

CCXXVIII.—*The Combination of Hydrogen and Oxygen
on the Surface of Platinum.*

By REGINALD PAUL DONNELLY and CYRIL NORMAN HINSHELWOOD.

THE experiments described in this paper were made with two independent objects. In the first place, since the homogeneous combination of hydrogen and oxygen between 500° and 600° is a chain reaction (*Proc. Roy. Soc.*, 1929, *A*, **122**, 610), it seemed possible that as the temperature of a platinum wire in a mixture of the two gases is gradually raised to the explosion point the reaction might cease to be purely heterogeneous, and reaction chains, initiated by the heterogeneous reaction, might spread into the gas. Although certain interesting observations have been made which are not easy

to explain except by assuming that chains are propagated, no conclusive proof can be said to be forthcoming.

In the second place, we wished to make kinetic measurements at ordinary pressures in order to compare them with the results obtained by Langmuir (*Trans. Faraday Soc.*, 1922, **17**, 621) at low pressures. Such a comparison seemed likely to throw light upon a question of some general importance raised by an observation of Schwab. Hinshelwood and Burk (J., 1925, **127**, 1114) had found that the decomposition of ammonia on tungsten at ordinary pressures was unretarded by the products of reaction, but Schwab (Diss., Würzburg, 1927; *Z. physikal. Chem.*, 1927, **128**, 161), working at low pressures, found a retardation, and concluded that since results valid at low pressures could obviously not be extrapolated to higher pressures, the simple Langmuir adsorption theory fails to account adequately for the kinetics of heterogeneous reactions. He interprets the changing behaviour in terms of a theory that multimolecular adsorption layers are formed; but an alternative, and in some ways preferable, explanation of the fact that a heterogeneous reaction may appear to proceed according to a different law in a different region of pressure is provided by Taylor's theory (*Proc. Roy. Soc.*, 1925, *A*, **108**, 105) that the catalytic surface possesses centres of varying activity. At low pressures the amount of gas may be small enough to be accommodated on the most active centres, which, in virtue of their activity, are more likely to be susceptible to poisons, and may even be poisoned by too large a pressure of the reacting gases. At higher pressures, where the total adsorption is much greater, the less active centres, being much more numerous, contribute the greater proportion of the total reaction. Since they may possess different adsorptive properties, the kinetic relationships may change completely.

The experiments to be described show, first, that the reaction follows a different law at normal pressures from that found by Langmuir at low pressures, and secondly, that active centres of different kinds do, in fact, exist on the platinum wire. These two results in conjunction lead us to believe that, in general, if the law which a heterogeneous reaction follows changes with pressure, the centres upon which reaction predominates also change.

The apparatus was the same as that described in previous investigations of catalytic reaction on heated wires (J., 1925, **127**, 327, 806). The reaction vessel was a cylindrical bulb of about 100 c.c. capacity, with a platinum wire about 15 cm. in length sealed along its axis. The bulb, placed so that the wire was vertical, was surrounded by ice, and all measurements of pressure were taken at 0°. It was connected by capillary tubes of negligible internal volume to a

capillary manometer on which the progress of reaction could be measured, and through taps to a vacuum pump and to gas holders containing oxygen, hydrogen, and any other gas which it was desired to introduce. Small glass spirals containing water and immersed in ice were inserted between the taps of the reaction vessel and the gas holders in order that the oxygen and hydrogen might be saturated at 0° at the beginning of the reaction and thus possess a constant water content throughout its course. This precaution, however, appears to have been unnecessary.

The temperature of the wire was determined from its resistance, which was controlled by an ammeter, voltmeter, and rheostat. The rate of reaction was measured by observing the fall in pressure caused by heating the wire for a suitable interval.

The oxygen was generated by heating potassium permanganate in a completely evacuated apparatus, and was purified by passage over caustic potash and phosphoric oxide. The hydrogen used was electrolytic hydrogen from a cylinder, freed from oxygen and carbon dioxide by passage, first over a glowing filament and then through caustic potash and phosphoric oxide in an all-glass apparatus, previously evacuated.

The catalytic activity of the wire was liable to vary, and in order to guard against systematic errors arising from this cause, the following procedure was adopted in determining how the rate of reaction varied with the pressures of the different gases. The pressure of one gas was varied over as large a range as possible, that of the other being kept constant. Between each pair of experiments of such a series "blank" experiments with a standard pressure of hydrogen and oxygen were made. The observed rate in any experiment, divided by the average of the rates of the "blank" experiments preceding and following it, gave a relative value which would be unaffected by a gradual drift in the activity of the wire. By careful treatment of the wire, such drift could actually be reduced to an almost negligible amount in the course of a given series of experiments; but if between two series the wire had been subjected to any unusual treatment, considerable changes often occurred.

