338. *The Kinetics of the Adsorption of Hydrogen and of Deuterium by Platinum.*

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Although the sorption of hydrogen by metals such as platinum is, in general, regarded as consisting of a surface stage, followed by a secondary process—possibly of solution—yet the resolution into these two stages is not very definite; and little is known with regard to the duration of the first stage or to the degree of implication of any intermediate stage corresponding with the penetration of the gas to less accessible inter-granular or inter-crystalline surface, for instance, along grain boundaries or through Smekal cracks. The adsorption—save for any low-temperature component of van der Waals type—in all probability involves linkage of a purely chemical nature; and its progress, after the initial external surface stage has been passed, has been regarded as being controlled by the velocity of diffusion or solution (Ward, *Proc. Roy. Soc.*, 1931, *A*, **133**, 522; *Trans. Faraday Soc.*, 1932, **28**, 399; Steacie, *J. Physical Chem.*, 1931, **35**, 2113; Steacie and Stovel, *J. Chem. Physics*, 1934, **2**, 581; Lennard-Jones, *Trans. Faraday Soc.*, 1932, **28**, 333). Further, the conception of an activated migration, *per saltum*, not only along the surface but also from the surface to the interior of the metal and subsequently within the metal itself, has also recently been put forward by Rideal (*Nature*, 1935, **135**, 737). In any case, these adsorption processes simulate or actually represent reactions associated with an activation energy in accordance with H. S. Taylor's theory of activated adsorption.

It was considered that evidence relative to the duration and sharpness of differentiation of the first stage and to the nature of the rate control might be obtained by further studying the kinetics of the adsorption and, particularly, by measuring any change in the rate or in the kinetic form which is introduced by substituting deuterium for hydrogen. It is usual to distinguish somewhat arbitrarily between a so-called primary, or substantially immediate, adsorption—which involves the bulk of the adsorbed gas—and a subsequent far slower secondary process; but this differentiation is not very satisfactory in the absence of precise figures relative to the early kinetics, and, for this reason, in the present work special weight has been laid on the early stages of adsorption, which have been followed by observations taken, where necessary, at intervals of a few seconds.

In order to compare rates of adsorption (*e.g.*, of deuterium relative to that of hydrogen), it is necessary to express the adsorption path in the form of a general equation which covers the observed kinetics. In the case of hydrogen on platinum, neither the total nor the secondary process follows either Ward's relationship, $x/\sqrt{t} = k$ [derived (*loc. cit.*) for the secondary adsorption of hydrogen on copper up to a not too advanced stage of adsorption; x is the volume adsorbed after time t] or the somewhat similar but wider expression of Bangham and Burt (*Proc. Roy. Soc.*, 1924, *A*, **105**, 481), according to which, for stages of adsorption which do not approach saturation, log x should vary linearly with log t. It has, however, been found that the early stages of the adsorption follow very exactly an equation of the type

$$\log a/(a - x) = kt^n \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

which is of the same form as that derived by Bangham and Sever (*Phil Mag.*, 1925, **49**, 938) for the course of adsorption in chemically neutral systems, such as that of carbon dioxide on glass, and in which a is the saturation capacity.

If the above expression be regarded as the integrated form of a rate equation which may be written

$$dx/dt = nk(a - x)t^{n-1} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

it will be seen that the constant expressing rate is represented by the product nk. Further, if equation (1) is expressed in its logarithmic form

$$\log\,[\log a/(a - x)] = \log k + n \log t \quad . \; . \; . \; . \; . \; . \quad (3)$$

the term on the left-hand side should vary linearly with log t.

The close agreement of the observed kinetics of the adsorption of hydrogen or deuterium by platinum with equations of the above type, and the influence of changes in temperature and in the mass of the adsorbed gas (by substituting deuterium for hydrogen) on the velocity constant, are discussed below.

EXPERIMENTAL.

