CCCXXI.—*The Combination of Hydrogen and Oxygen on the Surface of Nickel.*

By Reginald Paul Donnelly.

The investigation of the combination of hydrogen and oxygen on the surface of nickel has been undertaken as a sequel to the study of the same reaction on platinum (Donnelly and Hinshelwood, this vol., p. 1727). The mechanism of the heterogeneous reaction in the present case is different, however, and further, no evidence has been found that it initiates a homogeneous reaction spreading into the gas by a chain process.

The apparatus and procedure were similar to those used in the former investigation. The nickel surface was provided by a wire, 0·015 cm. in diameter (38 Imperial Standard Wire Gauge), stretched

axially in a cylindrical reaction vessel (2·0 cm. in diameter and about 15 cm. in length), which was connected to a mercury manometer, vacuum pump, and gas-holders. The ends of the wire, sealed through the glass, were connected in series with a storage battery, resistance, and ammeter, and in parallel with a voltmeter by means of which the temperature could be maintained steadily at any desired value.

In any experiment, reaction was allowed to proceed in presence of the heated wire for a suitable time, after which the heating current was interrupted and the fall of pressure determined; as the reaction vessel was kept immersed in ice and water, the measurements were made with the gas at 0°. Since the " complete reaction curves " (Fig. 3) are sensibly linear, the velocity of reaction may be measured by the average fall of pressure per minute for several intervals over the course of the reaction. It was found that individual measurements departed but little from the average, even when the rate of reaction reached values of 100—150 mm. (30—50% of the complete reaction) per minute.

Experiments were made in series, in any one of which the effect of only one variable was investigated. Although the activity of the nickel surface rarely altered during any one series, the method of correcting for variations in activity (used in the case of platinum, *loc. cit.*) has been adhered to, " blank " experiments being performed under standard conditions of temperature and concentration between each pair of experiments, and the rate of reaction in any experiment being divided by the average of the preceding and succeeding " blanks." Rates are thus referred to the " blanks " as unity, and are tabulated in this way for convenience.

In every experiment hydrogen was used in excess of the stoicheiometric proportion required for complete combination with oxygen in order to prevent the latter gas burning the wire.

In contrast with the results obtained with platinum, no evidence was forthcoming of initiation of chains from the hydrogen–oxygen reaction on nickel. In the first place a comparatively high rate of reaction could be obtained without its becoming non-isothermal and explosive. Also, exhaustive experiments, made over a series of rising temperatures up to the explosion temperature, have shown that argon and nitrogen have practically no influence either on the rate of reaction or on the explosion temperature. As with platinum, nitrogen peroxide was found to poison the heterogeneous reaction, so that its influence on any homogeneous reaction could not be apparent. Finally, the constant slope of the line connecting log k and $1/T_{\text{Abs.}}$ (Fig. 4) indicates that there is no homogeneous reaction superimposed on the heterogeneous reaction; for, if it existed,

such a reaction would become more pronounced with increased temperature.

Previous investigations of the combination of hydrogen with oxygen on nickel have been made by the " flow method," but this does not allow the different factors affecting the rate to be varied as easily and systematically as does the " hot-wire " method used in the present experiments. In agreement with Bone and Wheeler (*Phil. Trans.*, 1906, *A*, **206**, 1), it is now found that the rate is independent of the pressure of oxygen, and increases directly as the pressure of hydrogen. These authors suggested that the increase of rate with hydrogen pressure is accounted for by variation in the adsorption of hydrogen by nickel. This metal, however, readily becomes saturated with hydrogen, and the perfectly linear increase of rate with hydrogen pressure, maintained up to pressures which are probably beyond the saturation point, suggests rather that the reaction does not depend upon the adsorbed hydrogen, but is brought about by collision of hydrogen molecules with adsorbed oxygen, which probably exists as a film of active oxide on the metal (see Bevan and Hughes, *Proc. Roy. Soc.*, 1925, *A*, **117**, 101; Larson and Smith, *J. Amer. Chem. Soc.*, 1923, **45**, 346; Benton and Emmet, *ibid.*, 1926, **48**, 632; 1924, **46**, 2788). Benton and Emmet think that the mechanism of the reaction is the formation and reduction of an " incipient oxide " on the surface of the nickel, the metal catalysing the reduction of the oxide by an interfacial process : by " incipient oxide " they seem to mean nickel oxide which has not lost the energy set free in its formation.

