CCCCLIX.—*Studies in Gaseous Adsorption. Part II. The Heat of Adsorption Curve for Hydrogen on Platinum.*

By Edward Bradford Maxted and Nissim Hassid.

The variation in magnitude of the differential heat of adsorption of hydrogen on solid adsorbents with the stage at which a given small gas increment is added has been examined by a number of investigators with varying results. Thus, a type of curve in which the differential adsorption heat apparently rises from a relatively low value, then passes, as the adsorbed concentration is increased, through a maximum, and finally decreases with further adsorption, has been obtained by Fryling (*J. Physical Chem.*, 1926, **30**, 818) for hydrogen on nickel, by Kistiakowsky, Flosdorf, and Taylor (*J. Amer. Chem. Soc.*, 1927, **49**, 2200) for hydrogen on copper, and by one of us (J., 1930, 2093) for hydrogen on platinum.

The experimental measurement of adsorption heats, particularly in the two extreme regions, corresponding, respectively, with a very low and with a high adsorbed concentration, is complicated by a number of possible sources of error, which are different for these two extreme states and are relatively non-operative at intermediate adsorbed concentrations; and, for this reason, a revision of the heat measurements corresponding with the extreme portions of the curve is a subject of considerable interest.

The factors which cause a possible error during the addition of the first increments of gas, at which the total gas pressure is of a low order of magnitude, include, first a possible uneven temperature distribution, due to a preferential adsorption of the first small quantities of gas on those parts of the adsorbent with which they first come into contact and to the low thermal conductivity of finely divided metals of low gas pressures, and secondly, the operation of the so-called gas effect. Taylor, Kistiakowsky, and Perry, in a later series of measurements (*J. Physical Chem.*, 1930, **34**, 799) in which argon was employed as a buffer gas in the adsorption of various gases on platinum, also Garner and Kingman (*Trans. Faraday Soc.*, 1931, **27**, 322), by surrounding the whole of the apparatus in the immediate neighbourhood of the calorimeter by a carefully adjusted constant-temperature enclosure, were able to obtain heat of adsorption curves which exhibited no rise to a maximum, but in which the differential heat gradually decreased with an increase in the adsorbed concentration, the measurements of Garner and Kingman being for hydrogen on catalysts of an oxide type.

As the adsorbed concentration and consequently the residual gas pressure, increases, certain sources of possible error of another nature gradually become effective. The rate of adsorption becomes far slower and less complete; and the accurate assignment of the heat effect observed—corrected for losses by the extrapolation of the time–temperature charts—to a definite increase in adsorbed concentrations becomes more and more uncertain; moreover, the measurement, with a McLeod gauge, of the volume of gas adsorbed from gas increments added at a relatively high gas pressure, under conditions such that only a partial adsorption of the increment takes place, becomes of greater and greater difficulty.

In the work now described, the disturbing influence of the above factors has been minimised as far as possible by using a constant-temperature enclosure of considerable extent, as was done by Garner and Kingman, and by measuring—for more advanced adsorbed concentrations—heats of desorption in addition to heats of adsorption; since desorption takes place particularly quickly just in the region of high adsorbed concentrations, in which adsorption is slow, and the volume of gas desorbed for a given heat effect can be measured with a higher degree of accuracy than is possible for adsorption in this region.

In addition, an attempt was made to replace a thermometric determination of the heat effect by an ice-calorimetric method, for the reasons already stated; but the degree of accuracy obtainable with the relatively small heat quantities involved was, after considerable trial, found to be insufficiently high; and the heats were therefore determined by means of a copper–constantan thermocouple, as previously used, after testing for unevenness in the temperature distribution by employing helium as a buffer gas and by parallel experiments with calorimeters of two distinct types in one of which the gas was admitted initially to the outside and, in the other, to the inside of the adsorbing mass.

