206. *Studies in Gaseous Adsorption. Part III. The Thermal Activation Effect in the Adsorption of Hydrogen on Platinum and Nickel.*

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It has been noticed by several workers that the sorptive power of a metal for a gas such as hydrogen becomes increased if, instead of the gas being admitted to the previously evacuated metal at the temperature at which the adsorption is measured, the admission is made at a higher temperature. Thus, Firth (J., 1920, **117**, 171; 1921, **119**, 1120) found that, while the volume of hydrogen sorbed by palladium at liquid-air temperature is normally very small, a sorption of a greatly increased order of magnitude was obtained at – 190° by allowing the metal to cool to this temperature in a hydrogen atmosphere. Benton and White (*J. Amer. Chem. Soc.*, 1930, **52**, 2325) observed a similar effect with nickel, different results being obtained according to whether they operated exclusively at a low adsorption temperature or saturated the metal with hydrogen at a high temperature and afterwards cooled the system to the lower temperature.

This apparent activation, by thermal treatment, of adsorbing elements in the surface which are not normally available for adsorption is of considerable interest in connexion with the better understanding of the factors underlying adsorption generally, especially since the increased adsorption is usually considerably greater than the normal adsorption at any temperature within the range of heating and cooling; and, for this reason, the following work has been undertaken with the object of studying in greater detail the dependence of the activation effect on the range and position of the temperature change.

EXPERIMENTAL.

As adsorbing metals, nickel and platinum were employed, the former being prepared by the reduction, in the apparatus itself, of black nickel oxide—obtained by calcination of the nitrate—at a temperature not exceeding 300°. The platinum was made by reducing a solution of chloroplatinic acid with an alkaline formate solution, the metal being subsequently thoroughly washed, dried, and treated in the apparatus with hydrogen at 100°. These metals were contained in small adsorption pipettes, which could be brought, by immersion in suitable baths, to the temperature required.

For the measurement of gas volumes, it was found convenient to employ, for each adsorption pipette, two gas burettes, one of larger and one of smaller diameter, connected in parallel, volume changes being read off on the one or the other according to their magnitude. In this way it was possible to follow accurately relatively small volume changes while retaining a sufficiently large reserve of gas to avoid delays by the admission of gas from an external source. Correction for changes in the apparent volume of the adsorption pipette with temperature was facilitated by providing a compensating bulb of approximately the same capacity as the dead space in the adsorption pipette, immersed side by side with the adsorption bulb in the heating or cooling bath. The gas-measuring system was contained in a thermostat, and all readings were made telescopically.

Evacuation was carried out either by an automatic Sprengel pump or, where it was not necessary to measure the volume of gas pumped off, by a mercury-vapour pump backed by a Hyvac oil pump.

In the measurements carried out with nickel, this was first degassed at 250°, then cooled in a vacuum to the temperature chosen for adsorption; the normal adsorptive power at the temperature and at atmospheric pressure was then determined by the admission of hydrogen in the ordinary way. The nickel, after being used for some time, was found to be in a sufficiently stable condition to give check readings for the adsorptive power, after successive evacuations, agreeing within 0·2 c.c.

In order to determine the activation effect of a temperature change, the nickel was first allowed to adsorb the normal volume of hydrogen by the direct admission of the gas at a temperature, t_1. It was then heated, in contact with hydrogen, to a second temperature, t_2, and once more cooled to its original temperature, the increased adsorption induced by the heating and cooling being measured.

It should be noted that, if the adsorption at the higher temperature, t_2, be read off, this is found to be merely the normal adsorption for that temperature, the additional adsorption being obtained only on once more cooling the system to a temperature below t_2 : moreover, if the heating and subsequent cooling are carried out in a vacuum, in place of in a hydrogen atmosphere, the adsorption at t_1 undergoes no increase beyond its normal value. The adsorptive power is thus dependent on the highest temperature to which the metal has been heated in contact with hydrogen; and the result of such heating is to induce increased values for the adsorption at all temperatures below this point, but not to influence the adsorption at still higher temperatures.