Influence of Hydrogen at Constant Oxygen Pressure.—If the rate of reaction depends on the collision of molecules of hydrogen with adsorbed molecules of oxygen, it is governed by the rate at which molecules of hydrogen impinge on the catalytic surface. Thus (1) the rate should increase directly as the pressure of hydrogen, and (2) the relative increase of rate for a given increase of pressure should be independent of the temperature. Both these conditions are fulfilled, as is shown by the straight line in Fig. 1, which is based upon the following results obtained at several different temperatures.

Influence of Oxygen at Constant Hydrogen Pressure.—The results in Table II show that the rate is independent of the partial pressure of oxygen down to 50 mm., but below this it falls off sharply, as shown in Fig. 2. These two facts suggest that there is an equilibrium between adsorbed oxygen and gaseous oxygen of such a nature that the catalytic surface becomes saturated above a pressure of 50 mm., but is sufficiently denuded at lower pressures (*e.g.*, 10 mm.) to cause a fall in the rate.

The same behaviour is shown when any experiment is taken to

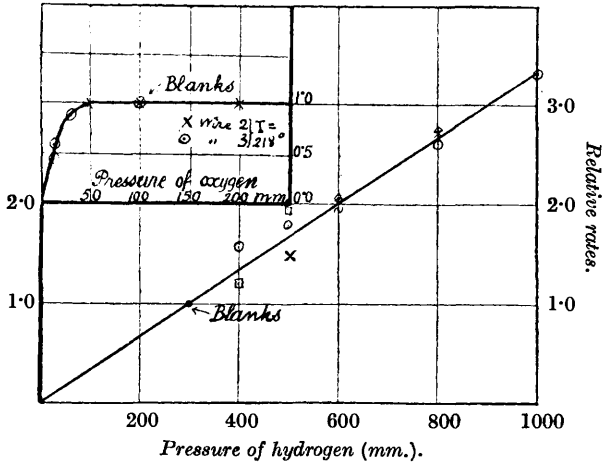
completion: in approaching the end-point, the rate suddenly diminishes and then becomes inappreciable 3—4% short of the theoretical end-point, *i.e.*, some oxygen remains uncombined. A comparison of the results obtained for Wire 3 at 218° (Table II) with the figures at the bottom of Table III, which show a rough proportionality between rates of reaction and corresponding estimated oxygen pressures towards the end-points of Expts. 2 and 3, tends to support the above suggestion.

FIG. 2.

Relation between rate of reaction and pressure of oxygen.

FIG. 1.

Relation between rate of reaction and pressure of hydrogen.



⊡ $T = 200°$ (*Wire* 1).
⊙ $T = 218°$ (*Wire* 2).
× $T = 266°$ (*Wire* 2).
△ $T = 244°$ (*Wire* 3).
~ $T = \begin{cases} 240° \\ 220° \end{cases}$,,

TABLE I.

$T = 200°$ (Wire 1). $O_2 = 50$ mm.		$T = 218°$ (Wire 2). $O_2 = 100$ mm.		$T = 244°$ (Wire 3). $O_2 = 100$ mm.	
H_2, mm.	Rate.	H_2, mm.	Rate.	H_2, mm.	Rate.
300	(1·0)	300	(1·0)	300	(1·0)
400	1·2	400	1·57	600	2·05
500	1·95	500	1·8	800	2·74
		800	2·61		
		1000	3·3		

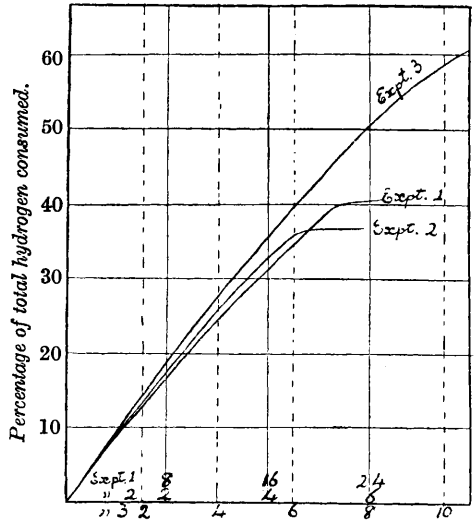
$T = 266°$ (Wire 2). $O_2 = 100$ mm.		$T = 240°$ (Wire 3). $O_2 = 100$ mm.		$T = 220°$ (Wire 3). $O_2 = 100$ mm.	
H_2, mm.	Rate.	H_2, mm.	Rate.	H_2, mm.	Rate.
300	(1·0)	300	(1·0)	300	(1·0)
500	1·44	600	1·95	600	1·98
600	2·05				
800	2·77				

TABLE II.

