269. *Sorption Processes on Diamond and Graphite. Part II. Reactions of Diamond with Oxygen, Carbon Dioxide, and Carbon Monoxide.*

By Richard M. Barrer.

The apparatus and method of analysis of gases used have been described in Part I (preceding paper), and the results on the diamond–oxygen–carbon oxide systems are now given.

In the sorption of oxygen by diamond four different temperature-dependent processes were observed; these merged gradually as transition regions of temperatures were traversed.

(1) At very low temperatures (—78°) a reversible van der Waals or physical sorption was obtained. Even at this temperature a slight chemisorption proceeded, however, as is also the case on charcoals (Barrer and Rideal, *Proc. Roy. Soc.*, 1935, *A*, **149**, 231).

(2) From 0° to 144° physical sorption was slight compared with an irreversible chemical sorption. After each admission of oxygen, subsequent admissions proceeded more and more slowly, until the sorption rates were negligible. In this region the sorbed oxygen was retained as a film, and the residual gas atmosphere was pure oxygen.

(3) At temperatures from 244° to 370° a burst of carbon dioxide occurred at each admission of oxygen, until, when all the oxygen was consumed, a gas atmosphere of nearly pure carbon dioxide remained. The amount of this carbon dioxide was very much smaller than the amount of oxygen originally taken, because nearly all the latter was chemisorbed to form a stable film.

(4) At still higher temperatures, the film itself commenced to decompose. Several reactions were observed, and the gaseous atmosphere consisted of carbon dioxide and monoxide.

These processes may now be considered in more detail. Fig. 1 gives the quantity–pressure curves for oxygen on diamond (2 g.) in the temperature range —78° to 144°; a remarkable increase has occurred in the saturation value for the sorption, *viz.*, from 0·05 to 0·15 c.c. (at N.T.P.). The former value is comparable with the limit for chemisorption of hydrogen of 0·03 c.c. (Part I). Since the sorption at — 78° was mainly physical it must be confined to external surfaces; the increased sorption at higher temperatures, which is a chemical process, must involve a continual penetration into the adsorbent. The isotherms therefore suggest that each (visible) diamond particle is invisibly subdivided into a mosaic of submicroscopic particles, into which penetration occurs with increasing facility as the temperature is raised. The necessary mosaic structure doubtless has its origin in the grinding processes required to form the powder. Even with large crystals, however, laminar structure (Robertson, Fox, and Martin, *Phil. Trans.*, 1935, *A*, **232**, 463) and cracks (Andrade and Martindale, *ibid.*, **235**, **69**) in the crystal surface have been noted in certain cases.

Kinetics and Energetics of Oxygen Sorption.—The rate of sorption is

$$-dp/dt = k(1 - \theta)p = k[1 - a(\text{Film})]p \quad . \quad . \quad . \quad . \quad . \quad (1)$$

if θ is the fraction of surface covered, k and a are constants, and p is the pressure. This equation does not include a reverse process, because sorption is irreversible. It is, however, of limited applicability, because the ease of penetration decreases as sorption increases; *i.e.*, k is a function of the amount of film formed. This variation is well shown by plotting $d \log p/dt$ against the amount of the film formed, the curious family of curves given in Fig. 2 being obtained. At low temperatures over a limited range of film increase, equation (1) is valid. The curve then turns and approaches the x axis asymptotically. At higher temperatures $d \log p/dt$ tends initially to be constant, at a value not greatly dependent on temperature, so that here the sorption equation is $\log p_0/p = kt$. By examining the curves of Fig. 2, one can infer that the high-temperature curves also approach the x axis asymptotically, producing an **S**-shaped curve.

FIG. 1.

Sorption of oxygen by diamond.

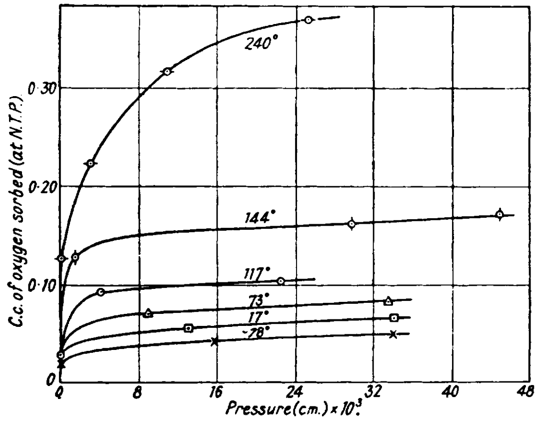
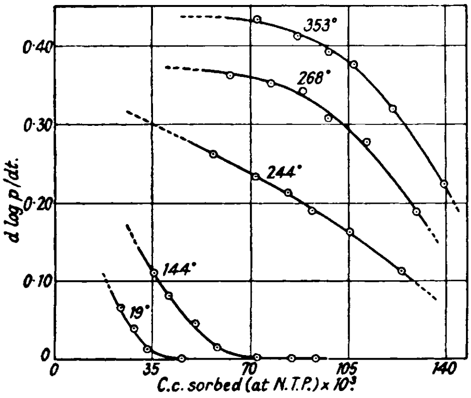


