268. *Sorption Processes on Diamond and Graphite. Part I. Reactions with Hydrogen.*

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Since sorption of hydrogen by "amorphous," *i.e.*, microcrystalline, carbon has recently been thoroughly investigated (Barrer and Rideal, *Proc. Roy. Soc.*, 1935, *A*, **149**, 231; Barrer, *ibid.*, p. 253; *Trans. Faraday Soc.*, 1936, **32**, 481), it was of interest to study the sorption of hydrogen by diamond and graphite, and also the interactions of oxygen and of oxides of carbon with diamond. It was hoped to correlate differences in behaviour with the different crystalline structures of the adsorbents, both of which were found to give very stable reproducible surfaces. Diamond, which forms unusually perfect macrocrystals, should be very constant in such properties as energy of activation for sorption, absence of active centres (of "lockerstellen" type) and heat of sorption. The sequel will show how these views require modification for powdered diamond.

The main phenomena of oxygen sorption (*e.g.*, Langmuir, *J. Amer. Chem. Soc.*, 1915, **37**, 1139; Bull, Hall, and Garner, J., 1931, **837**; Allmand and Shiels, *Trans. Faraday Soc.*, 1932, **28**, 225) by charcoal are well known. Few data exist on the corresponding diamond adsorbents. Storfer (*Z. Elektrochem.*, **1935**, **41**, 868) reported no high-temperature hydrogen uptake by diamond, but it will be shown that there is a small but vigorous chemisorption. Oxygen is known to oxidise diamond to carbon dioxide (Lambert, *Trans. Faraday Soc.*, **1936**, **32**, 452), but the details of oxygen sorption have not been examined. Study of oxygen–diamond systems leads to the study of primary oxidation processes, of the reactions of carbon oxides with diamond surfaces, and the interaction of hydrogen with oxide-covered diamond. The influence of oxide films on the chemisorption kinetics and isothermals of hydrogen may be three-fold, according as hydrogen attacks only the bare carbon surface, displaces oxygen as water, or forms surface hydroxyl groups.

EXPERIMENTAL.

The static method of measuring sorption equilibria was employed. The sorption apparatus and hydrogen generator have been described elsewhere (Barrer and Rideal, *loc. cit.*). Oxygen was prepared from out-gassed potassium permanganate, and passed through a trap at − 78°. Carbon dioxide was prepared in small quantity by oxidation of diamond at 400°, and separated by liquid air. Carbon monoxide was also prepared by the interaction of the dioxide with diamond at higher temperatures (800°), and purified by use of liquid air. The stored gases were admitted in suitable doses to the adsorbent, which was contained in the double-walled silica bulb already described (*idem, ibid.*). Before use, the diamond was out-gassed at 830° for 24 hours, and the graphite for a similar period at 900°.

Gas analyses of CO–CO_2–O_2 mixtures was carried out at the low pressures of the experiments (10^{-1} to 10^{-3} cm.) by using Langmuir's hot platinum-filament method. A sample of gas was isolated from the adsorption bulb, and absence of water and condensable gases shown with solid carbon dioxide at − 78°. The carbon dioxide content was measured with liquid air, and the residual permanent gases were removed by means of a Toepler pump to the catalyst (thoroughly out-gassed platinum wire at 900°). There, if any oxygen as well as carbon monoxide was present, oxidation occurred, and the carbon dioxide was frozen out in an appendage immersed in liquid air. The nature of the residual gas (either carbon monoxide or dioxide) was determined by addition of a small excess of oxygen and reheating the filament. In cases where oxides of carbon were formed at all readily, no gaseous oxygen whatever remained. Further, no water or condensable gas was ever observed in the resultant CO–CO_2 mixtures.