The greater part of the gas is adsorbed immediately; and the rate of subsequent adsorption rapidly sinks, being very low after the first few minutes. The figures given in Table I represent adsorptions after 30 minutes. All measurements are at atmospheric pressure, and all gas volumes are in c.c. at *N.T.P.* The weight of nickel employed was 7·0 g.

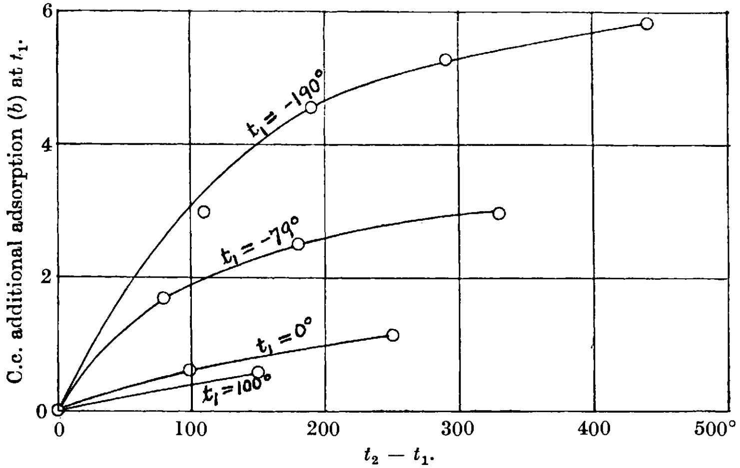
TABLE I.

			Adsorption (c.c.) at t_1 after heating to t_2 and re-cooling to t_1. t_2 =			
Series.	t_1.	Normal adsorption at t_1, c.c.	−79°.	0°.	100°.	250°.
1	−190°	2·70	5·67	7·27	7·97	8·52
	− 79	3·84	—	5·54	6·34	6·82
	0	4·78	—	—	5·38	5·93
	100	5·09	—	—	—	5·72
	250	3·50				
2	−190	2·76	5·62	7·32	7·75	8·17
	− 79	3·88	—	5·88	6·61	7·21
	0	5·02	—	—	5·82	6·47
	100	5·03	—	—	—	5·73
	250	3·36				

If the increase in adsorption (*b*) at a given temperature (t_1) is plotted against the range of heating and cooling ($t_2 - t_1$) inducing the increase, curves of the type shown in the figure are obtained : the total thermally activated adsorption, contained in Table I, is expressed in the form $v = a + b$, in which a is the normal adsorption.

From the figure it will be seen, first, that the activation effect, *b*, for a given rise and fall in temperature, is the greater the lower the position of t_1 on the temperature scale. Thus the effect of a 100° rise and fall at an adsorption temperature of — 190° is to induce an adsorption increase of nearly 3 c.c., compared with an increase of only about 0·2 c.c. if the initial temperature is 100°. Secondly, for any value of t_1, the activating effect of each additional degree of temperature in the heating and cooling range becomes progressively less as this range is extended. A more detailed expression of b as a function of t_1 and of the activation range, $t_1 - t_2$, is of considerable interest in connexion with the mechanism of the effect.

The activation is, moreover, approximately additive, in the sense that the additional adsorption caused by heating and cooling through a given range is approximately the sum of the values observed if the heating and cooling are carried out in successive small stages in place of in one step. The degree of experimental agreement between the sum of the four smaller values of b observed if an activation range of — 190° to 250° is covered in four successive steps and the larger value obtained by a one-step temperature change within the same limits is shown in Table II.



In some series, however, there seemed to be a small but persistent tendency for the sum of the smaller activation effects to be slightly greater than the one-step effect. This may be either inherent in the process or due to the accumulation of small observation errors in the measurement of the successive small adsorption increments.

With platinum, results similar to those observed with nickel were obtained; but, with the specimen of metal employed, which had a relatively high adsorptive power and had not been exposed to a temperature above 100°, there was evidence, even at this temperature, of slow but appreciable sintering, small quantities of adsorbed

TABLE II.

Temperature step.		
t_1.	t_2.	Value of b (c.c.).
$-190°$	$-79°$	2·97
-79	0	1·70
0	100	0·60
100	250	0·61
		Total 5·88
-190	250 (one stage)	5·82

gas being evolved, at an approximately constant rate, if the platinum, after previous saturation with hydrogen at 100°, was maintained in contact with the gas without change of temperature or pressure. By virtue of this sintering, the adsorptive power fell slightly with each heating to 100° and, consequently, with each degassing.