The results obtained appear to indicate, not only the absence of a maximum in the first part of the curve, but also the absence of any appreciable diminution in value of the heat effect as the adsorption is continued; indeed, in some series, slightly higher heat values were obtained at relatively high adsorbed concentrations. In other words, the differential heat of adsorption of hydrogen on platinum is apparently constant throughout the whole of the range studied.*

EXPERIMENTAL.

The apparatus employed was, in the main, similar to that previously used (J., 1930, 2093), save that a thermally insulated enclosure, fed with air at a carefully regulated constant temperature, was built round the whole of the parts in the neighbourhood of the calorimeter. Time–temperature graphs were, as before, recorded on a revolving drum in order to permit, by extrapolation, the correction for heat loss during the time of adsorption. For the desorption measurements now made in order to determine with greater accuracy the differential heat at relatively high adsorbed concentrations, the heat effect was of course negative. All determinations relate to adsorptions at 20°.

In the first place, the course of three measurements of the relative rates of adsorption at different initial hydrogen concentrations has been summarised in Table I, in order to show the decrease in the rate of adsorption from an approximately equal gas increment as the adsorbed concentration at which the gas is added increases.

TABLE I.

Platinum = 12 g.

Initial H_2 content, c.c.	H_2 increment admitted, c.c.	H_2 (c.c.) adsorbed after (mins.)			
		1.	2.	5.	10.
0	0·486	0·455	0·480	0·486	0·486
2·36	0·410	0·262	0·308	0·355	0·338
5·83	2·51	0·289	0·330	0·360	0·371

In addition to the above-mentioned decrease in rate, shown by the course of adsorption from 0·4—0·5 c.c. of admitted gas by the platinum containing initially 2·36 c.c. of hydrogen, compared with adsorption by the degassed metal, it will be noted, first, that, at the still higher initial adsorbed concentration, a far greater volume of gas must be admitted in order to obtain approximately the same adsorption rate, and secondly, that adsorption by platinum containing a relatively high initial adsorbed concentration of hydrogen becomes less complete and does not so quickly reach a maximum.

In regard to heat measurements, Table II summarises the results of four typical series of measurements with 12·0 g. of platinum-black, previously exposed to an excess of hydrogen and degassed at

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* Since the above statement was written, Ward (*Proc. Roy. Soc.*, 1931, **133**, *A*, 506) has published results for copper which, from analogy, apparently confirm those now reported for platinum.

100° for 10—14 hours by means of a combined mercury diffusion and Hyvac pump and contained in a platinum calorimeter, as previously described. The differential heat of adsorption given is in calories per g.-mol. of hydrogen, and is calculated on the basis of the heat evolution observed during the adsorption of the corresponding gas increment. The heat effects have been measured at various convenient adsorbed concentrations up to the limit of pressure measurable on the McLeod gauge used, the approximate adsorbed concentration at which the determination is made and the residual hydrogen pressure being indicated in cols. 4 and 5. Series 2 differs from the others in that the platinum was degassed at room temperature instead of at 100°. The platinum therefore, in this case, contained initially considerably more hydrogen than in the other series; and the hydrogen pressures corresponding with the possession of a given additional adsorbed concentration are consequently abnormal.

TABLE II.

Series.	H_2 increment admitted, c.c.	Hydrogen adsorbed.		Press. of H_2, mm.	Differential heat of adsorption.
		Increment.	Total.		
1	0·570	0·570	0·570	—	16,600
	0·535	0·535	1·10	—	16,500
	0·630	0·630	1·73	—	15,800
	0·765	0·752	5·2	0·06	16,000
	1·00	0·530	13·0	0·52	17,200
	2·80	0·59	16·6	3·0	17,200
2	0·692	0·668	0·7	0·002	15,800
	0·765	0·515	3·4	0·23	16,200
	1·50	0·27	5·2	2·3	16,500
	7·1	0·51	6·0	7·3	16,500
3	0·371	0·371	0·37	—	15,000
	0·456	0·456	0·83	—	14,500
	0·549	0·543	1·37	—	13,300
	0·397	0·391	1·75	—	13,500
	0·530	0·510	2·76	0·005	14,700
	0·586	0·523	3·29	0·02	13,800
	0·709	0·546	3·86	0·10	13,200
4	0·241	0·241	0·241	—	15,900
	0·245	0·238	0·72	—	15,800
	0·256	0·245	1·3	0·005	15,800
	0·371	0·358	2·6	0·015	14,900
	0·755	0·415	5·0	0·40	14,500
	2·97	0·662	5·7	1·68	16,700
	2·52	0·30	6·2	3·0	17,500