The Stability of the Adsorbents.—No changes in sorptive capacity of the graphite were observed during numerous chemisorptive experiments with hydrogen and physical sorption experiments with various gases. No permanent changes were observed with diamond which were not due to chemical attack by oxygen. Even these changes were of secondary importance. It should be noted that the 2 g. of diamond powder employed had a small surface area and were therefore covered by small traces of gas only. The 20 g. of Acheson graphite used, with a much greater surface, could suffer negligible contamination by traces of foreign gases, when once thoroughly out-gassed and held in a vacuum. There remained the possibility of the diamond–graphite transformation. The diamond not only appeared the same visually after the longest treatments at 830°, but also gave β-ray photographs (kindly taken by Mr. C. S. Lees of this laboratory) after such treatments which indicated only a diamond structure. Since a 15 A. layer of graphite is detectable, it was concluded that the diamond remained stable under rigorous treatment.

Isothermals for Chemisorption of Hydrogen by Diamond.—It was first shown that diamond, like graphite, is capable of chemisorbing hydrogen, the contrary result of Storfer (*loc. cit.*) being due possibly to inadequate out-gassing. Numerous isothermals were measured, all showing similar characteristics. They were rectangular, sorption being completed even at 820° at very low pressures (*ca.* 10^{-1} cm.). This indicates a high heat of sorption. The saturation limit usually increased with increased duration of out-gassing [Fig. 1, isotherms (I), (II), (III)]. The increase was not always permanent, and the various fluctuations in activity were all found to be due to the influence of traces of surface oxide (see below).

On the assumption that the molecule of hydrogen is adsorbed as atoms, but that always the *same* pair of atoms desorbs to give back the molecules, the isotherm is that of Langmuir, $\theta = ap/(1 + ap)$. Statistical mechanics (Fowler, *Proc. Camb. Phil. Soc.*, 1935, **31**, 260) gives

$$p = \frac{\theta}{1 - \theta} \frac{(2\pi m^{3/2})(kT)^{5/2}}{h^3} \cdot \frac{bg(T)}{Vs(T)} e^{-\Delta H/RT}$$

where $bg(T)$ is the partition function for the internal states of the gaseous hydrogen molecules and $Vs(T)$ the partition functions for its set of adsorbed states (as two atoms). When $\theta = \frac{1}{2}$, $\theta/(1 - \theta) = 1$. Half saturation was observed at 1033° Abs. when $p = 2{\cdot}2 \times 10^{-3}$ cm. Putting these values (p in dynes/cm.^{2}) in the above expression, we obtain for ΔH, the heat of sorption, in cals./g.-mol. of hydrogen

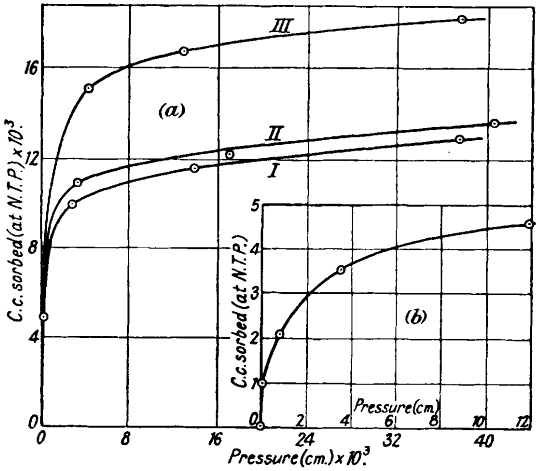
$$\Delta H = 58{,}000 + 4{,}750 \log bg(T)/Vs(T)$$

Although ΔH cannot be determined uniquely from this expression, since the state sum $Vs(T)$ is not known, one sees that, save where $bg(T)/Vs(T)$ is very small, ΔH is large, as indicated by the rectangularity of the isotherms.

The isotherm at 1063° Abs. on graphite (Fig. 1b) was of Langmuir type, as is also true of chemisorption on charcoals (Barrer and Rideal, *loc. cit.*). The isotherm, however, is not so rectangular as those on diamond. The pressure of half saturation is 2·1 cm., so that the expression for ΔH is

$$\Delta H = 45{,}000 + 4{,}950 \log bg(T)/Vs(T)$$

FIG. 1.