The apparatus employed for the measurement of rate of adsorption was the same as that used for the adsorption of ethylene (*Trans. Faraday Soc.*, 1936, **32**, 1375), save that a simple bulb, containing 15·2 g. of platinum-black made by Mond, Ramsay, and Shields's method (*Phil. Trans.*, 1895, *A*, **186**, 657), was substituted for the calorimeter illustrated. The hydrogen was prepared by desorbing electrolytic hydrogen from palladium, and the deuterium by passing the vapour of heavy water (purity 99·2%) over heated and previously carefully degassed zinc in an apparatus from which any water adsorbed on the Pyrex or silica walls had been removed by heating in a vacuum.

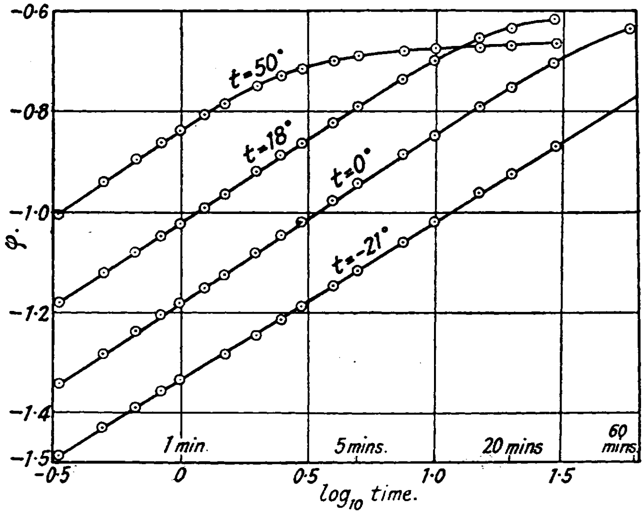
Before beginning the measurements, the original oxygen content of the platinum was removed by repeated treatment with hydrogen, followed in each case by degassing; and the metal was then stabilised by being maintained at 200° for several hours, all subsequent degassing (in each case for 12 hours, by means of a combined Hyvac and mercury-vapour pump) being carried out at 100°. The changing from hydrogen to deuterium or *vice versa* involved repeated treatment with the new gas in order to displace the residue of the original gas not removed by degassing; and, both with hydrogen and with deuterium, the series of measurements was only begun when the metal was shown by duplicate adsorption measurements to be in a steady state.

The adsorption of hydrogen was, at each temperature studied, found to be considerably faster than that of deuterium. This may be compared with the results of Pace and Taylor (*J. Chem. Physics*, 1934, **2**, 578), who report an equal rate for the adsorption of hydrogen and deuterium by nickel supported on kieselguhr; but it is possible that this difference may be due to the present very careful precautions to displace one gas by the other before making the comparison and to avoid traces of water or of other hydrogen compounds which might introduce complications by deuterium–hydrogen exchange. The increased speed of adsorption with hydrogen was maintained in series carried out both before and after corresponding series with deuterium.

Adsorption of Hydrogen : Influence of Temperature.—The degree of conformity of the kinetics of the adsorption to equations (1)—(3) is shown by the typical rate graphs summarised in Fig. 1, in which ϕ is log [log $a/(a - x)$]. This type of graph was given in all cases and at all the temperatures examined; and the accuracy with which the linear path was followed—which was seen very clearly on plotting the graphs on a large scale—was very striking. The early values of the adsorption were in every case read off at intervals of 10 seconds; and the value of the saturation capacity of the platinum for hydrogen—approximately 1·5 c.c. per g.—was determined by an adsorption measurement prolonged over several weeks.

The initial stage during which the above equations are obeyed persists over a period of time which becomes continuously shorter as the velocity of the adsorption is increased by increasing the temperature. For instance, at − 21° (and still more so at − 79°, the graph for which has been omitted from the diagram since it involves values of ϕ too low for convenient inclusion), the linear form persists beyond the limit of the time scale shown in the figure. At 0° the break begins at about 30 mins. and is very apparent at 60 mins.; whereas at 18° and at 50° it occurs respectively after about 15 and after 2—3 mins. At higher temperatures, the duration of the initial stage of adsorption becomes too short to be followed with accuracy by means of readings at intervals of 10 seconds. The adsorption at which the deviation occurs does not change greatly with temperature, although there was apparently a slight fall (from 0·6 to slightly less than 0·5 c.c. of hydrogen per g. of platinum) as the temperature was raised from 0° to 100°.

