171. *The Catalytic Hydrogenation of Simple Molecules by Light and by Heavy Hydrogen.*

By H. W. MELVILLE.

THE discovery of the heavy isotope of hydrogen has raised a number of new problems in chemical kinetics. As has already been demonstrated, the velocity of reaction of the two isotopes is, in certain cases, widely different—a circumstance which allows of their separation. The first question to arise is whether separation is to be obtained in every chemical reaction involving either the production or the disappearance of hydrogen as molecules or as atoms, the reactions occurring in the gas phase or in presence of a catalyst. It is probable that the energies of activation for reaction will be somewhat different for hydrogen and for deuterium. On account of the large difference of mass, however, another important factor must be taken into consideration, for Eyring and Polanyi (*Z. physikal. Chem.*, 1931,

12, *B*, 279) have pointed out that the zero-point energy of the hydrogen molecule, which is 6·1 kg.-cals. for H_2 and 4·4 kg.-cals. for D_2 (Urey and Rittenberg, *J. Chem. Physics*, 1933, 1, 137), would certainly make an important contribution to the energy of activation of the reaction.   In those reactions in which the energy of activation is small, a relatively large difference in velocity coefficients is to be expected.   In addition, it may happen, on account of the small mass, that the probability of the quantum-mechanical leakage of hydrogen and of deuterium through energy barriers is responsible for part of the difference in chemical reactivities, but Cremer and Polanyi (*Z. physikal. Chem.*, 1932, 19, *B*, 443) have shown that this factor is not nearly so great as that calculated theoretically.

The first problem in kinetics is thus to find the relative magnitudes of the velocities of reaction of the isotopes, and to see whether any difference is to be explained on the basis of the different zero-point energies of the hydrogen and the deuterium compound.   That this point of view does explain the principal cause of the separation has already been demonstrated quantitatively by Farkas and Farkas (*Proc. Roy. Soc.*, 1934, *A*, 144, 467) for the diffusion of hydrogen–deuterium mixtures through palladium.   It is the object of the present investigation to find if similar variations can be obtained in a somewhat more complicated reaction, *viz.*, the hydrogenation of simple molecules on a metal catalyst. The results with palladium have shown that it is necessary to work at low temperatures to ensure separation.   The choice of catalysts was therefore restricted, and nickel was employed.

EXPERIMENTAL.

The four reactions chosen were the hydrogenation of carbon monoxide, oxygen, nitrous oxide, and ethylene, since these all occur readily on a suitably prepared nickel catalyst at a temperature favourable for the separation.   Highly active nickel catalysts spread upon an inert support are very sensitive to poisons, adsorb a considerable amount of the reactants, and do not give accurately reproducible results.   A spiral of nickel wire was therefore employed, for although the activity could not be made so great as that of a bulk catalyst, yet the ease of temperature control and reproducibility offered great advantages.   It required repeated oxidation and reduction before it was sufficiently active.   After this treatment it was fairly easily poisoned, but its previous activity could, in general, be restored by oxidation and reduction (sometimes reduction alone sufficed).   It was necessary to study the kinetics of these hydrogenations over a wide range in order to find suitable pressure and temperature regions.

The apparatus consisted of a reaction tube of 15 c.c. capacity attached to a capillary mercury manometer and to a glass-spring gauge, the latter being used for measuring pressures down to 1 mm.   The nickel wire was 50 cm. long and 0·01 cm. in diameter.   It was placed in a bridge circuit for temperature control; the temperatures were calculated from the resistance, no end corrections being applied.   Calcium chloride was placed in the bottom of the reaction tube to absorb water vapour in those reactions where it was formed.   The reaction tube was kept in ice, and the pressure readings were only made when the filament was switched off.   Exhaustion of the apparatus was effected by a mercury condensation pump.

The carbon monoxide was prepared by dropping formic acid into an evacuated flask containing warm concentrated sulphuric acid; it was then passed over soda–lime and phosphoric oxide and through a liquid-air trap.   Nitrous oxide was obtained from a cylinder and purified by fractional distillation.   Oxygen from potassium permanganate was purified in the same manner as the carbon monoxide.   Electrolytic hydrogen was freed from oxygen by palladised asbestos.   Deuterium–hydrogen mixtures were prepared by decomposing water containing a known percentage of D_2O on a well out-gassed tungsten filament; if necessary the gas could be further purified by diffusion through palladium.   Preliminary experiments with ordinary water showed that hydrogen prepared by the two methods reacted with the same velocity. The deuterium content of the mixture was checked by analysis by the thermal conductivity method (this was kindly done by Drs. L. and A. Farkas).