T = 200° (Wire 1). H_2 = 500 mm.		*T = 218° (Wire 2). H_2 = 500 mm.	
O_2, mm.	Rate.	O_2, mm.	Rate.
50	1·29	52	0·99
100	1·03	100	(1·0)
120	0·97	200	1·03
200	(1·0)		
T = 266° (Wire 2). H_2 = 500 mm.		*T = 218° (Wire 3). H_2 = 300 mm.	
O_2, mm.	Rate.	O_2, mm.	Rate.
52	1·0	100	(1·0)
100	(1·0)	25	0·86
200	0·9	13	0·57
		12	0·44

* These results are plotted in Fig. 2.

FIG. 3.



Time (mins.) — separate scale for each experiment.
Complete reaction curves.

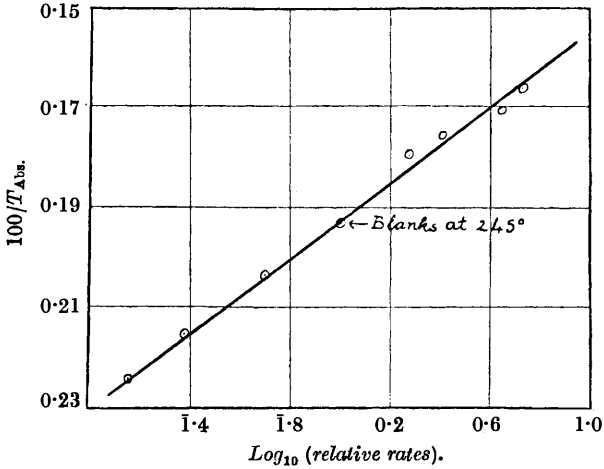
The complete reaction curves (Fig. 3), in which the percentage of hydrogen combined, x (see Table III), is plotted against time (t, in mins.), seem to be of the first order with respect to the hydrogen, and would thus bear out the conclusions already reached, *viz.*, that the rate is proportional to the pressure of hydrogen. Owing to the necessity of working with excess of hydrogen in all experiments, however, the full unimolecular form of the curves cannot be made apparent.

TABLE III.

Expt. 1. T = 218° (Wire 2). H_2 = 500 mm. O_2 = 106 mm.		*Expt.* 2. T = 266° (Wire 2). H_2 = 500 mm. O_2 = 100 mm.		*Expt.* 3. T = 266° (Wire 3). H_2 = 300 mm. O_2 = 100 mm.	
t.	x.	t.	x.	t.	x.
2	5·3	1	9·4	1	7·2
4	9·0	2	17·6	2	14·5
6	13·4	3	25·6	3	21·3
8	17·3	4	32·9	4	27·7
11	23·3	4·5	35·8	5	33·9
14	28·5	5	36·8	6	39·5
16	31·5			7	44·3
18	34·7			9	55·0
20	37·8			11	61·8
22	40·0			12	63·4
23	40·3			13	63·7
25	40·3				

Expt. No.	Interval.	Rate in interval relative to average rate in expt.	Average pressure of O_2 in interval.
2	t = 4 — 4·5	0·72	14 mm.
2	t = 4·5— 5	0·24	8 mm.
3	t = 9 —11	0·56	12 mm.

FIG. 4.



The Temperature Coefficient of the Reaction.—The temperature coefficient of the reaction has been measured over a range of 150°. The temperature at which any experiment is performed is calculated from the ratio of the corrected resistance of the wire during the experiment to its resistance at 0°, Somerville's values of the temperature coefficient of nickel (*Physical Rev.*, 1910, **31**, 261) being used. The correction is to allow for the resistance of the cold ends where the wire is sealed into the reaction vessel. The results, which are given below, are plotted in Fig. 4 as $100/T_{Abs.}$ against the Briggsian

logarithm of the rate relative to the "blanks," which were all performed at a constant temperature of 245°. The temperature coefficient per 10° over the range 173—245° is therefore 1·34, and over the range 245—329·5°, 1·22.

Temp.	173°	191·5°	218°	245°	284°	297°	313°	329·5°
Rate (mm./min.)	1·5	3·5	8·2	17	34	46·5	62·7	76·5
Rate relative to rate at 245°	0·12	0·233	0·494	(1·0)	1·88	2·54	4·18	5·45

Summary.

1. Systematic experiments performed on the effect of variations in the proportions of hydrogen and oxygen at various temperatures confirm the views of other workers that the combination of hydrogen and oxygen on nickel takes place by molecules of hydrogen striking adsorbed molecules of oxygen.

2. No evidence has been obtained that the foregoing heterogeneous reaction initiates a homogeneous reaction spreading into the gas by a chain process, but in view of the marked difference between the mechanisms of the reaction on nickel and on platinum, this is not surprising.

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