CCLXVIII.—*Heats of Adsorption and Isotherms in the System Platinum–Hydrogen.*

By Edward Bradford Maxted.

If the differential heat of adsorption of hydrogen on certain metals—*viz.*, the function dQ/dC, in which Q is the heat evolved and C the adsorbed hydrogen content—is plotted against this adsorbed hydrogen content, curves are obtained which confirm in a remarkable way the non-uniformity in the degree of unsaturation of a catalytic surface. Thus, Fryling (*J. Physical Chem.*, 1926, **30**, 818) found that the heat of adsorption of hydrogen per mol. on nickel rose from a low value to a maximum of about 32,000 cals. as the hydrogen content was increased, this value falling once more with further increments in the adsorbed hydrogen content. Somewhat similar results were obtained by Kistiakowsky (*Proc. Nat. Acad. Sci.*, 1927, **13**, 1); further, Kistiakowsky, Flosdorf, and Taylor (*J. Amer. Chem. Soc.*, 1927, **49**, 2200) observed a curve of this form, with a maximum heat of adsorption of about 18,000 cals. per mol., for hydrogen on copper. These curves resemble those obtained by Garner and McKie (J., 1927, 2451) for the adsorption of hydrogen on carbon.

In a recent paper by Taylor, Kistiakowsky, and Perry (*J. Physical Chem.*, 1930, **34**, 799), the heats of adsorption of a number of gases on platinum have been measured, and results have been obtained which differ somewhat from those cited, in that no rise to a maximum value of the heat of adsorption was observed, this heat decreasing continuously with each increase in the adsorbed hydrogen content.

Since the form of the heat of adsorption curve possesses considerable importance from the standpoint of the catalytic activation of hydrogen, it is of interest to ascertain whether the non-occurrence of a maximum with platinum depends on certain conditions, which include those employed by the last-named investigators, or whether, with this metal, the form is general. A further object of the work now described was to determine the effect of the "ageing" of a hydrogenation catalyst on the heat of adsorption and on the hydrogen isotherm. It will be seen that the keeping of a catalyst such as platinum black for a considerable period of time causes a diminution both in the differential and in the integral heat of adsorption, as well as in the adsorptive capacity for hydrogen at a given pressure, the latter effect being especially marked with hydrogen at relatively low pressures. These effects of ageing seem to correspond with a breaking down or stabilisation of the highly active areas which are usually assumed to be responsible both for abnormally energetic adsorption and for the specific or pseudo-chemical adsorption component (Langmuir, *J. Amer. Chem. Soc.*, 1918, **40**, 1361; Benton, *ibid.*, 1923, **45**, 887), *viz.*, for that part of the total adsorption which is influenced relatively little by gas pressure. It is well known that ageing, under the conditions employed, usually gradually diminishes the activity of platinum black for catalytic hydrogenation.

EXPERIMENTAL.

The calorimeter and manometer connexions employed were similar to those used by Garner and his collaborators (see, especially, McKie, J., 1928, 2870), save that the quartz vacuum calorimeter was provided with a water jacket through which water from a thermostat could be circulated; and the author wishes to express his thanks to Prof. W. E. Garner for familiarising him with the construction involved. In this apparatus, small known quantities of hydrogen could be admitted to a known mass of finely divided platinum, the rise in temperature being photographed, by means of a copper–constantan thermocouple and a Moll galvanometer illuminated by a " Pointolite " lamp, on a rotating drum.

For evacuation, a mercury diffusion pump, backed by a Hyvac rotary oil pump, was used. Measurements of gas pressure were made with two McLeod gauges, suitable together for a pressure range from 0·0001 to 2 mm., beyond which upper limit measurements were not undertaken.

The same specimen of platinum black, weighing 9·48 g., was used throughout. It was prepared as described by Mond, Ramsay, and Shields (*Phil. Trans.*, 1895, *A*, **186**, 657) by reducing a dilute solution of hydroplatinic acid with potassium formate, and was placed, after being washed and dried, in a cylindrical cage of fine-meshed platinum gauze, approximately 5 cm. high and 1·5 cm. in diameter, surrounded by a small glass container and suspended by fine glass links within the vacuum calorimeter. The thermocouple, which was sheathed in as thin glass as possible, was inserted approximately in the centre of the platinum mass. The hydrogen employed was prepared by electrolysis and purified from oxygen by being passed over the filament, heated to dull redness, of an electric lamp, followed by phosphoric oxide.