The Carbon Monoxide Hydrogenation.—The first experiments with a nickel catalyst (Sabatier and Senderens, *Ann. Chim.*, 1905, 4, 424; *Compt. rend.*, 1902, 134, 514, 689) indicated that the reaction was $CO + 3H_2 = CH_4 + H_2O$.   Later, flow experiments by Armstrong and Hilditch (*Proc. Roy. Soc.*, 1923, *A*, 103, 25) showed, however, that the reaction was $2CO + 2H_2 = CO_2 + CH_4$.   First, it was therefore necessary to find which of these reactions occurred in the static system with a wire catalyst.   The second scheme may be represented by the equations

CO + H₂ = CH₄ + H₂O, CO + H₂O = CO₂ + H₂, and consequently, if the water vapour is removed continuously during the reaction, the water-gas reaction should not occur, and the products ought to be methane and water. Qualitative experiments supported these assumptions, for if the reaction was allowed to proceed with the tube at 0°, both carbon dioxide and water vapour were formed, but if the reaction tube was kept in carbon dioxide–ether at − 80° (water vapour pressure less than 10^{-3} mm.; the stationary concentration near the surface of the wire would naturally be higher), no carbon dioxide could be detected in the products of the reaction. In the experiments to be described below, calcium chloride was used to prevent the occurrence of the water-gas reaction. At first, owing to the low activity of the wire, a measurable reaction could only be obtained at about 400°; but carbonisation of the filament was extremely rapid and therefore reproducible results could not be obtained. Even at 271° it was difficult to get accurately reproducible results, and consequently experiments with deuterium were not carried out. In Table I two series of runs with varying p_{CO} and p_{H_2} are given to show that the reaction probably occurs by the adsorption of hydrogen on the portions of the nickel surface which are not covered by carbon monoxide, for this gas is a strong inhibitor and the reaction velocity is nearly proportional to the hydrogen pressure; t is the time (in minutes), Δp the change of pressure (in mm.), and r the initial rate of reaction (mm./min.).

TABLE I.

	Temp. 271°.	Effect of carbon monoxide.				Effect of hydrogen.		
p_{CO}	10·0	20·6	41·8	101·4	10·6	10·4	10·8	10·8
p_{H_2}	199·8	197·8	199·2	198·6	199·8	101·0	50·2	25·8
t.	Δp.	Δp.	Δp.	Δp.	Δp.	Δp.	Δp.	Δp.
2	10·4	6·4	7·0	3·6	7·2	4·6	2·8	0·8
4	18·8	14·8	10·8	7·0	13·4	9·6	—	—
6	—	23·0	16·0	10·2	19·4	13·0	6·4	2·2
8	—	31·4	21·8	13·2	21·2	16·8	—	—
10	—	—	—	—	—	21·4	10·0	3·2
15	—	—	—	—	—	—	13·8	4·2
r	5·65	3·9	2·75	1·80	3·7	2·3	1·2	0·39

Hydrogenation of Nitrous Oxide.—With the same catalyst as before, the hydrogen–nitrous oxide reaction was rapid at about 150° (cf. Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 278). The observed rate was not due to the oxidation of the wire by nitrous oxide and immediate reduction by hydrogen, for the rate of decomposition of the nitrous oxide as measured by a McLeod gauge was at least 100 times slower. If the water was allowed to accumulate, it appeared to exert no inhibitory action. Nevertheless, this may mean that the reaction velocity is independent of p_{H_2O} over a wide range, and that actually a layer of water is present during the whole course of the reaction. The water takes a fraction of a second to reach the absorbent and thus a small stationary concentration must exist in the gas phase, which may be sufficient to keep the surface saturated.

As will be shown below, the kinetics of this reaction do not obey any simple equation, and hence series of runs have been made over the whole of the available range, in order that well-defined and known conditions may be found for a comparison of the rates of reaction of the two isotopes.

In Table II, typical results are given. The initial rate of reaction is plotted against p_{N_2O} in Fig. 2, from which it will be observed that in this pressure range nitrous oxide behaves similarly

TABLE II.

