CCI.—*The Interaction of Hydrogen and Nitrous Oxide on the Surface of Gold.*

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IN catalytic reactions at surfaces considerable variety is found in the relations which exist between the rate of reaction and the concentrations of the several reacting substances. Examples of different kinds have been given in a number of previous papers. The most general relation, when there is one reacting substance only, is that the rate increases with concentration according to a curve of the same form as an adsorption isotherm. When there are two reacting substances, the rate may actually pass through a maximum and decrease again as the pressure of one gas increases, the decrease being due to the displacement of the other gas from the surface. But it may happen that the two reacting substances are independently adsorbed on different active parts of the surface. Saturation can then be reached with respect to each gas without displacement of the other. Examples of these two kinds of behaviour are given in J., 1925, **127**, 806, 1546. For the sake of completeness in classifying the various types of heterogeneous reaction, further instances may be useful.

We have now investigated the kinetics of the interaction of hydrogen and nitrous oxide on the surface of a gold wire. The results can be interpreted by assuming that hydrogen and nitrous oxide are adsorbed on the surface independently of each other, and that interaction can take place between adjacent molecules. The reaction rate increases with increase in the pressure of nitrous oxide, and reaches a limiting value at approximately 300 mm., after which it remains constant up to the highest pressure used, *viz.*, 500 mm. The absence of any fall in the rate at the higher pressures may be taken to show that, even after saturation is reached, there is no appreciable tendency for the nitrous oxide to displace the hydrogen from the surface.

Increase of hydrogen pressure has a similar effect, except that the limiting value of the rate is not quite reached within the experimental limit of 500 mm.

A second effect was traced to the hydrogen, namely a steady decrease in the activity of the wire, especially when it was heated in mixtures containing hydrogen in excess. On a wire, the activity of which had been reduced in this way to less than one-fifth of its initial value, it was found that the influence of the nitrous oxide on the rate was more nearly proportional to its pressure, and that the limiting or saturation value could not be reached. It is suggested that hydrogen gradually dissolves in the body of the metal—this solution being distinct from its primary adsorption on the surface—and decreases the adsorptive power towards nitrous oxide. This would result, not only in a decrease in the rate of reaction due to the smaller number of nitrous oxide molecules present on the surface, but also in a change in the actual adsorption isotherm.

The method of procedure was that already described (*loc. cit.*), the change in pressure giving a measure of the reaction

$$N_2O + H_2 = N_2 + H_2O \text{ (liquid).}$$

A correction was necessary for the vapour pressure of liquid water at 0° in those cases where no drying agent was present. The experimental work was complicated by the continually decreasing activity of the catalyst. Heating to dull redness in air caused a partial but only temporary recovery, for it rendered the wire very susceptible to the further action of hydrogen. The following method was therefore employed to correct for the variable activity, and to reduce the results to values which are comparable with one another. Initial rates of reaction only were observed, and in any series, the first, third, and odd-numbered experiments were performed under standard conditions of concentration of the reactants (for convenience, 100 mm. of each), and in the even-numbered experiments the initial pressure of one or other reactant was varied. The ratio of the observed initial rate in an even-numbered experiment to the mean value of the rates observed in the reference experiments on either side of it gives a value which is strictly comparable with the others in a given series, even if the state of activity of the catalyst drifts to some extent.

Owing to this gradual poisoning of the catalyst, and also on account of the complicated relation which would be required to express the velocity in terms of the concentration of both reactants, no attempt was made to evaluate velocity coefficients, nor to determine the heat of activation. The experiments were carried out in the usual manner at two temperatures with a number of different wires, and in the tables which follow it will be seen how the initial rate of reaction depends upon the initial pressure of nitrous oxide and of hydrogen. If, as seems probable, the rate is determined by the amount of adsorption or surface concentration, these figures represent also the relative degrees of saturation of the active parts of the surface with the gas in question.

Influence of Nitrous Oxide.—On a fresh active wire the initial rate reaches a limit at a pressure near 300 mm. and remains constant up to a pressure of at least 500 mm.

Table I.

Pressure of hydrogen = 100 mm.

	Pressure of N_2O (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1·00	1·40	1·64	1·91	1·80	Wire 1	704°
,, ,, ...	1·00	1·18	1·34	1·37	1·38	Wire 2	
,, ,, ...	1·00	—	1·25	—	1·26	Wire 3	
,, ,, ...	1·00	—	1·77	—	1·89	,,	880°

With a wire in a highly poisoned and inactive state, as a result of the prolonged action of hydrogen, saturation was not reached, and the rate varied considerably more extensively with the initial pressure of nitrous oxide.

Table II.

Pressure of hydrogen = 100 mm. (Wire poisoned.)

	Pressure of N_2O (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1·00	1·50	2·10	2·50	—	Wire 2	704°
,, ,, ...	1·00	1·76	2·56	3·13	3·68	,,	880°

Influence of Hydrogen.—The influence of the pressure of hydrogen on the rate appears to be independent of the state of the wire, as the figures of Table III show. Saturation is not reached so readily as in the case of nitrous oxide.

Table III.

Pressure of nitrous oxide = 100 mm.

	Pressure of H_2 (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1·00	1·33	1·58	1·97	2·22	Wire 4	704°
,, ,, ...	1·00	1·21	1·50	1·78	1·92		
,, ,, ...	1·00	1·18	1·43	1·40	1·81	Wire 2 (poisoned)	880°

Influence of Water Vapour.—Experiments were performed in which phosphoric oxide was present either in the bulb or in a small side tube sealed to it. The rate was reduced somewhat, as compared with that observed on the same wire before the introduction of the phosphoric oxide, and a certain recovery took place when the side tube containing it was sealed off, but the change was not fundamentally important. Further, a comparison of the results contained in Tables IV and V with those already discussed shows that the adsorption isotherms remain of the same form, whether water vapour is present or not.

This reaction possesses some interest in connexion with the general classification of heterogeneous reactions, as it represents

TABLE IV.

Pressure of hydrogen = 100 mm. (Fresh wire.)

	Pressure of N_2O (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1·00	1·34	1·56	1·59	(1·31)	Wire 5	704°

TABLE V.

Pressure of nitrous oxide = 100 mm. (Fresh wire.)

	Pressure of H_2 (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1·00	1·63	—	2·00	2·73	Wire 5	704°

one of the most general cases. But rather will it be in certain special circumstances, for example, with very small or very large adsorption of one reactant, that further theoretical inferences will become possible.

Summary.

The relation between the rate of interaction of nitrous oxide and hydrogen at the surface of a gold wire and the concentrations of the two gases has been examined at 704° and 880°. The reaction is of the type where the two gases are adsorbed independently of each other. The rate of reaction tends to a limiting value as the pressure of each gas is increased.

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