(a) *Hydrogenation of* 2 *g. of diamond at* 1092° *Abs. Experiments in order* I, II, III.

(b) *Hydrogenation of* 22 *g. of Acheson graphite at* 1063° *Abs.*

From previous work (*idem, ibid.*) the Clapeyron equation gave for chemisorption of hydrogen on charcoal $\Delta H = 50{,}000 \pm 5000$ cals./g.-mol.; hence $\log bg(T)/Vs(T)$, which will be approximately the same for diamond and graphite, is quite small. Hydrogen is chemisorbed more vigorously therefore by diamond than by graphite, and the heats are of the order 58,000 and 45,000 cals., respectively.

Energy of Activation for Chemisorption on Diamond and Graphite.—The kinetic processes for chemisorption of hydrogen by diamond and graphite resemble those observed on charcoals (*idem, ibid.*). An initially rapid velocity was followed by a steady decrease in speed; when $\log (p_t - p_\infty)$ is plotted against time, the graphs show a curvature. For not too great surface densities, the equation

$$d \log (p_t - p_\infty)/dt = k(1 - \theta)e^{-E/RT}$$

may be used. In the case of diamond, the total surface was very small and the curvature is due more to the term $(1 - \theta)$ than to changes in the energy E. The converse is the case with graphite. Fig. 2 shows $d \log (p_t - p_\infty)/dt$ plotted against the percentage saturation of the surface for diamond. For both substances the former decreases as the latter increases; but *also* the temperature coefficient of the former increases as the latter increases. This function was used, modified where necessary at greater surface densities,* to calculate the values of E. These are given for two temperature ranges for diamond in Table I. The means of numerous experiments at temperatures ranging from 418° to 733° are given for graphite in Table II.

Comparison of Energy of Activation and Percentage Saturation Curves.—The same characteristic energy–charge curves were observed on all the graphitic carbons; E was initially small and increased at first rapidly then more slowly until a constant or nearly constant value was reached. Fig. 3 shows energy–charge curves for diamond, and for the following three graphitic carbons, the volumes (corrected to N.T.P.) relating to physical sorption of hydrogen per g. at saturation: (1) Acheson graphite, 0·1% ash; 1·1 c.c. (2) Sugar carbon, 0·01% ash; 18 c.c. (3) Sugar carbon, 0·1% ash; 57 c.c.

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* At large surface density the equation which must be employed is

$$d \log (p_t - p_\infty)/dt = k[p_0/(p_0 - p_\infty) - \theta]e^{-E/RT}$$

This expression is derivable from the differential equation $-dp/dt = k_1p_t(1 - \theta) - k_2\theta$, and the equilibrium condition $k_1p_\infty(1 - \theta) = k_2\theta$. An analysis of the absolute reaction rates will be given elsewhere.

TABLE I.

Sorption of hydrogen on 2 g. of diamond powder.

C.c. sorbed at N.T.P.	Energy (kg.-cals./mol.).		Mean energy (kg.-cals./mol.).
	Between 563° and 450°.	Between 450° and 615°.	
0·00175	15·7	13·7	14·5
0·00350	16·1	14·9	15·5
0·00525	17·1	15·4	16·3
0·00700	18·2	15·8	17·0
0·00825	21·8	19·3	20·5
0·0105	22·4	21·3	22·0
Saturation value 0·030 c.c.			

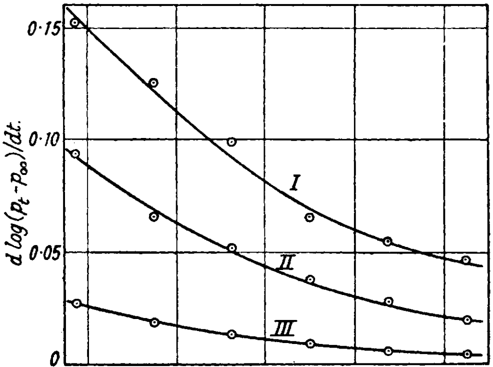
TABLE II.

Sorption of hydrogen on 22 g. of graphite.