	Temp. 123°.						Temp. 135°.		
p_{N_2O}	10·0	200·0	20·6	20·2	443·4	689·2	3·76	3·80	26·27
p_{H_2}	202·6	199·8	20·4	377·6	20·2	21·0	3·76	14·72	3·63
t.	Δp.	Δp.	Δp.	Δp.	Δp.	Δp.	Δp.	Δp.	Δp.
2	3·2	1·6	2·2	—	7·8	4·6	0·31	0·30	0·50
4	5·6	—	4·6	0·8	11·0	8·2	—	—	—
5	—	—	—	—	—	—	0·61	0·64	1·14
6	6·2	4·8	6·2	—	11·2	10·2	—	—	—
8	—	—	—	—	11·2	10·6	—	—	—
10	6·4	9·8	10·0	1·8	—	—	1·04	1·39	2·10
15	—	16·6	13·0	2·8	—	—	1·41	1·87	2·82
20	—	23·8	15·8	3·6	—	—	1·71	2·40	—

to carbon monoxide, in that it inhibits the reaction and apparently displaces the hydrogen from the nickel surface. But this explanation is not sufficient, for the rate of reaction with 200 mm. is not 10 times that with 20 mm. of hydrogen.

The non-linearity between rate and hydrogen pressure was further investigated at higher hydrogen pressures in order to see whether it was possible to displace nitrous oxide from the nickel surface. For this purpose, a much smaller nitrous oxide pressure was employed, *viz.*, 20 mm. (Fig. 1). Where necessary, a correction was applied for the increasing activity of the catalyst. The drift is systematic, for when nitrous oxide is in excess, the activity decreases, and when hydrogen is in excess, it increases; *e.g.*, in No. 35, $r = 1.68$; in No. 41, $r = 1.88$ (hydrogen in excess); in No. 37, $r = 2.37$; in No. 45, $r = 3.30$; in No. 46, $r = 1.08$; in No. 50, $r = 0.74$ (nitrous oxide in excess).

FIG. 1.   FIG. 2.
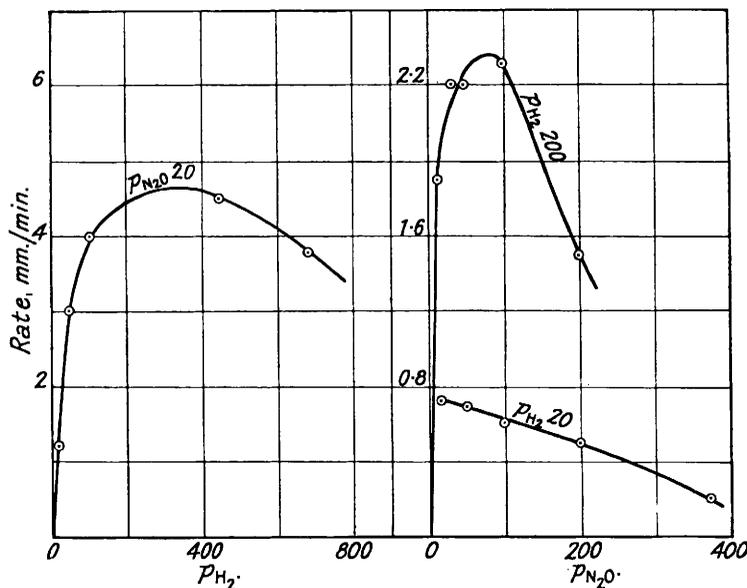
It is apparent from a comparison of Figs. 1 and 2 that nitrous oxide is more strongly adsorbed than hydrogen, for the maximum in the rate–pressure curve occurs at a lower pressure and is sharper. The maxima are, however, sufficiently close to show that down to low pressure the nickel surface must be completely covered. Experiments were therefore made at lower total pressures to see if the reaction rate became proportional to the pressure of hydrogen and of nitrous oxide. Although these anticipations are realised by the results in Fig. 3, yet there is a tendency at higher pressures for both curves to bend round in such a way as to show that, above 4 mm., hydrogen and nitrous oxide are still quite strongly adsorbed.