The curves representing the complete course of the reaction are given in Fig. 1, which is plotted from the data given in Table I.

After a short period of induction, the curves are almost linear over a considerable range, and the slope of the linear part of the curve is used as a measure of the rate of reaction.

A comparison of the curves for excess of oxygen and excess of hydrogen suggests that the rate of reaction is independent of the pressure of hydrogen and dependent on that of oxygen. That the

FIG. 1.

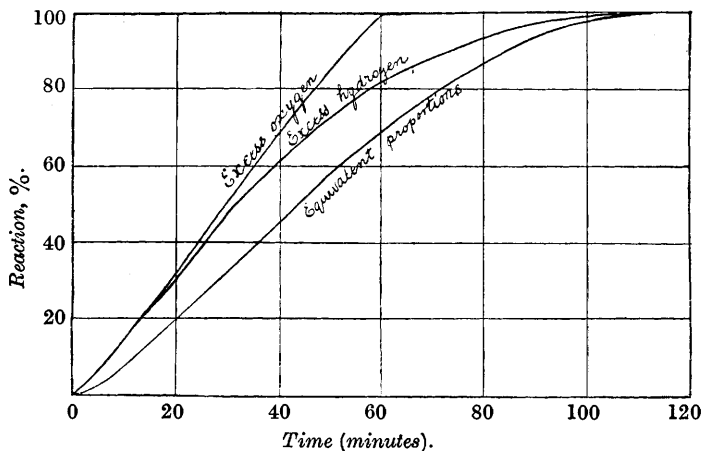


TABLE I.

[t = time (in minutes), x = total change in pressure (in mm.)]

142° (Wire 2). H ₂ = 100 mm. O ₂ = 102 mm.				143° (Wire 1). H ₂ = 200 mm. O ₂ = 56 mm.				142° (Wire 2). H ₂ = 102 mm. O ₂ = 54 mm.			
t .	x .	t .	x .	t .	x .	t .	x .	t .	x .	t .	x .
3	5	39	104	5	12	56	129.7	6	4	61	106
6	12.5	48	126	10	25	66	142.5	12	14.5	67	116.5
9	21	54	139.5	15	37	81	157.5	18	25.5	74	126
15	36	60	152	20	50.3	90	162	24	36.5	84	135
21	54	63	152.5	25	65	101	165	30	48	90	142
27	71	66	153	36	93.5	106	165	36	61	96	148
33	88	76	153	46	112.6			42	74	102	151
								48	84	108	152.5
								54	94		

rate is independent of the hydrogen concentration is confirmed by the following table, where in each case, rates of reaction are given relatively.

143° (Wire 1).				142° (Wire 2).			
O ₂ = 200 mm.		O ₂ = 50 mm.		O ₂ = 100 mm.		O ₂ = 100 mm.	
H ₂ , mm.	Rate.	H ₂ , mm.	Rate.	H ₂ , mm.	Rate.	H ₂ , mm.	Rate.
50	0.99	100	(1.00)	13.5	1.0	100	(1.00)
100	1.16	200	1.07	22	1.05	200	1.03
200	(1.00)	300	1.07	100	(1.00)	300	1.10
250	1.02	400	1.07	300	1.09	350	1.20
300	0.84			500	1.22	500	1.33
400	1.24						
500	0.82						

The rate of reaction increases with the pressure of oxygen, the increase being less marked at higher pressures than at the lower

(see Table II). There is, however, no evidence of definite saturation, except in one series of experiments in which the wire was in an abnormally active state. The form of the curves (see Fig. 2) varies considerably with the state of the wire, but is always similar to that which would be obtained by superposition of two Langmuir isotherms, one with a small saturation limit soon reached, and the other with a much larger saturation limit less easily reached (see inset in Fig. 2).

FIG. 2.