In order to minimise the " gas effect," the temperature of the calorimeter jacket and stoppers, also that of the cold junction of the thermocouple, was adjusted before each run to that of the adsorbing mass, determined by the galvanometer deflexion. The effect of a small partial pressure of helium was also determined, with the object of improving the conductivity of the platinum mass as low hydrogen pressures; but, under the conditions employed, the addition of helium was found to produce no appreciable effect on the curve. Helium, supplied in a pure condition through the courtesy of Prof. M. W. Travers, was also used for the calibration of the volume of the apparatus. Access of traces of mercury vapour to the platinum, from the pump, manometers, or gas burettes, was prevented by isolating the catalyst, by means of taps, at all times save during actual measurements, and by the insertion of traps containing aluminium and silver gauze.

The platinum was at no time exposed to a temperature greater than 100°, in order to avoid the possibility of structural changes in the active areas, it having been shown by Kistiakowsky, Flosdorf, and Taylor (*loc. cit.*) that the heat treatment of copper leads to adsorption curves containing no maximum. In the present work, accordingly, the " degassing " of the metal was made as complete as possible by using very efficient methods of evacuation rather than by unduly raising the temperature.

Measurements of the Heat of Adsorption.—In all, four series of measurements were made, the first at 0° and the remainder at about 20°. Of these, Series 1 was probably less accurate than the other three, owing to experimental difficulties of working, with the apparatus employed, at temperatures differing greatly from that of the laboratory. In Series 4, a small partial pressure (0·01 mm.) of helium was present throughout the measurements. Before each series, the platinum was degassed for at least three hours at 100°, by means of the combined Hyvac and diffusion pumps, the pressure obtained being lower than could be measured on the McLeod gauge. Save in Series 1, successive small increments of hydrogen were added, the rise in temperature being photographed in the manner already described; and the platinum was allowed to cool approximately to the original temperature before a fresh addition of hydrogen was made. The results of these four series are contained in Table I.

If, for any of the above series, the total adsorbed hydrogen content be plotted against the total heat evolved, sinuous curves are obtained. In general, the total heat evolved during the acquisition of a given adsorbed hydrogen content decreases with the age of the catalyst. Thus, the relatively freshly prepared catalyst evolved about 8 cals. in adsorbing a total of about 8 c.c. of hydrogen, whereas a catalyst which had been kept in the apparatus for 40 days evolved only slightly over 4 cals. for approximately the same adsorption; but the heat of adsorption appeared then to have become steady, since it was only slightly less for a catalyst that had been kept for a total of about 90 days. It should be noted that these heats of adsorption refer to the first, and more energetic, part of the adsorption curve; and the heats are consequently greater than those

TABLE I.

Series.	Age of catalyst, days.	Hydrogen adsorption, c.c.		Heat evolution, cals.	
		Increment.	Total.	Increment.	Total.
1	2—3	—	0·513	—	0·232
		—	1·26	—	0·93
		—	1·66	—	1·47
		—	2·52	—	2·08
		—	3·23	—	2·48
2	8—9	0·764	0·76	0·50	0·50
		0·694	1·46	0·67	1·17
		1·35	2·81	1·55	2·72
		1·98	4·79	2·88	5·60
		1·60	6·39	1·29	6·89
		1·05	7·44	0·77	7·66
		0·51	7·95	0·40	8·06
3	40	1·16	1·16	0·80	0·80
		1·14	2·30	0·88	1·68
		1·38	3·68	0·75	2·43
		1·37	5·05	0·84	3·27
		0·79	5·84	0·44	3·71
		0·49	6·33	0·26	3·97
		0·44	6·77	0·19	4·16
4	89	0·66	0·66	0·25	0·25
		0·70	1·36	0·36	0·61
		1·35	2·71	0·93	1·54
		1·68	4·39	1·17	2·71
		1·03	5·42	0·66	3·37
		0·68	6·10	0·31	3·68
		0·35	6·45	0·14	3·82
		0·35	6·80	0·12	3·94

measured by Mond, Ramsay, and Shields (*Z. physikal. Chem.*, 1898, **25**, 656) for the total adsorption. These authors found that 9·74 g. of platinum adsorbed a total varying between 7·4 and 8·3 c.c. of hydrogen with a heat evolution varying between 4·6 and 5·2 cals., the catalyst being probably less completely degassed than is possible with the vacuum pumps now available.