The reaction has been studied under three different conditions, *viz.*, (*a*) each reactant only moderately strongly adsorbed, (*b*) nitrous oxide displacing hydrogen, (*c*) hydrogen displacing nitrous oxide. From the Langmuir adsorption isotherm expressing the amounts of gas adsorbed under these conditions, the following three equations are obtained,

$$- d[\mathrm{N_2O}]/dt = k_1[\mathrm{H_2}][\mathrm{N_2O}] \; e^{-(\lambda_\mathrm{R} - \lambda_{\mathrm{H_2}} - \lambda_{\mathrm{N_2O}})/RT},$$

$$- d[\mathrm{N_2O}]/dt = k_2[\mathrm{H_2}][\mathrm{N_2O}]^{-1} \; e^{-(\lambda_\mathrm{R} - \lambda_{\mathrm{H_2}} + \lambda_{\mathrm{N_2O}})/RT},$$

$$- d[\mathrm{N_2O}]/dt = k_3[\mathrm{H_2}]^{-1}[\mathrm{N_2O}] \; e^{-(\lambda_\mathrm{R} + \lambda_{\mathrm{H_2}} - \lambda_{\mathrm{N_2O}})/RT},$$

where k_1, k_2, k_3 are constants nearly independent of temperature, λ_R is the energy of activation of the surface reaction, and $\lambda_{\mathrm{H_2}}$ and $\lambda_{\mathrm{N_2O}}$ are the heats of adsorption of hydrogen and of nitrous oxide. The kinetics at any given temperature are thus in agreement with the simple assumptions made in deriving these equations. The apparent energy of activation ought, however, to be different in the three cases, and moreover, it should be possible to determine λ_R, $\lambda_{\mathrm{H_2}}$, and $\lambda_{\mathrm{N_2O}}$ from the three equations. Measurements were therefore made for (*a*) and (*b*), but instead of

(c), the temperature coefficient was measured at the maximum of the r–p_{H_2} curve, in which circumstance the kinetic equation becomes

$$- d[N_2O]/dt = k_4[N_2O]\ e^{-(\lambda_R - \lambda_{N_2O})/RT}.$$

From Table III the surprising result is found that the apparent energy of activation is independent of the nature of the reaction. Two alternatives are open : (i) λ_{H_2} and λ_{N_2O} are negligible in

TABLE III.

	Low pressure. $p_{H_2} = 3\cdot7;\ p_{N_2O} = 3\cdot7.$			High pressure (H$_2$ in excess). $p_{H_2} = 200;\ p_{N_2O} = 20.$			High pressure (N$_2$O in excess). $p_{H_2} = 20;$ $p_{N_2O} = 230.$	
Temp.	r.	$\log_{10} 100r$.	$10^3/T$.	r.	$\log_{10} 100r$.	$10^3/T$.	r.	$\log_{10} 100r$.
136°	0·086	0·935	2·442	1·39	1·143	2·442	1·38	1·140
117·5	0·032	0·505	2·628	0·65	0·813	2·628	0·56	0·748
100	—	—	—	0·21	0·322	2·68	—	—
152	0·180	1·256	2·354	2·52	1·402	2·354	—	—
163	0·39	1·591	2·296	6·1	1·786	2·296	4·6	1·67
136	0·126	1·101	2·442	1·80	1·256	2·442	1·38	1·140
	$\lambda = 16\cdot8$ kg.-cals.			$\lambda = 16\cdot4$ kg.-cals.			$\lambda = 16\cdot4$ kg.-cals.	

FIG. 3.
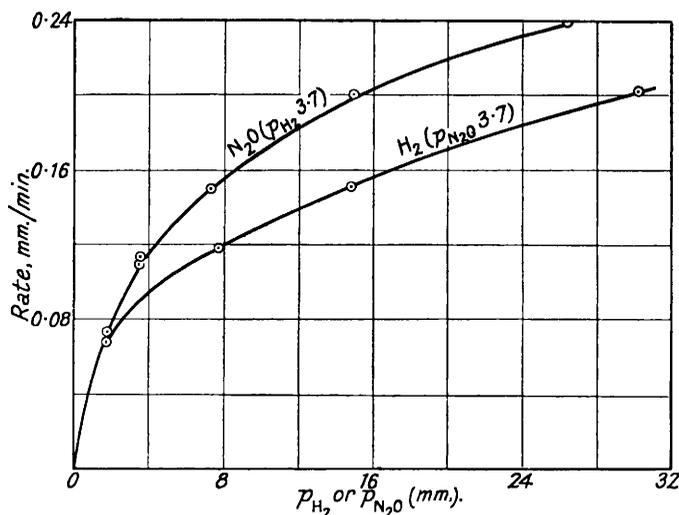
comparison with λ_R; (ii) the mechanism postulated above does not hold at all, and adsorption processes do not occur in the reversible manner necessary for these equations to remain valid. The first alternative is unlikely since the apparent energy of activation is not large. Further discussion is delayed until the experiments with deuterium are described.

