. This is to be expected, for when re-radiation begins to appear, the fraction of the excited atoms removed by hydrogen molecules will be higher than that by HD or D_2, and therefore the rate of production of hydrogen atoms will be a little greater. For the conditions used above, *i.e.*, 47% deuterium and about 50% of the absorbed light radiated, the correction only amounts to 10%. The maximum ratio for very low pressures and for pure deuterium is again $\sqrt{2} : 1$, as may be seen from the following : The rates at which hydrogen and deuterium atoms are produced when the mean life (τ) of the excited mercury atom is greater than the time between the collisions of hydrogen molecules and mercury atoms are respectively proportional to $\sigma_{H_2}^2(M_{H_2})^{-\frac{1}{2}}\tau$ and $\sigma_{D_2}^2(M_{D_2})^{-\frac{1}{2}}\tau$; *i.e.*, ratio $= \sqrt{2} : 1$.

TABLE II.

Low pressures, palladium surface.

		Hydrogen : oxygen = 2 : 1.			Hydrogen : nitrous oxide = 2 : 1.		
Initial press., mm.		0·1480.	0·1635.		2·90.	2·89.	11·54.
	t.	Δp.	Δp (47% D).	*t.*	Δp (47% D).	Δp.	Δp.
	1	0·0135	0·0105	2	0·13	0·18	0·22
	2	0·0275	—	5	0·35	0·38	0·54
	4	0·0455	0·0375	10	0·54	0·55	1·04
	6	0·0580	0·0545	15	0·64	0·67	1·54
	10	0·0740	0·0660	20	0·67	0·72	—
				25	0·70	0·74	—

Water vapour was withdrawn by phosphoric oxide.

The velocity of the hydrogen–nitrous oxide reaction fell off at a somewhat higher pressure. At 11·54 mm. (3·84 mm. N_2O) the initial rate was 0·106 mm./min., and at 2·89 mm. (0·96 mm. N_2O) 0·077 mm./min., thereafter falling rapidly, as can be seen from the results in Table II. For comparison, a complete high-pressure run is also given to demonstrate that zero order is maintained for a considerable portion of the reaction.

The hydrogenation of ethylene follows a similar course. The reaction with excess hydrogen is of zero order until the ethylene pressure falls approximately to 1 mm., which is in agreement with experiments of Olson and Meyers (*J. Amer. Chem. Soc.*, 1926, **48**, 389). In Table III, the first run is at a comparatively high pressure, but the value of $d(\Delta p)/dt$ rapidly decreases as the ethylene disappears, as may be seen from col. 4 in the table. The second run is at lower pressure, where $d(\Delta p)/dt$ falls off from the start; the third, with heavy hydrogen, was therefore made at the same pressure as the second, and comparison of the Δp values shows that again there is no separation.

TABLE III.

Hydrogenation of ethylene; palladium surface, temp. 20°.

p_{H_2}		5·80		2·90	2·88 (47% D)
$p_{C_2H_4}$		1·97		0·97	1·03
t.	$p_{C_2H_4}$.	Δp.	$d\Delta p/dt$.	Δp.	Δp.
1	1·57	0·40	0·40	0·17	0·14
2	1·21	0·76	0·36	0·33	—
3	0·85	1·12	0·32	0·39	0·29
4	0·64	1·33	0·23	0·47	—
6	0·43	1·54	0·13	0·58	0·53
8	0·25	1·72	0·07	0·70	—
10	0·19	1·78	0·04	0·77	0·75
12				0·81	0·80

The mechanism usually postulated (cf., *e.g.*, Taylor, *Trans. Faraday Soc.*, 1926, **21**, 560) for the hydrogenation of ethylene by atomic hydrogen is $C_2H_4 + H \longrightarrow C_2H_5$, $C_2H_5 + H_2 \longrightarrow C_2H_6 + H$, which is a chain process. It is probable that the second step is the slower and requires considerable activation, and therefore the rate of hydrogenation ought to increase with temperature. Moreover, if deuterium or HD be substituted for hydrogen, a decrease in velocity should occur as in the photochemical synthesis of hydrogen chloride and hydrogen bromide. In one set of experiments at 339°, the initial rate was 0·13 mm./min., and at 20°, 0·12 mm./min. at a pressure of 4·75 mm. of hydrogen and 1·55 mm. of ethylene. Experiments with a 66% deuterium mixture gave exactly the same speeds at both temperatures. Runs with excess ethylene were not made on account of complications due to polymerisation. The facts, *viz.*, similar quantum yields at high and at low temperatures and no separation, not only agree but definitely exclude a chain mechanism. The second step in the reaction is probably between the ethyl radical and a hydrogen atom on the walls or in the gas phase, depending on the total pressure.

Since the velocity of these hydrogenation reactions in the palladium tube falls off at about 1 mm., and if it be assumed that the reactions are bimolecular, then the collision efficiency is of the order of 10^{-3}, which corresponds to an energy of activation of only 4 kg.-cals. If, however, a third molecule is necessary to effect stabilisation of the complex, every ternary collision would lead to the removal of the hydrogen atom.

Having regard to the results of these and previous experiments, it would appear that leakage phenomena do not play any important part in determining the kinetic behaviour of light and of heavy hydrogen. The observation of this effect may be frustrated by the fact that in many reactions the potential barrier is so small that it can practically be neglected, and both hydrogen and deuterium atoms react with the same collision efficiency. In those examples, *viz.*, the emission of particles from unstable atomic nuclei, where leakage has been employed to explain why the rate of emission is much larger than classical theory allows, the experimental methods are extremely sensitive and indeed detect the emergence of single particles from the barrier. In chemistry, however, the collision efficiencies must be considerable in order that the reaction velocity may be measured at all. It is therefore not necessarily true to say that leakage does not exist in chemical reactions; rather, in general, its detection is rendered exceedingly difficult by the operation of collision frequency and zero-point energy factors.

It is fortunate that matters are so arranged, for it permits the application of deuterium to some problems in kinetics and, as has been shown, decides, without especial regard to the finer details of reaction mechanism, that, *e.g.*, in the hydrogen–oxygen reaction, the rate-determining step involves a hydrogen molecule (or compound, HO_2), whereas the hydrogen–nitrous oxide chains proceed through the intermediary of an atom. Its use in this respect may be compared with the intensity law in photochemical reactions which decides unequivocally the type of collision responsible for the termination of the chains.

SUMMARY.

The mercury-photosensitised reduction by hydrogen and by deuterium of oxygen, nitrous oxide, and ethylene has been studied at 20° and at higher temperatures.

At 20° with excess hydrogen, both isotopes react at the same speed. With excess of

the gas undergoing reduction, *e.g.*, oxygen, a difference in reaction speeds is obtained, and is shown to be due to a collision-frequency factor.

At higher temperatures, 250—400°, where chains are propagated in the hydrogen–oxygen and –nitrous oxide reactions, separation occurs in the former but not in the latter reaction. The separation decreases with increasing temperature. In the ethylene reaction there is no separation and no chain propagation.

The significance of these results is discussed, and it is concluded that with due allowance for collision-frequency factors, zero-point energy differences are adequate to explain the magnitude of the separation obtained. In no case could separation be reasonably attributed to the leakage of the atoms through potential barriers.

The author is greatly indebted to Prof. E. K. Rideal for constant advice and encouragement. He also thanks the Royal Commissioners of the Exhibition of 1851 for a Senior Studentship and the Chemical Society for a grant.

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