C.c. sorbed at N.T.P.	Mean energy (kg.-cals./mol.).	C.c. sorbed at N.T.P.	Mean energy (kg.-cals./mol.).	C.c. sorbed at N.T.P.	Mean energy (kg.-cals./mol.).
0·0260	22·0	0·400	29·0	1·20	35·2
0·0461	24·6	0·60	30·6	1·40	34·2
0·0625	25·4	0·80	31·6	1·60	34·1
0·0750	26·4	1·00	33·2	1·80	33·8
				Saturation value 5·8 c.c.	

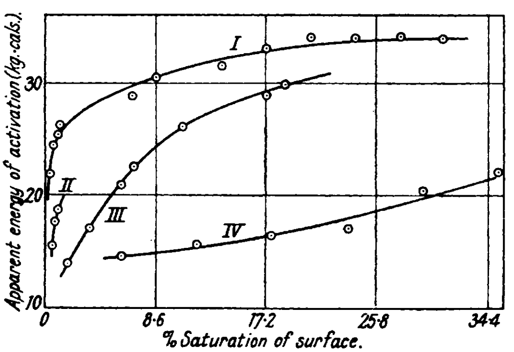
FIG. 2.

Rates of sorption of hydrogen on diamond.



I. 615°; II. 563°; III. 450°.

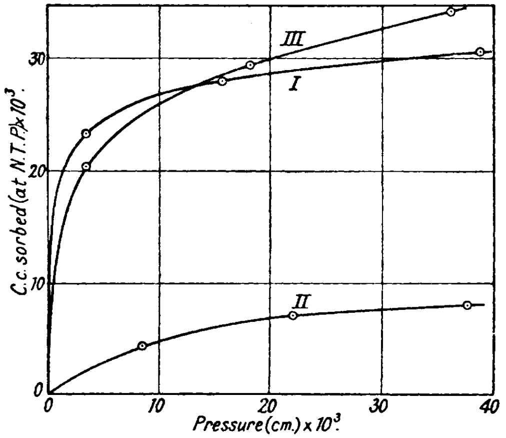
FIG. 3.



I. *Acheson graphite,* 0·1% *ash.*
II. *Sugar carbon,* 0·01% *ash.*
III. *Sugar carbon,* 0·1% *ash.*
IV. *Diamond.*

The saturation value is a rough measure of the size, and therefore degree of perfection, of the component crystallites. Very small microcrystals of graphite (10—30 A.) show a marked increase in inter-laminar distance with decreasing size (Randall and Rooksby, *Nature,* 1932, **129**, 280; Arnfelt, *Arkiv Mat. Astron. Fysik,* 1932, **23**, *B*, No. 2), and probably a sliding of laminæ across one another (Warren, *Physical Rev.*, 1934, **45**, 763). The graphite is most nearly perfect. Its *E* values should therefore most rapidly approach constancy, and should commence nearest to that constant value. Carbon (2) should lie intermediate between graphite and carbon (3), as regards both its initial *E* value and the speed with which a constant *E* is approached. Carbon (3), having the greatest range in structure, should have the smallest initial *E*, and should take longest to reach a constant *E* as charge increases. Examination of Fig. 3 shows that all these expectations are fulfilled. Thus the properties of the curves are explicable upon the assumption only of the variable carbon–carbon distances in the materials. There is no connexion with total ash content : on this basis one would expect carbon (2) to have by far the most constant *E* as charge increases. Only upon an adsorbent composed of perfect crystals would the energy *E* be a constant for all values of charge, and to this condition diamond may approach. It is, in fact, observed that the E–x curve is of an entirely different shape from those for charcoals and graphite : E remains nearly constant by comparison with that for graphite ; the curve is concave to the x axis, and not convex ; and it does not commence with the very small E value at small x. These curves stress a difference in the sorptives which has not previously been revealed. Chemisorption of hydrogen, except for the first traces, should proceed more easily on diamond than on graphite, area for area. The principal spacing likely to be involved in diamond is the C–C distance of 1·56 A., while graphite has two such distances, 1·42 and 3·4 A. (both of which, especially the latter, vary with crystal size). Finally, it is probable that the variable energies are to be ascribed to variable C–C distances rather than to an activated migration to internal surfaces following upon chemisorption upon external surfaces, since in all cases the surface available for van der Waals sorption is *greater* * than that for chemisorption. Thus the process does not involve activated flow to parts not accessible to Knudsen flow.