Since λ has the same value in each case, experiments with deuterium were only carried out at low pressures. Three runs were made, the first and third with ordinary hydrogen, the second with a mixture of known deuterium content. Any drift in the activity of the wire could thus be checked. Two series of runs are shown in Fig. 4 and it will be seen that the rate of reaction of the 30% deuterium mixture is somewhat less than that of ordinary hydrogen. To demonstrate more clearly the quantitative differences, the ratio of the times (t) required for the pressure to fall by a given amount (Δp) are given in Table IV.

Two further series of results gave relative velocities of 1·17 at **133°** and 1·16 at **124°**. The maximum possible ratio, on the assumption that deuterium reacts very slowly compared with hydrogen, is 1·41.

The Hydrogen–Oxygen Reaction.—First, a preliminary survey of the kinetics was made in order to see whether this reaction bore any similarity to the preceding one. The reaction velocity decreases with oxygen pressure above 1 mm., but is nearly proportional to the hydrogen pressure (Table V). The spring manometer was not sufficiently sensitive to measure reaction velocities

TABLE IV.

Temp. 192°. $p_{N_2O} = 11.08$; $p_{H_2} = 3.72$.				Temp. 159°. $p_{N_2O} = 11.10$; $p_{H_2} = 3.70$.			
$\Delta p.$	t (H$_2$).	t (30% D).	Ratio.	$\Delta p.$	t (H$_2$).	t (30% D).	Ratio.
0·74	0·32	0·40	1·25	0·74	1·76	2·10	1·19
1·11	0·52	0·61	1·18	1·11	2·64	3·22	1·22
1·48	0·73	0·85	1·17	1·48	3·68	4·42	1·20
1·85	0·99	1·15	1·16	1·85	4·76	5·70	1·20
2·20	1·30	1·55	1·19	2·20	5·90	7·25	1·23
2·59	1·75	2·15	1·23	2·59	7·42	9·50	1·28
2·96	2·48	3·30	1·33	2·96	9·50	13·90	1·32
		Mean	1·19			Mean	1·22

FIG. 4.

Hydrogen–nitrous oxide reaction.
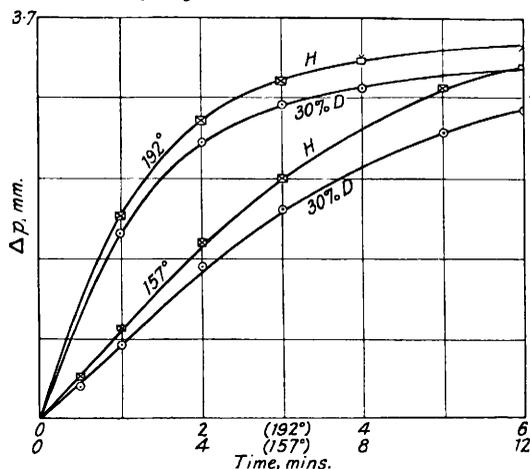
FIG. 5.

Hydrogen–oxygen reaction.
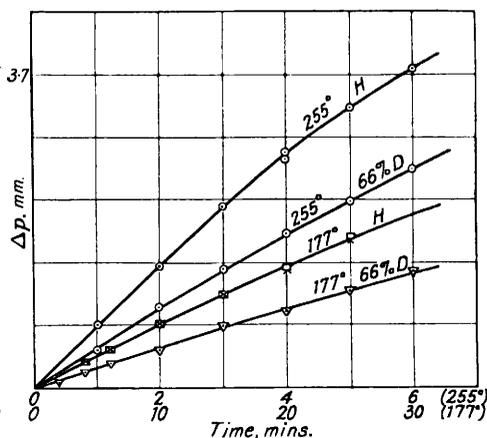
TABLE V.

The Hydrogen–Oxygen Reaction.