FIG. 2.

Sorption of oxygen by diamond.



The temperature coefficient of the quantity $d \log p/dt$ increases very strongly as the amount of film increases, and the apparent energy of activation calculated therefrom increases to an extent more marked than in any hydrogen–carbon system (Part I) (Table I).

TABLE I.

Absorption on 2 g. of diamond powder.

Film (c.c. O_2 at N.T.P. × 10^3).	Temp. range.	Temp. coeff.	E (apparent) (kg.-cals.).	Film (c.c. O_2 at N.T.P. × 10^3).	Temp. range.	Temp. coeff.	E (apparent) (kg.-cals.).
35	144—244°	2·75	4·3	84·6	144—244°	206·0	23·0
45·5	,,	4·63	6·6	93·4	,,	284·0	24·4
58·8	,,	19·7	12·0				
73·2	,,	77·0	18·6	45·8	19—144	281	13·8

Since a certain amount of chemisorption occurs at − 78°, one may infer that on an exposed surface E(true) is small. The rising values of the energy with increased sorption cannot be interpreted exclusively as indicating that certain crystal distances on the exposed surface favour reaction more than others, producing a stepped energy–charge curve, because the larger energies are associated with amounts of oxygen greater than those needed to cover the external surface completely. Instead, they are probably connected with processes of penetration to internal surfaces of the mosaic (whose existence is indicated by the sorption isotherms). The less accessible the internal surface, the greater the cohesion of its component crystallites. Thus, of the energy of activation a small part is needed for chemical reaction, and an increasing fraction is expended to overcome cohesion as penetration proceeds. This power of penetration is a specific property of the oxygen–diamond system, because the analogous process occurs only to a minor extent with hydrogen. Where the temperature coefficient is negligible, and the sorption equation is log $p_0/p = kt$, one may suppose sorption to be limited by simple diffusion, whose temperature dependence is slight.

Mechanism, Kinetics, and Energetics of Carbon Dioxide Formation.—Between 240° and 370° pure carbon dioxide was the primary product of the reaction between oxygen and diamond. Most of the oxygen, however, was sorbed. When all the oxygen was used up, a little more carbon dioxide was liberated as a secondary process. The rate of liberation steadily diminished, ultimately leaving a stable film.

The primary liberation may be due either to interaction of gaseous or physically sorbed oxygen with the uncovered surface of the diamond, or to decomposition of the oxide film. To decide between these possible mechanisms, successive equal admissions of gaseous oxygen were made. Oxygen pressure, carbon dioxide pressure, and amount of film were measured simultaneously, as functions of time. Between each admission the film was allowed to attain a stable state until no carbon dioxide was evolved. The sorption of oxygen decreased in velocity after each admission. Thus more and more gaseous oxygen remained at any time, *t*, after each admission; and less and less newly-formed film was present at the same time. If the carbon dioxide liberation depends on the *gaseous* oxygen pressure, the amount liberated in time *t* will increase with every admission of oxygen. If it depends on freshly-formed film, the amount will decrease with every admission. Always when the pressure of oxygen, the amount of freshly formed film, and the amount of carbon dioxide were plotted as functions of time, the carbon dioxide yield was observed to be increased by decrease in the rate of oxygen sorption. Therefore, this primary process involves the gaseous oxygen and *not* the newly-formed film. But the formation of carbon dioxide may involve gaseous oxygen and bare surface, or gaseous oxygen and oxide film. The two mechanisms give two reaction expressions :

FIG. 3.

Test of equation $(dp/dt)_{CO_2} = k . p_{O_2}[1 - a(\mathit{film})]$.