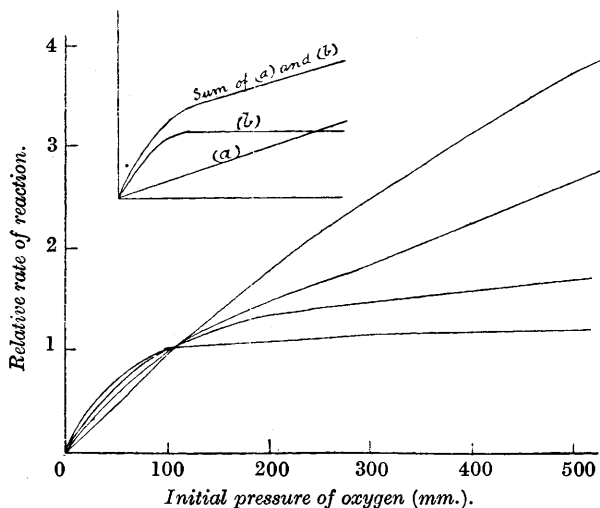


TABLE II.

143° (Wire 1).		143° (Wire 1).		115° (Wire 1).	
H ₂ = 200 mm.		H ₂ = 300 mm.		H ₂ = 100 mm.	
O ₂ , mm.	Rate.	O ₂ , mm.	Rate.	O ₂ , mm.	Rate.
60	0.55	38	0.47	50	0.72
100	(1.00)	54	0.49	74	0.85
200	1.35	100	0.81	100	(1.00)
300	1.50	150	(1.00)	300	1.16
400	1.58	200	1.22	500	1.15
		300	1.25		
		350	1.35		
142° (Wire 2).		150° (Wire 2).		101° (Wire 2).	
H ₂ = 100 mm.		H ₂ = 100 mm.		H ₂ = 100 mm.	
O ₂ , mm.	Rate.	O ₂ , mm.	Rate.	O ₂ , mm.	Rate.
50	0.60	100	(1.00)	100	(1.00)
100	(1.00)	250	2.21	200	1.72
315	1.95	500	3.79	300	1.85
500	2.70			500	2.83

According to Langmuir, the rate of reaction at low pressures and below 300° is directly proportional to the pressure of oxygen and

inversely to that of hydrogen. This indicates that hydrogen displaces oxygen from those centres on which reaction predominates. The present results, on the other hand, show that at normal pressures, although hydrogen saturates the surface, it does not displace oxygen to any appreciable extent, since the rate is independent of the pressure of hydrogen over the whole range.

The form of the curve expressing the relation between rate and oxygen pressure shows that oxygen itself is adsorbed, and does not react merely by striking adsorbed hydrogen—a process which would lead to a strictly linear relation. The centres, therefore, on which hydrogen and oxygen are adsorbed cannot be the same. Further, the exact relation between rate and oxygen pressure varies considerably with the state of the surface. This fact renders improbable the suggestion that the oxygen is adsorbed in a second layer on the primary hydrogen layer, for the constant nature of the surface thus presented to the oxygen should give a constant form of curve. However this may be, the surface on which reaction takes place is not the same at normal pressures as that at the low pressures of the Langmuir experiments.

Several experiments of different kinds were made to see if evidence could be found that propagation of chains from the wire into the gas occurred. At first an attempt was made to discover whether the relation between the rate of reaction and the pressure of hydrogen or oxygen changed with increasing temperature in such a way as to indicate that spreading of chains into the gas took place. The only significant result of these experiments was that the maximum rate at which reaction could take place on the wire without causing ignition of the gas was rather surprisingly small, being only 4% per minute with Wire 1 and 200 mm. of hydrogen and 100 mm. of oxygen.

It was next found that the presence of nitrogen or argon definitely lowered the temperature to which the wire could be heated without causing explosion from about 200° to 180°. With 400 mm. of nitrogen and less than 50 mm. of oxygen the gas mixture did not explode, but at a temperature where the reaction in absence of nitrogen would still have been fairly slow, a very rapid surface reaction took place, raising the wire to incandescence. It was found too that nitrogen or argon caused an acceleration of the isothermal reaction, 300—500 mm. increasing the rate of reaction by 20—30%. A similar effect of these foreign gases is characteristic of the homogeneous combination of hydrogen and oxygen, in which it is due to the lengthening of chains, and the result obtained here suggests that there may be some homogeneous reaction spreading out from the wire.

It is a little difficult to see how argon or nitrogen could accelerate the heterogeneous reaction itself. It should be mentioned that the effect was independent of the total conductivity of the gas mixture.

Experiments were next made on the influence of small amounts of nitrogen peroxide, since this gas is known to initiate reaction chains very readily in mixtures of hydrogen and oxygen at higher temperatures. Its only effect, however, was to poison the heterogeneous reaction, 0.5 mm. of nitrogen peroxide reducing the rate to about half. The explosion temperature was correspondingly raised.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD.

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