Effect of oxygen. Temp. 226°.						*Effect of hydrogen.* Temp. 255°.			
p_{H_2}	3·74	3·70	3·70	3·74		p_{H_2}	3·70	16·56	11·10
p_{O_2}	3·68	18·48	7·36	1·74		p_{O_2}	3·70	3·70	3·67
$t.$	$\Delta p.$	$\Delta p.$	$\Delta p.$	$\Delta p.$		$t.$	$\Delta p.$	$t.$	$\Delta p.$	$\Delta p.$
2	0·77	0·50	0·56	0·67		1	1·19	0·5	1·80	1·53
4	1·39	1·02	1·06	1·37		2	2·11	1·0	3·96	2·53
6	1·91	1·42	1·73	2·04		3	2·85	1·5	6·18	3·67
10	3·09	2·16	2·58	3·56		4	3·44	2·0	8·06	4·55
15	4·17	2·95	3·58	5·07		5	4·07	2·5	9·76	—
r	0·33	0·24	0·28	0·34		6	4·48	3·0	10·36	6·07
						r	1·04		4·07	2·51

in the region where oxygen is only weakly adsorbed. The maximum in the r–p_{O_2} curve must, however, occur at about 1 mm., for the run with 1·74 mm. of oxygen apparently goes faster as the oxygen is used up, but falls off again towards the end of the reaction. The two reactions are thus similar qualitatively, and oxygen is more strongly adsorbed than is nitrous oxide. The apparent energy of activation is higher, *viz.*, 23 kg.-cals. from 195° to 256° for a 1 : 1 mixture at 7·40 mm.

The experiments with deuterium were made at pressures where the oxygen is just beginning to inhibit the reaction. The temperatures required to obtain a measurable velocity are higher than those for nitrous oxide, and therefore in addition to the 30% mixture, one containing 66% of deuterium was employed. The Δp–t curves are shown in Fig. 5. The separation of the 66% curve is much greater than that for 30%. The average of the ratios of the times required for

Δp to reach a given series of values is summarised below. From these data the relative rates of reaction of hydrogen and deuterium are easily calculated.

p_{H_2}.	p_{O_2}.	Temp.	D_2 content, %.	Ratio of times.	p_{H_2}.	p_{O_2}.	Temp.	D_2 content, %.	Ratio of times.
3·73	3·70	226°	30	1·15	3·70	3·70	177°	66	1·63
3·70	3·70	226	30	1·18	3·70	3·70	255	66	1·60

The Hydrogenation of Ethylene.—A few experiments on this reaction were made to find whether the separation was quantitatively the same as that for the two preceding reactions. Experiments to be described elsewhere have shown that the reaction is much more complicated than had hitherto been supposed, and it is therefore not satisfactory to use kinetic data alone to follow the rate at which hydrogen and deuterium react. Nevertheless, some results are given in order (*a*) to compare this reaction with the others on the same catalyst, and (*b*) to show that deuterium reacts more slowly in spite of the more complicated mechanism.

The kinetics are simpler, the rate being proportional to the hydrogen and to the ethylene pressures except that, at high ethylene pressures (*ca.* 400 mm.), the r–$p_{C_2H_4}$ curve begins to bend over, showing that ethylene is rather more easily adsorbed than hydrogen. These four reactions have therefore a close similarity in that the molecule to be hydrogenated is more easily adsorbed than hydrogen. The nickel surface was more easily poisoned for the ethylene than for the other hydrogenations, but the activity could be restored by heating the wire in presence of several hundred mm. of hydrogen at 330° for $\frac{1}{2}$ hour, thus pointing to poisoning by oxygen. Table VI summarises the effect of hydrogen and of ethylene at 135°.

TABLE VI.

p_{H_2}.	$p_{C_2H_4}$.	r.	$r/p_{C_2H_4}$.	$t_{1/2}$.	p_{H_2}.	$p_{C_2H_4}$.	r.	r/p_{H_2}.	$t_{1/2}$.
48·8	23·8	1·8	0·071	—	51·0	50·0	3·9	0·077	9·0
50·2	50·8	3·0	0·059	11·5	102·8	50·0	6·5	0·067	4·35
50·0	101·0	6·0	0·059	5·67	195·2	50·8	11·7	0·059	2·50
51·0	198·0	9·6	0·049	3·76	396·6	50·0	20·0	0·050	1·62
50·6	367·5	11·3	0·031	3·1	51·8	50·2	5·0	0·077	7·0

A comparison of the second, sixth and last experiments shows that the activity of the wire is increasing. The values of r/p_{H_2} and $r/p_{C_2H_4}$ are corrected for this drift. Neither r/p_{H_2} nor $r/p_{C_2H_4}$ is constant, but the latter decreases more quickly than the former. One peculiarity about this reaction is that the apparent energy of activation, which is nearly zero between 190° and 155°, increases to about 5 kg.-cals. between 121° and 83°. At high pressures, the energy of activation (*E*) tends to decrease at high temperatures, as shown :