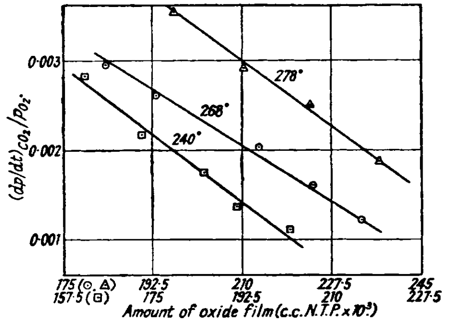
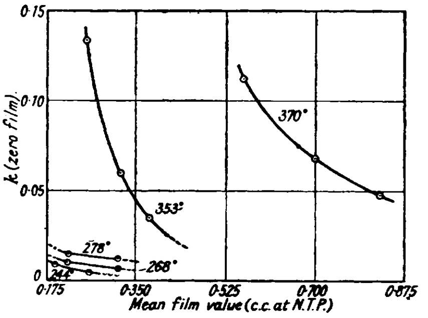


FIG. 4.

Velocity constants in CO_2 *formation as a function of the amount of oxide film.*



$$(dp/dt)_{CO_2} = kp_{O_2}(1 - \theta) \qquad (dp/dt)_{CO_2} = k_1p_{O_2}\theta$$

where θ, the fraction of surface covered, is equal to a(amount of film). In both cases $(dp/dt)_{CO_2}/p_{O_2}$ should be a linear function of the amount of film formed, in the former case decreasing as θ increases, and in the latter case increasing. Fig. 3 shows some graphs of $(dp/dt)_{CO_2}/p_{O_2}$ plotted against the amount of film formed. The carbon dioxide formation is poisoned by film formation, so that the reaction which primarily liberates carbon dioxide is one between gaseous or physically sorbed oxygen and diamond surface free from chemisorbed oxygen. The poisoning effect is a *linear* function of θ, over not too wide a range in the value of θ. When these graphs are extrapolated back to zero film the intercepts on the ordinate are the values of k in the equation $(dp/dt)_{CO_2} = kp_{O_2}(1 - \theta)$. Fig. 4 shows that k diminishes steadily as the amount of film formed increases. Thus those parts which would most easily evolve carbon dioxide are those which most readily sorb oxygen.

This is in agreement with the supposition that the most *active* centres in both processes are the most *exposed* surfaces. From the graphs of Fig. 4 it was possible to obtain a consistent set of temperatures coefficients for *k*, over a narrow range of film formation, *viz.*, 0·235—0·280 c.c. of oxygen per 2 g. of diamond (Table II). The graphs of Fig. 4 at 353° and 370° show, however, that the temperature coefficients steadily increase over an extended increase in the amount of film. Thus the apparent energies recorded in Table II are correct only in the range 0·235—0·280 c.c. at N.T.P.

TABLE II.

Temp. range.	Temp. coeff.	Amount of film (c.c. at N.T.P.).	Apparent energy of activation (kg.-cals.).	Temp. range.	Temp. coeff.	Amount of film (c.c. at N.T.P.).	Apparent energy of activation (kg.-cals.).
353—268°	16·5	0·235	22·2	353—268°	14·8	0·280	21·5
353—244	26·4	,,	19·3	353—244	27·3	,,	19·6
353—278	10·0	,,	21·2	353—278	8·8	,,	20·0

It was observed that, in addition to the primary burst of carbon dioxide, the film decomposed, though more and more slowly, when no gaseous oxygen remained. This secondary liberation of carbon dioxide increases in velocity as the temperature increases, becoming important at high temperatures (600—830°) as the primary process in film decomposition.

The result indicates that a very small fraction of the oxide itself is not stable, and decomposes preferentially, at quite low temperatures (*ca.* 300°), leaving a stable film. About 5% of the film decomposes in this way at 300°, compared with about 80% of the film at 800°. At the higher temperature secondary reactions also occur which will be discussed later.

Film Decomposition at High Temperatures.—The composition of the gas was studied at various temperatures between 330° and 820° to find how it varied with time and with successive desorptions, and whether any approach was made to the equilibrium value for C–CO–CO_2. Each successive quantity of gas desorbed (at pressures of 10^{-1} to 10^{-3} cm.) gave a greater and greater carbon monoxide content, and a desorption rate which decreased more rapidly than the amount of oxide film. Table III summarises these results.

TABLE III.

0·470 C.c. at N.T.P. per 2 g. of diamond. Temp. 333°.