Fig. 4.



Curves I and III : H_2 *on out-gassed diamond before and after oxide formation at* 819°.
Curve II : H_2 *on " oxided " diamond surface at* 819°.

Chemisorption of Hydrogen by Oxide-covered Diamond.—In seeking an explanation for the fact that saturation for physical sorption exceeds saturation for chemisorption of hydrogen, in contrast to the diamond–oxygen system (Part II), we must envisage the following possibilities : (1) Chemisorption occurs only on certain parts of a bare carbon surface (as was assumed for charcoals) ; (2) chemisorption would occur at all points but that an oxide film of great stability occupies a great part of the surface. Physical sorption proceeds largely undiminished on such a film.

That oxygen has an important influence upon chemisorption of hydrogen by diamond was shown as follows. A hydrogen isothermal was determined ; a little oxygen was admitted, gaseous oxides of carbon removed, and the hydrogen isothermal redetermined. Finally, the sorbent was out-gassed, and the isothermal again measured. These are respectively curves I, II, III of Fig. 4, all at 819°. Oxygen is clearly a strong poison for chemisorption of hydrogen. The two possible reactions with the oxygen film, *viz.*,

$$(1)\ H_2 + {>}CO_{2(\text{surface})} \longrightarrow {>}C(OH)_{2(\text{surface})}$$

$$(2)\ H_2 + C{\cdot}CO_{(\text{surface})} \longrightarrow CH{\cdot}C(OH)_{(\text{surface})}$$

are ruled out by the poisoning of hydrogen sorption by the oxide film. Reactions (1) and (2) would not decrease the amount of hydrogen sorbed. The possibility of a reaction $H_2 + CO_{(\text{surface})} \longrightarrow C + H_2O_{(\text{vapour})}$ was eliminated by testing the gas atmosphere for water with solid carbon dioxide in acetone. Even at 820° this film was chemically inert towards hydrogen, and chemisorption can proceed only upon oxygen-free surfaces. It has been stated (Schilow, Shatunovska, and Chmutov, *Z. physikal. Chem.*, 1930, *A*, **149**, 211) that there are several surface oxides on carbon. It was therefore thought possible that hydrogen might react with a low-temperature oxide film. This film was formed at 333°, and hydrogen sorption measured on it at that temperature. The film remained inert, no hydrogen was sorbed, and no water vapour was formed. One therefore has reason to suppose that suggestion (2) is the correct one.

The *rates* of chemisorption of hydrogen both in presence and in absence of oxide film at 820° were not measurably different. In both cases sorption was complete in several

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* The surfaces available for chemisorption were less than 10% of those available for physical sorption. The physical sorption experiments will be discussed in another paper.

minutes. At the same time the oxide film underwent its usual slow decomposition (see Part II) into oxides of carbon. This rate was also the same in a vacuum as when hydrogen was present.

SUMMARY.

Diamond chemisorbs hydrogen very vigorously at temperatures from 400° upwards. The isotherms indicate, by their rectangular form, a more energetic sorption than occurs on graphite. An estimate of the heats of sorption gives 58 kg.-cals./g.-mol. for diamond, and 45 kg.-cals./g.-mol. for graphite. The energy of activation–percentage saturation curves are of different forms for diamond from those for graphite and charcoals. All the results are explicable in terms of the varying degrees of perfection of the crystals. By admission of a little oxygen a very stable oxide film is formed on diamond which is chemically inert towards hydrogen up to 820°. This film poisons the chemisorption of the hydrogen, which gas can therefore occupy only the bare carbon surface.

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