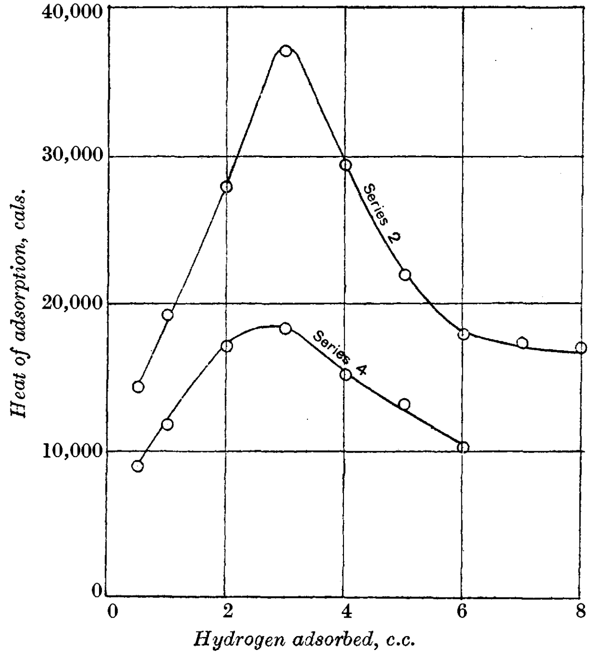
When tangents are drawn to the above curves in order to determine the differential heat of adsorption per mol. for various contents of adsorbed hydrogen, curves with well-defined maxima are obtained. The indications of a maximum are least in Series 3, this being possibly due to insufficiently complete degassing. The molecular heats of adsorption obtained in this way are given in Table II.

Of these curves, Series 2 and 4 have been reproduced in Fig. 1. The general effect of ageing is to flatten the curve by the elimination of the peak portion, as well as to lower the integral heat of adsorption; but, while the form of all the curves is similar, the actual curve obtained for a given specimen of platinum is dependent on its history and on conditions such as the degree of degassing applied prior to the adsorption measurement. The order of magnitude agrees fairly well with those obtained for other metals, and with the bulk of Taylor, Kistiakowsky, and Perry's values for platinum, the

TABLE II.

Content of adsorbed hydrogen, c.c.	Differential heat of adsorption, cals. per mol. of hydrogen.			
	Series 1.	Series 2.	Series 3.	Series 4.
0·5	14,500	14,200	15,700	8,900
1	23,400	19,100	20,000	11,700
1·25	32,000	—	—	—
1·5	27,100	—	19,400	—
2	16,600	27,800	18,500	17,000
2·5	16,300	—	—	—
3	14,800	37,000	14,800	18,200
4	—	29,300	13,600	15,100
5	—	21,900	13,200	13,900
6	—	17,900	13,200	10,200
7	—	17,300	13,000	—
8	—	17,000	—	—

FIG. 1.



non-observance of a maximum under the experimental conditions employed by the last-named investigators being possibly due to the employment of a relatively high temperature (250—350°) for degassing. This similarity of the value for the heats of adsorption of hydrogen on various metals suggests that the main heat effect measured is due to a common process, specific to the hydrogen and independent of the metal.

Measurements of Isotherms.—The variation in the isotherms with the gradual ageing of a catalyst is a subject of considerable interest. Müller and Schwabe (*Z. Elektrochem.*, 1929, **35**, 165) have shown that all the platinum metals, when reduced from their oxides by hydrogen, adsorb initially a far greater volume of hydrogen than is the case if the metal is degassed and allowed to re-adsorb; and this diminution appears to continue if the catalyst is allowed to remain.

In the adsorption of hydrogen at low pressures by platinum, the bulk of the gas is adsorbed almost instantaneously; and this stage is followed by a relatively slow adsorption, in such a way that equilibrium between the adsorbed and the free gas phases is only approximately reached after a time of the order of several days. This effect has been found in other cases of gas adsorption and is illustrated by the typical isotherm reproduced in Table III, in which a relatively large volume (3·3 c.c.) of hydrogen was introduced into the apparatus, at 17°, containing the platinum black, previously degassed at 100°. The third column gives the completeness of the adsorption, expressed as a percentage of the gas ultimately adsorbed.

TABLE III.

Time, mins.	Hydrogen pressure, mm.	% of total adsorption.	Time, mins.	Hydrogen pressure, mm.	% of total adsorption.
0	1·119	—	40	0·0274	99·2
3	0·0867	93·9	60	0·0253	99·5
7	0·0590	96·4	75	0·0232	99·6
14	0·0405	97·0	105	0·0211	99·7
20	0·0341	98·5	24 hrs.	0·0189	—
30	0·0312	98·9			

Even with the relatively large volume of gas admitted, about 94% of the total adsorption takes place during the first 3 minutes, and over 96% in the first 7 minutes. In the measurements of the heat of adsorption already described, the volume of gas admitted was, in general, less than 3 c.c.; accordingly, any error due to adsorption " drift " during the period of the recording of temperature (10 mins.) will not be appreciable.