Desorption No.	Time allowed (mins.).	Residual film, c.c. at N.T.P.	Press. developed $\times 10^3$ (cm.).	Composition, %. CO.	CO_2.
1	900	0·453	7·2	59	41
2	300	0·449	1·85	67·6	32·4
3	560	0·444	2·23	77·8	22·2
4	900	0·438	3·10	91·9	8·1
5	5400	0·411	14·3	95·1	4·9

The equilibrium values for the system C(diamond) + $CO_2 \rightleftharpoons 2CO$ were calculated as follows :

(*a*) $\text{C(graphite)} + CO_2 \rightleftharpoons 2CO;\ K'_p = [CO]^2/[CO_2]$

$$\Delta F_1{}^0 = 40910 - 4{\cdot}9T \,.\, \log t + 0{\cdot}00455T^2 - 0{\cdot}0_6 51T^3 - 12{\cdot}66T.$$

(*b*) $\text{C(diamond)} \longrightarrow \text{C(graphite)}$

$$\Delta F_2{}^0 = \Delta H - T \,.\, \Delta S;\ \Delta H = 260 \text{ cals.*};\ \Delta S = -\ 0{\cdot}6 \text{ cal./deg.*}$$

(*c*) $\Delta F_3{}^0 = \Delta F_1{}^0 + \Delta F_2{}^0;\ \Delta F_3{}^0 = -\ RT \,.\, \log K_p;\ K_p\text{(diamond)} = [CO]^2/[CO_2].$

From these three expressions, one calculates the following typical values of K_p and K'_p :

Temp.	333°	660°	810°	823°
K_p(diamond)	$1{\cdot}41 \times 10^{-6}$	$2{\cdot}63 \times 10^{-2}$	6·3	7·5
K'_p(graphite)	$1{\cdot}78 \times 10^{-6}$	$4{\cdot}2 \times 10^{-1}$	11·2	13·2

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* Values from Lewis and Randall, " Thermodynamics." Later work of Rossini (*Bur. Stand. J. Res.*, 1934, **13**, 21) indicates a very similar figure for ΔH of 220 ± 70 cals.

All pressures are expressed in atmospheres. Over diamond the equilibrium gas is richer in carbon dioxide at high pressure (1 atm.) but poorer in carbon dioxide at low pressure, as compared with graphite. To determine the actual compositions at equilibrium the quadratic equation derived from the relations

$$[CO]^2/[CO_2] = K_p; \; [CO] + [CO_2] = \text{total pressure}$$

was solved for each case. Table IV shows the variation in composition of the gas samples desorbed, and a comparison with the equilibrium values. Thus the trend at 330° noted in Table III is *away* from the equilibrium value, whilst at higher temperatures it was *toward* this. In all cases, however, the trend is simply towards a carbon monoxide-rich gas phase and has probably nothing to do with the establishment of equilibrium. The monoxide may have its origin by direct decomposition of surface oxide. Also, however, by an independent set of experiments it was shown that carbon dioxide is reduced at diamond surfaces to carbon monoxide. Even when liquid air is used to condense carbon dioxide as soon as it is formed, there is an appreciable period during diffusion of the dioxide through the powder when it continually encounters the reducing medium. The ratios of CO : CO_2 in the resultant gas are then governed simply by the relative velocities of the reactions :

TABLE IV.

			Actual composition, %.		Composition at equilm., %.	
Temp.	Time (mins.).	Total press. (cm.) × 10^3.	CO.	CO_2.	CO.	CO_2.
333°	900	7·2	59·0	41·0	11	89
660	40	19·5	77·4	22·6	99·89	0·105
810	40	266·0	89·5	10·5	99·95	0·05
823	800	123·0	94·8	5·2	99·978	0·022
823	1400	22·5	98·8	1·2	99·9978	0·0022

$$\begin{aligned}&\text{(i)}\quad >\mathrm{CO(chemisorbed)} \longrightarrow \mathrm{CO(gas)}\\ &\text{(ii)}\begin{cases} >\mathrm{CO_2(chemisorbed)} \longrightarrow \mathrm{CO_2(gas)}\\ \mathrm{CO_2(gas)} + \mathrm{C(diamond)} \longrightarrow \mathrm{2CO(gas)}.\end{cases}\end{aligned}$$

The Reduction of Carbon Dioxide by Diamond.—A quantity of carbon dioxide was admitted to the diamond, at a pressure of 10^{-2} cm., and the carbon monoxide and dioxide content measured as a function of time. The surfaces on which the carbon dioxide decomposed were less than 10% covered with oxide film, so that, θ being small, $(1 - \theta)$ was nearly unity and reduction on a simple surface should follow a law $-(dp/dt)_{CO_2} = kp_{CO_2}$. It was found, however, that $d(\log p)/dt$ decreased as the reaction proceeded, and that the temperature coefficient increased correspondingly. Thus Table V shows the time (in mins.) of $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{2}{3}$ decomposition of carbon dioxide, at initial pressures of 15×10^{-3} cm., at various temperatures.