After several evacuations and adsorptions at 100°, however, the surface became sufficiently stable to allow of the investigation of the thermal activation effect in a similar way to that used for nickel. The results contained in Table III represent, as before, the adsorption obtained at t_1, by raising and lowering the temperature through a range, $t_2 - t_1$, in contact with hydrogen. The weight of platinum taken was 7·05 g.

TABLE III.

			Adsorption at t_1, after heating to t_2 and re-cooling to t_1. t_2 =			
Series.	t_1.	Normal adsorption at t_1, c.c.	$-79°$.	0°.	25°.	50°.
1	$-190°$	13·60	16·60	—	—	16·92
2	-190	13·19	14·61	15·34	—	—
2	-79	10·77	—	11·87	—	12·18
2	0	11·02	—	—	11·38	11·45

Owing to the gradual sintering of the platinum surface at 100°, the heating and cooling could not in this instance be extended to the neighbourhood of this temperature; and in the above table only the results from − 190° to 50° have been inserted. These show clearly a general activation effect analogous to that observed with nickel, the additional adsorption, b, varying with the position of t_1 and with the value of $t_2 - t_1$ just as for nickel.

From the standpoint of a better understanding of the energetics of the process—which may be regarded either as the effect of a temperature change on a two- or more-component adsorption, the components of which are distinct adsorption types associated, respectively, with higher and lower activation energies (Taylor, *J. Amer. Chem. Soc.*, 1931, **53**, 578), or as being due to an adsorption, which is not necessarily composite, on an energetically heterogeneous surface—it was considered of interest to compare the extent of the possible desorption at various temperatures of hydrogen bound as the result of thermal activation with that of hydrogen adsorbed in the normal way. The volume of hydrogen which is retained by the metal when the superincumbent hydrogen pressure is reduced to a constant low value, *e.g.*, to 10^{-3} mm., is, for a given specimen of metal at a given temperature, approximately constant, in that, at any temperature, a certain volume of gas, which is reproducible within the limit of experimental error, can be quickly pumped off as the pressure is reduced to that given, and that further evacuation at the same temperature, even if prolonged, gives only a negligible further quantity.

The effect of degassing, at various temperatures, 7 g. of nickel, which had previously been allowed to adsorb hydrogen in the normal way at − 190° and, in the second series, had been subsequently also heated to 250° and re-cooled to − 190° in contact with the gas, is seen from the figures collected in Table IV. In addition to the total volumes of gas desorbed at the temperature stated, the volume increments obtained by raising the temperature from the next lower stage, at a constant pressure of 10^{-3} mm., are also given. The increments given in this way for 250° are for a temperature change from 100° to 250°, since the figure for 150° for the normal adsorption was not measured.

TABLE IV.

	C.c. of hydrogen desorbed.			
	Normal adsorption at −190°.		Thermally activated adsorption at −190°.	
Temperature of degassing.	Total.	Increment.	Total.	Increment.
−190°	1·10	—	1·30	—
− 79	1·27	0·17	2·29	0·99
0	1·33	0·06	3·30	1·01
100	1·42	0·09	5·35	2·05
150	—	—	6·30	—
250	2·98	1·56	7·88	2·53
C.c. of H_2 previously adsorbed	2·78		7·98	

It will be seen that, in each case, the total volume of gas previously adsorbed at − 190° is recovered at the degassing temperature (250°). There are, however, considerable differences—even having regard to the larger volume involved in the second mode of adsorption—in the relative degree of release of gas at a given temperature for hydrogen bound in the one or in the other way. For instance, while the volumes desorbed at − 190° are approximately equal for both methods of adsorption and the increments evolved between 100° and 250° do not differ by more than about 50%, the volume of gas which can be recovered at intermediate temperatures—*e.g.*, between 0° and 100°—is many times greater for the abnormal than for the normal adsorption.