Fig. 1.



It is important to note that there is no kinetic evidence for an adsorption phase involving the immediate adsorption of any considerable bulk of gas and distinct from the process which is apparently complete within a few minutes after the admission of hydrogen. The subsequent far slower adsorption, after the completion of the stage corresponding with the linear portion of the graph, may be a distinct secondary process, *e.g.*, of solution; or, if the first phase has included penetration into the interior of the metal itself—as distinct from penetration to the less accessible inter-granular or inter-crystalline surface—the deviation may be due to the attainment of a stage at which the smaller platinum particles are saturated. Bangham and Sever (*loc. cit.*) have pointed out that the attainment of this condition should, if the rate control is by internal diffusion, render the subsequent kinetics less simple. In any case the total adsorption process is not complete even after many weeks.

It is proposed in the present work to deal principally with the first stage of the adsorption. In order to illustrate the method employed for expressing these rates in a form suitable for comparison, a typical measurement is given in full in Table I. The gas burette could be read to 0·01 c.c., corresponding with an accuracy of about 0·001 c.c. per g. of platinum. The temperature was 18°.

TABLE I.

t, secs.	Vol. H_2 adsorbed (c.c. at N.T.P.) per g. Pt.	ϕ.	*t*, mins.	Vol. H_2 adsorbed (c.c. at N.T.P.) per g. Pt.	ϕ.	*t*, mins.	Vol. H_2 adsorbed (c.c. at N.T.P.) per g. Pt.	ϕ.
10	0·171	−1·282	1	0·293	−1·025	5	0·463	−0·795
20	0·211	−1·182	1·25	0·312	−0·995	7·5	0·514	−0·739
30	0·238	−1·123	1·5	0·330	−0·967	10	0·549	−0·704
40	0·260	−1·083	2	0·360	−0·924	15	0·592	−0·656
50	0·278	−1·049	2·5	0·383	−0·892	20	0·618	−0·637
			3	0·403	−0·867	30	0·643	−0·614
			4	0·437	−0·825	60	0·664	−0·595

From these results, the values of *k* and *n*, and consequently of the rate constant *nk*, may be determined by the appropriate substitution of values of ϕ in the equation $\phi = \log k + n \log t$. If the observed values of ϕ for 1 and for 5 mins. in Table I are taken for this calculation, values of 0·0944 and 0·329 are obtained for *k* and *n* respectively, whence $nk = 0{\cdot}0311$; or, if the calculation is made from, *e.g.*, the points $t = 1$ and $t = 10$ on a smoothed graph, the closely agreeing values $k = 0{\cdot}0955$, $n = 0{\cdot}326$, and $nk = 0{\cdot}0311$ are derived.

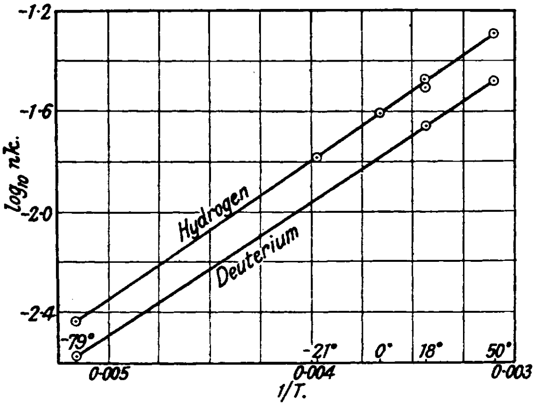
The quantitative effect of temperature on the adsorption velocity is summarised in Table II.

TABLE II.