TABLE V.

Temp.	780°	720°	830°	690°	737°
$t_{\frac{1}{4}}$	3	8·5	1·5	25·0	6·0
$t_{\frac{1}{2}}$	10·2	35·0	3·0	95·0	24·0
$t_{\frac{2}{3}}$	18·5	72·0	4·5	210·0	53·0

The values of $\log t_{1/n}$ plotted against $1/T$ (T = absolute temperature) give graphs (Fig. 5) whose slope is $E/2{\cdot}303R$. The values of E are respectively 54, 50, and 45 kg.-cals., when calculated from the $\frac{2}{3}$, $\frac{1}{2}$, and $\frac{1}{4}$ lines.

There are two possible modes of reduction of the carbon dioxide :

$$\begin{aligned}&(a)\quad \mathrm{C(diamond)} + \mathrm{CO_2} \longrightarrow \mathrm{CO(adsorbed)} + \mathrm{CO(gas)}\\ &(b)\quad \mathrm{C(diamond)} + \mathrm{CO_2} \longrightarrow \mathrm{2CO(gas)}.\end{aligned}$$

In Fig. 6 the full curve II shows the actual carbon monoxide content of the gas as a function of time, while the dotted curves III and I show the theoretical content according to the two mechanisms given above. It is apparent the mechanism is that indicated by (*b*). The experimental curve usually lies between the two calculated curves, however, showing that a small part of the oxygen is retained as a film.

Reaction of Carbon Monoxide with Diamond.—This film may be formed by transference of an oxygen atom from the carbon dioxide at the instant of reaction or by subsequent chemisorption of carbon monoxide. To test this, the diamond (2 g.) was thoroughly out-gassed at 830°, and carbon monoxide at that temperature admitted. A very slight sorption ensued, as indicated by the following figures :

FIG. 5.

Reduction of CO_2 *by diamond.*

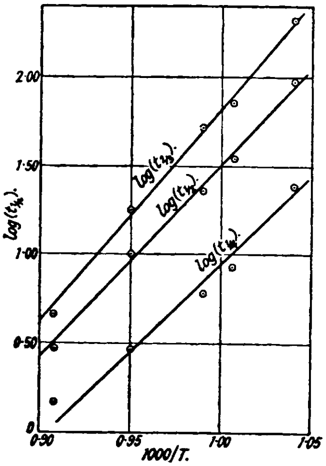
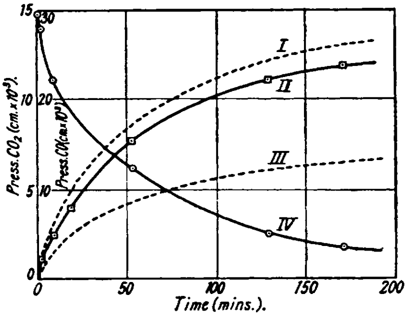


FIG. 6.



I. CO *pressure calculated from* $CO_2 + C \longrightarrow 2CO$(*gas*).
II. *Observed* CO *pressure.*
III. CO *pressure calculated for* $CO_2 + C \longrightarrow CO$(*adsorbed*) + CO(*gas*).
IV. *Observed* CO_2 *pressure.*

Press. × 10^3 (cm.) ...	23·0	22·2	22·1	21·9	21·8	21·2	21·0	20·9
Time (mins.)	0	1·5	3·0	5·0	8·0	16·0	24·0	34·0
C.c. sorbed × 10^3......	0	2·8	3·15	3·65	4·20	5·30	7·00	7·35

This sorption, although very small even at 830°, is sufficient to cover the difference between the experimental curve of Fig. 6 and the curves indicated by (*b*).

DISCUSSION.