Perhaps the most suggestive result of the desorption measurements was the observation that hydrogen adsorbed as the result of thermal activation cannot be desorbed without raising the temperature. Accordingly, the reversible part of the adsorption, *viz.*, the volume of hydrogen which can be pumped off at the adsorption temperature, is unchanged by additional adsorption induced by thermal activation. The constancy, within the limits of observation, of the desorbable portion at a given temperature, for various ranges of thermal activation, is illustrated in Table V.

TABLE V.

t_1.	t_2.	Total adsorption, c.c.	C.c. of hydrogen desorbable at t_1.	C.c. of hydrogen not desorbed.
−80°	−80°	3·85	1·10	2·75
−80	0	6·08	1·03	5·05
−80	100	6·75	1·05	5·70
−80	250	7·29	0·83	6·46
0	0	5·18	1·28	3·90
0	100	5·96	1·26	4·70
0	250	6·46	1·00	5·46
100	100	5·00	2·25	2·75
100	250	5·60	2·39	3·21

This result suggests that the binding of hydrogen during thermal activation takes place on adsorbing elements other than those which are able to adsorb—or to desorb, if the gas pressure on the adsorption complex is reduced to a sufficiently low value—at the normal adsorption temperature t_1, and apparently supports the conception of an adsorbing surface made up of elements differing from one another in energy, these elements becoming active for adsorption or desorption at temperatures dependent on their individual energy content.

It appears possible, indeed, to explain the thermal activation effect and certain other aspects of adsorption without the necessity for assuming the existence of distinct adsorption types, although in certain cases two types of adsorption may exist (Taylor and Williamson, *J. Amer. Chem. Soc.*, 1931, **53**, 2168). If the adsorbing surface be energetically heterogeneous, in the sense that the energy of the individual adsorbing elements is not identical but varies continuously or discontinuously from a lower to a higher value according to the position or mode of formation of the element, a varying critical increment, dependent for its value on the original energy of the adsorbing element, is required to bring this either to the lower limit, E_1, necessary for adsorption or to a higher critical value, E_2, needed for initiating desorption, then the adsorption of an impinging hydrogen molecule by a given element will depend on the possession of an energy sum between E_1 and E_2.

At any temperature, therefore, only those elements the original energies of which lie within a certain range should adsorb immediately and further adsorption will depend on the acquisition of the necessary critical increment. Moreover, the greater the critical increment required by an individual adsorbing element the less will be the probability of its acquisition within a given time.

The general effect of a rise in temperature, both on a bare surface element and on an already formed adsorption complex, will be to raise its energy. Thus, according to the energy value of the particular element, a temperature rise may cause a passage over the critical value E_2, *i.e.*, it may cause desorption from an adsorption complex stable at a lower temperature, or the temperature rise may cause surface elements of energy below E_1 to become potentially adsorptive. At gas pressures maintained continuously at a low value, the hydrogen molecules necessary for the second effect (adsorption) are relatively absent; and a rise in temperature should, as is found, cause mainly the first effect, *viz.*, a progressively greater effect of desorption as the temperature is raised. Indeed, this progressive desorption, at each temperature step, of a definite and limited volume of gas which is controlled, above all, by the temperature and only to a subsidiary degree by the time of the evacuation, may, from this standpoint, be viewed as a necessary consequence of the progressive passage of the individual metal–hydrogen complexes, in the order of their energies, over the critical value, E_2, in the course of the general increase in the energy of the surface as a whole caused by the temperature rise.

If the gas in contact with the metal is at a relatively high pressure, a rise in temperature will operate in both of the above ways, the difference in the two effects representing the normal change in adsorptive power with temperature; but a subsequent fall in temperature should allow the adsorption complexes of energies between E_1 and E_2 to retain their hydrogen even if some of these fall below E_1, and at the same time should bring those adsorbing elements of energies slightly above E_2 to values below this, thus rendering them able to adsorb and causing an increase in the total adsorption. This, apparently, is the thermal activation effect of heating and subsequent cooling.

It should be noted, finally, that an energy distribution among the individual adsorbing elements, such that the fractional number of elements associated with a given original energy decreases as the value of this individual energy content increases, would give, qualitatively at any rate, a variation of the quantity, b, with adsorption temperature and with the activation range, $t_2 - t_1$, of the nature found experimentally.

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