It will be seen that the differential heats, measured at various stages of adsorption, show no indication of a regular increase or decrease as the adsorbed concentration advances, but vary round a mean value for each series. The hydrogen pressure corresponding with a given total adsorption varied from series to series, this being probably due principally to slight differences in the extent of the preliminary degassing; further, as has also been observed previously, the adsorption at a given hydrogen pressure was especially high during the first series for which the platinum was used.

In addition, a series of adsorption measurements was carried out in a copper calorimeter of a type such that the hydrogen was admitted initially to the centre of the adsorbing mass instead of to the outside. The platinum-black used weighed 8·4 g. Somewhat lower results were obtained for the adsorption heats, this being possibly due to differences in the condition of the platinum; but here again the values varied round a mean. The results in this series are given in Table III.

TABLE III.

H_2 admitted, c.c.	Hydrogen adsorbed.		Differential heat of adsorption.
	Increment.	Total.	
0·509	0·317	0·3	10,400
0·519	0·285	0·6	12,800
0·573	0·315	1·0	11,700
0·615	0·329	1·3	11,700
0·824	0·399	1·7	12,500
1·113	0·471	2·2	13,000
1·653	0·641	2·8	13,000
2·216	0·871	3·6	13,000

Measurements of the heats of desorption were made by evacuating the whole of the apparatus, with the exception of the part actually containing the platinum. On opening the stopcock connecting the calorimeter with the evacuated portion of the apparatus, a small volume of hydrogen was relatively quickly desorbed, provided that the initial adsorbed hydrogen concentration was not too low; and the negative heat effect could be determined in the usual way.

Table IV contains the results of a number of desorption measurements at various initial gas pressures, those at high pressures corresponding with relatively high adsorbed concentrations. The differential heats of desorption were, like the adsorption heats, found to vary round a mean value. If anything, there was a tendency for the experimentally determined heats at high adsorbed concentrations to be somewhat high; but this slight variation is probably due to the higher rate of desorption in this state and the consequent decreased effectiveness of heat losses by radiation or other means, and in any case the variation from the mean value is not greater than the limit of accuracy of the apparatus. The weight of platinum used in this series was 12 g. In all, 23 desorption measurements were made, the average heat of desorption being 17,300 cals. per g.-mol. of hydrogen.

In conclusion, it may be pointed out that while a uniform heat of adsorption is perhaps not inconsistent with the theory of a surface

TABLE IV.

Initl. equil. press. of H_2, mm.	H_2 desorbed, c.c.	Diffl. heat of desptn., cals.	Initl. equil. press. of H_2, mm.	H_2 desorbed, c.c.	Diffl. heat of desptn., cals.
4·99	0·24	−18,700	1·71	0·25	−15,000
4·91	0·37	−18,500	1·60	0·30	−18,000
3·30	0·32	−17,500	1·30	0·32	−15,700
2·32	0·25	−15,400	1·18	0·20	−15,800
2·31	0·32	−15,500	1·15	0·18	−16,000
2·29	0·22	−18,700	0·81	0·22	−19,100
2·20	0·25	−16,000	0·60	0·17	−15,000

possessing a non-uniform degree of unsaturation, as postulated by Taylor, it is at least more difficult to reconcile with this conception than is the case for a heat effect which decreases with an increase in the adsorbed concentration.

DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY OF BRISTOL.

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