	$p_{H_2} = 3\cdot70$; $p_{C_2H_4} = 11\cdot10$.				$p_{H_2} = 50\cdot0$; $p_{C_2H_4} = 50\cdot0$.		
Temp.	190°	155°	121°	83°	152°	135°	117·5°
r	0·268	0·268	0·204	0·105	5·5	4·8	3·6
E		0·0	2·7	4·9		2·8	5·2

A considerable difference in the Δp–t curves was obtained with the 30% deuterium mixture :

Temp. 159°; $p_{H_2} = 3\cdot70$; $p_{C_2H_4} = 11\cdot10$.

t	2	4	6	8	10
Δp	0·25	0·47	0·73	1·12	1·50
Δp (30% D)	0·16	0·32	0·54	0·77	1·10

No quantitative calculations can be made with these results, for it has been found that, in addition to hydrogenation, some substitution also takes place. The relative rates of these reactions depend on the temperature and activity of the catalyst.

DISCUSSION.

It is at once apparent that the ratio of the rates of reaction of hydrogen and of deuterium is greater than could be accounted for simply by a collision factor involving the mass of the two atoms; the maximum ratio in this case would be $\sqrt{2} = 1\cdot4$. On the other hand, had the zero-point energies of the molecules been responsible for the separation, the ratio of the rates for the 66% mixture ought to have been about 3·5, account being taken of the presence of HD molecules. The experimental data for the hydrogen–oxygen and –nitrous

oxide reactions yield ratios much lower than this. For comparison the results are summarised in Table VII. In the last column, E has been calculated from the formula $r_H/r_D = e^{E/RT}$.

TABLE VII.

Reaction.	Mixture; D_2, %.	Temp.	Ratio (r_H/r_D).*	E (kg.-cals.).
H_2–N_2O	$\{$ 30	192°	2·10	0·69
	$\{$ 30	159	2·44	0·75
H_2–O_2	$\{$ 30	226	1·80	0·59
	30	226	2·09	0·74
	66	177	2·42	0·78
	$\{$ 66	255	2·31	0·88

* The results in this column have been calculated on the assumption that the rate is directly proportional to the deuterium content.

It is important to observe that E is about half the value of the difference in zero-point energies of the hydrogen and the deuterium molecule (Urey and Rittenberg, *loc. cit.*). Calculations from band-spectroscopic data of metallic hydrides have, however, shown that when the atom is relatively heavy, such as nickel, the zero-point energy difference for Me–H and Me–D is about half that of H_2 and D_2. Eyring and Sherman (*J. Chem. Physics*, 1933, **1**, 348) estimated that for nickel this difference is 0·7 kg.-cal., which is in very good agreement with the values of E in Table VII. It may therefore be reasonably concluded that the greater reactivity of hydrogen is due predominantly to the larger zero-point energy of the Ni–H molecule adsorbed on the nickel surface.

This explanation is supported by some photochemical experiments on the mercury-sensitised reaction, in which it is probable that the steps leading to reaction are $H + N_2O \longrightarrow OH + N_2$ and $OH + H_2 \longrightarrow H_2O + H$. The first step is the slower, and hence controls the rate (Melville, *Proc. Roy. Soc.*, 1933, *A*, **142**, 524; *Trans. Faraday Soc.*, 1933, **29**, 1255; also unpublished experiments). Comparing this sequence of reactions with that for the photosynthesis of hydrogen chloride, *viz.*, $H + Cl_2 \longrightarrow HCl + Cl$, $Cl + H_2 \longrightarrow HCl + H$, where it is now well established that the second reaction is the slower, we see that if deuterium is substituted for hydrogen, the rate of reaction at room temperature is decreased many-fold (Farkas and Farkas, *Naturwiss.*, 1934, **22**, 218). This is due mostly to the lower zero-point energies of the D_2 and the HD molecule. With the hydrogen–nitrous oxide reaction, on the other hand, zero-point energy should not enter into the velocity equation, for the hydrogen and deuterium atoms are free. Polanyi has, however, suggested (*Proc. Roy. Soc.*, 1934, *A*, **144**, 16) that in a reaction of this nature it may be that the deuterium atom will react more quickly than the hydrogen atom, owing to the difference in zero-point energies of the OH and OD molecules. As can be seen from Table VIII, there is practically no difference in velocity for ordinary hydrogen and for a 66% deuterium mixture; indeed, it would seem that deuterium reacts slightly more quickly.