Temp.	*n*.	*k*.	*nk*.	Temp.	*n*.	*k*.	*nk*.
−79°	0·231	0·0158	0·00365	18°	0·331	0·1018	0·0337
−21	0·315	0·0524	0·0165	18	0·332	0·1015	0·0337
0	0·332	0·0744	0·0247	18	0·331	0·1015	0·0336
18	0·331	0·0940	0·0311	50	0·331	0·1535	0·0508

The approximate constancy of the index, *n*, save at low temperatures at which some van der Waals adsorption is probably present, may be noted; further, the velocity of the adsorption increases continuously with increasing temperature.

FIG. 2.



That the product *nk* is a true measure of rate is supported by plotting log *nk* against $1/T$, whereupon the usual linear relationship between rate and temperature is seen to be followed. The degree of this conformity is shown in Fig. 2, which also contains the corresponding points for deuterium. From the slope of the line the apparent activation energy of the process may be calculated to be slightly less than 2500 cals., corresponding with a temperature coefficient of 1·16 for a 10° rise at 15°. This low value suggests control by diffusion—for instance, to the less accessible inter-granular surface—even during the primary stage of the adsorption; but the presence, as a rate-controlling factor, of a true adsorption process having an energy of activation of this order is by no means excluded; and it was considered that information on this point might be obtained from the relative rate of adsorption of deuterium.

It is necessary in making comparisons of the adsorption rate to measure carefully—by duplicate determinations at intervals under identical conditions—any slow drift in the activity of the platinum that may be caused, for instance, by prolonged exposure to a higher temperature (in this case to 100°) during the degassing process, and to apply a correction for this. With platinum-black previously stabilised by being heated to 200°, the ageing effect was small; *e.g.*, three consecutive runs at 18° showed a fall in activity of the order of 1% for each 12 hours' degassing at 100°. At an earlier stage, the ageing effect was a little greater; but it was in any case small in comparison with the change of velocity observed on changing either the temperature or the nature of the gas—a rise in temperature from − 79° to 50° results in a rise in velocity to about 14 times the original value.

Adsorption of Deuterium.—The adsorption of deuterium follows, as would be expected, a path identical in form with that followed by hydrogen and capable of being represented by the same general kinetic equation. Further, the stage of adsorption up to which the linear relationship between ϕ and log t is followed (0·5—0·6 c.c. of deuterium per g. of metal) was the same for both gases.

The velocity of adsorption was, however, in all cases and at all temperatures studied, slower than that of hydrogen under corresponding conditions. This is illustrated by the series of rate values at various temperatures contained in the following table; the experiments were carried out with the same platinum immediately before the hydrogen series of Table II, the relative adsorption velocities being thus directly comparable.

Temp.	−79°	18°	18°	18°	50°
n	0·222	0·316	0·312	0·318	0·328
k	0·0120	0·0703	0·0702	0·0695	0·1009
nk	0·00267	0·0222	0·0219	0·0221	0·0331

The ratios of the velocities of adsorption of hydrogen and of deuterium at the three temperatures at which comparative measurements were made are shown below:

Temp.	−79°	18°	50°
Ratio	1·4	1·4—1·5	1·5

These experimentally determined ratios are only approximate, owing to the necessity for thoroughly replacing one gas by the other before comparative rate measurements can be made—which prevents the immediate juxtaposition of a hydrogen and of a deuterium run—but the order of magnitude of the ratio persisted whether the hydrogen measurements preceded those with deuterium or *vice versa.* The nearness of the ratio to the square root of the relative masses of deuterium and of hydrogen is again suggestive of possible control by diffusion to the internal surface. Further, the apparent energy of activation of the adsorption of deuterium has a calculated value of about 2,400 cals., corresponding with a temperature coefficient of 1·15 for a 10° rise at 15°, the slope of the line obtained by plotting the logarithm of the velocity against $1/T$ being approximately equal to that for hydrogen, as shown in Fig. 2.

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[*Received, September 17th,* 1936.]