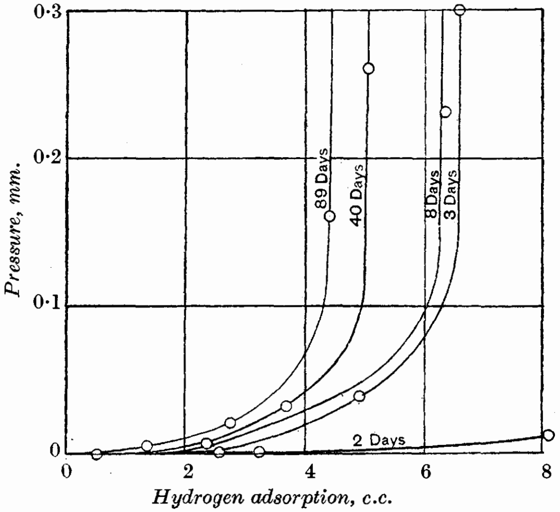
In the following isotherms, the pressure 7 minutes after the admission of hydrogen has been taken throughout. The results refer to the same specimen (9·48 g.) as was used for the measurements of the heat of adsorption; indeed, the isotherms were, for the greater part, measured in conjunction with these. Before the first series, the platinum was treated with excess of hydrogen at room temperature and degassed for 3 hours at 100°. The figures for this series are abnormal, a result which is of interest in connexion with the well-known high activity of freshly prepared catalysts and with the observations of Müller and Schwabe (*loc. cit.*).

The form of the isotherms and the effect of ageing are seen more clearly on plotting these graphically. The wide range of pressure

TABLE IV.

Age of catalyst, days.	Press. of H_2, mm.	Vol. of H_2 adsorbed, c.c.	Age of catalyst, days.	Press. of H_2, mm.	Vol. of H_2 adsorbed, c.c.
2	0·0008	0·51	40	0·0067	2·30
	0·0014	3·23		0·032	3·68
	0·0120	8·11		0·26	5·05
3	0·0017	2·52		0·66	5·84
	0·0396	4·89		1·26	6·33
	0·300	6·58		2·35	6·77
8	0·00084	1·46	89	0·0025	0·66
	0·0059	2·81		0·0063	1·36
	0·0733	4·79		0·0206	2·71
	0·230	6·39		0·16	4·39
	1·14	7·44		0·56	5·42
	2·02	7·95		1·56	6·10
				2·20	6·45
				2·98	6·80

FIG. 2.



involved precludes the inclusion of all points on a single diagram ; but the isotherms for pressures up to 0·3 mm. have been plotted in Fig. 2. The curves, with the exception of the first—in which substantial saturation was not reached—are all of the type observed by Gauger and Taylor for nickel, namely, of a form in which a relatively large change of pressure, once the preliminary stage has been passed, does not greatly influence the adsorbed hydrogen content ; and the gradual shift, with time, towards the pressure axis is well seen.

It would appear that both the heat of adsorption and the hydrogen isotherms are properties which, like catalytic activity, are specific, not only to an individual specimen of a hydrogenation catalyst, but also to its condition and to its history. The possession of a high differential heat of adsorption and of a high primary adsorptive capacity—primary adsorption being that component which relatively rapidly attains substantial saturation even at low pressures—should be intimately related to the possession of a relatively high catalytic activity, since it would be expected that a given point in the catalytic surface must possess at least a certain critical free energy in order to bring about, by this adsorption, activation of the hydrogen and, consequently, catalysis. Further, this necessary critical energy should be greater for a difficult hydrogenation, such as the saturation of a benzenoid ring, which requires a relatively active catalyst, than for a relatively easily saturated bond such as an ethylenic or an acetylenic linkage. This point is being tested, and the apparent occurrence of a maximum in the heat of adsorption for non-sintered catalysts is being further investigated by a modification of the ice calorimeter method used by Mond, Ramsay, and Shields for the total heat; since it is recognised that the initial rises in temperature take place under conditions in which accurate thermometric determinations are rendered difficult, both by the low thermal conductivity of non-coherent, finely divided metals at low pressures—although this effect should be eliminated by the use of an inert conducting gas, such as helium or argon—and by the probability that the adsorption of the first quantities of gas takes place preferentially, or even exclusively, on those parts of the metal which first meet the gas to be adsorbed, *viz.*, on the outside portions of the adsorbing mass, which are, in general, farthest removed from the seat of measurement of temperature. These factors, unless controlled by experimental conditions, would, for thermometrically determined heats, in themselves tend to give too low apparent initial heats of adsorption even if the rise to a maximum value were not an inherent part of the adsorption itself.

In addition to the acknowledgments already made, the author wishes to express his indebtedness, for the purchase of part of the apparatus, to a grant from Imperial Chemical Industries, Ltd.

UNIVERSITY OF BRISTOL. [*Received, June* 11*th*, 1930.]