TABLE VIII.

Cool Cathode Mercury Lamp. Temp. 20°. Hg *vap. press.* 0·001 *mm.*

Reaction mixture.

	$p_{H_2(HD,D_2)}$.	p_{N_2O}.	t.	2.	5.	10.	15.	20.	25.
H_2	3·70	3·67	Δp	0·30	0·95	1·70	2·41	2·96	3·66
66% D_2	3·73	3·70	Δp	0·30	1·00	2·15	2·96	3·44	—
H_2	3·70	3·70	Δp	0·41	1·04	1·85	2·51	3·11	—

There is, then, additional evidence to support the statement that, in the heterogeneous catalysis, the above explanation of the differences in velocities of reaction is adequate. This, in turn, throws a new light on the mechanism of these hydrogenation reactions, but only with regard to the slowest step in the reaction. In general, and especially at low temperatures, the rate of adsorption of hydrogen on nickel is very much faster than the rate of reaction (cf., *e.g.*, Bonhoeffer and Farkas, *Trans. Faraday Soc.*, 1932, **28**, 242), and hence the separation must be due to some reaction on the surface. Having regard to the probable mechanism of the diffusion of the two isotopes through palladium, it would

appear to follow that in the hydrogen–nitrous oxide reaction the rate-governing step is the migration of hydrogen atoms on the nickel surface to adsorbed oxygen, which is formed by the impact of oxygen or nitrous oxide on the bare nickel surface (or on a hydrogen-covered surface) immediately these gases are admitted to the reaction tube.

Since the temperature coefficient of the hydrogen–nitrous oxide reaction is independent of the displacement effects described previously, then, in order to form a reasonable picture of the mechanism, it must be supposed that the nickel surface (assumed for simplicity to be homogeneous) is always covered with hydrogen and oxygen, and that the proportion covered with, say, the former atoms, will depend primarily on the composition of the gas mixture. Temperature will thus not alter the fraction of the surface covered, but will perhaps change the relative amounts of the two types of atom adsorbed for a given composition in the gas phase. If this latter effect is small, the apparent energy of activation is really the true energy of activation of the surface reaction. In this case, the hydrogen–oxygen and –nitrous oxide reactions should have the same temperature coefficients, but the difference is not great; 17 kg.-cals. might be taken as the energy of activation for the migration of the hydrogen atom. The data do not, however, provide any information as to whether *part* of this energy is required for bringing the oxygen atom into a reactive state.

To explain the effect of hydrogen and nitrous oxide pressure, it is necessary to assume that the reaction rate will be a maximum when the surface composition attains a certain value; this does not imply that equal numbers of oxygen and of hydrogen atoms are to be adsorbed. For a given nitrous oxide pressure, the rate will increase with hydrogen pressure, reach a maximum, and then fall off after the optimum surface concentration is reached. A similar behaviour will be obtained when the pressure of nitrous oxide is varied. Hence the reaction will not be bimolecular at the lowest pressure used in these experiments, which is in agreement with the results in Table IV, for which the corresponding r–$p_{H_2(C_2H_4)}$ curves bend round quite rapidly to exhibit displacement phenomena similar to those at high pressure.

SUMMARY.

The kinetics of the interactions of hydrogen and of deuterium with carbon monoxide, oxygen, nitrous oxide, and ethylene have been studied on a nickel wire catalyst at temperatures from 100° to 300° and pressures from 1 to 760 mm.

The velocity of reaction of hydrogen with nitrous oxide and with oxygen is about twice that of deuterium from 160° to 250°. This is about the degree of separation expected if the different velocities are due solely to the difference in zero-point energies of the Ni–H and Ni–D molecules. A similar variation is obtained with ethylene, but owing to complications, the results cannot be interpreted quantitatively.

Combining these results with the kinetic measurements for the H_2–O_2 and H_2–N_2O reactions, the mechanism would appear to be as follows : The nickel surface is always covered with H and O atoms, the proportion depending on the temperature, composition, and pressure of the gas with which it is in contact. The slowest step is the migration of the H or D atom to the adsorbed O atom, and this determines the magnitude of the separation observed. The energy of activation of this process is less than 20 kg.-cal.

In the mercury photosensitised H_2–N_2O reaction, where the H atom is free and therefore zero-point energy does not contribute to the energy of activation, the ratio of rates is nearly unity.