It has been noted that, although oxygen appears to penetrate into diamond, hydrogen attack is confined mainly to certain specific parts. Further discussion of this is desirable, with a view to giving reasons for this difference. The diamond powder before out-gassing is regarded as being covered on internal and external surfaces by a chemisorbed oxygen layer. When out-gassing proceeds, oxygen from external surfaces is lost as oxides of carbon. There is produced a two-dimensional concentration gradient, and at high temperatures the chemisorbed oxygen in the interior migrates towards the exterior. Under any normal condition of out-gassing, this process is never completed, but by out-gassing at similar temperatures for a given time the same condition of the external surfaces is producible more or less indefinitely. Hydrogen is chemisorbed on vacant spaces on external surfaces, forming C–H bonds. This hydride undergoes no marked lateral migration down slip-planes because available spaces in the interior are increasingly covered with an oxide layer chemically inert to hydrogen, as demonstrated experimentally, which blocks the diffusion process. The additional assumption must be made that hydrogen in surface hydride is less mobile than oxygen in at least one type of surface oxide, because in oxygen sorption after out-gassing penetration occurs, though with a rapidly increasing apparent energy of activation, and an isobaric quantity–temperature curve which increases rapidly with temperature and cannot represent an equilibrium condition. A suggestive mechanism for diffusion is as follows. The film formed is initially a dioxide or peroxide, on external parts of the surface. The oxygen is passed on, all or in part, to other less exposed carbon atoms and so diffuses inwards. This relatively unstable oxide tends to decompose into the more stable atomic monolayer of the type postulated by Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 1139), which is very hard to desorb and relatively immobile. It is the latter film which remains on parts of the carbon surface even after prolonged out-gassing at 830°.

All the chemical facts observed in oxygen–carbon oxide–diamond systems are explained by the following processes: a chemisorption of oxygen; a primary interaction between oxygen (either gaseous, or physically sorbed) and bare carbon surface, giving carbon dioxide; a decomposition of oxide film into carbon dioxide, and possibly simultaneously into carbon monoxide; a reduction of carbon dioxide to carbon monoxide; and a slight chemisorption of carbon monoxide. Each process commences in its appropriate temperature zone, but at high temperatures all occur simultaneously. Analysis is only possible by studying as wide a range of temperatures as possible, and working at low pressures. It is a characteristic of the observable processes that the apparent energy of activation increases with increased covering of the surface by oxide, or as the reaction proceeds towards completion.

There are analogies between reactions with diamond and reactions with graphite or charcoal, but there are also certain differences. Langmuir (*loc. cit.*) found that, when carbon dioxide was reduced by graphite filaments, the reaction was $CO_2 + C(graphite) \longrightarrow CO(adsorbed) + CO(gas)$. In this paper it has been found that the reaction with diamond is mainly $CO_2 + C(diamond) \longrightarrow 2CO(gas)$.

The apparent energy of activation is also larger for the reaction on diamond. Mayers (*ibid.*, **1934**, **56**, 70), also working at low pressures, gives E(app.) = 38—32 kg.-cals. for graphite compared with 54—45 kg.-cals. on diamond. On diamond also, we have observed two primary processes for production of oxides of carbon: $>C + O_2(gas) \longrightarrow CO_2(gas)$ at low temperatures (370° upwards), and breakdown of surface oxides at high temperatures (about 600° upwards). Graphite also gives these reactions, but two additional processes have been reported by Lothar Meyer (*Z. physikal. Chem.*, 1932, *B*, **17**, 385), *viz.*,

$$4C + 3O_2 \longrightarrow 2CO + 2CO_2 \text{ (below 1300°; } E = 20\text{—}30 \text{ kg.-cals.)}$$
$$3C + 2O_2 \longrightarrow 2CO + CO_2 \text{ (above 1500°; } E = 90 \text{ kg.-cals.)}$$

which have so far no counterpart in the oxidation of diamond. Neither graphite nor diamond chemisorbs carbon monoxide to a marked extent.

SUMMARY.

1. The sorption of oxygen by diamond is nearly all physical at − 78°. A slight chemisorption is superposed. From 0° to 144° the oxygen is chemisorbed, but no oxides of carbon liberated. The surface involved is much greater than that involved in physical sorption of oxygen, or chemisorption of hydrogen. The apparent energy increases rapidly (from 4·3 to 20 kg.-cals., as the amount sorbed increases from 0·035 to 0·093 c.c. at N.T.P.).

2. From 244° to 370° pure carbon dioxide is liberated by interaction between gaseous or physically sorbed oxygen and uncovered diamond surface. The poisoning effect of oxide film has been clearly demonstrated. The apparent energy of activation was *ca.* 20 cals. at small oxide coverings of the surface, but increased as the amount of surface oxide increased. The amount of primary carbon dioxide formed was slight compared with the amount of oxygen chemisorbed.

3. At higher temperatures the oxide film commences to decompose into a mixture of carbon oxides. The carbon monoxide and dioxide content did not always approach the thermodynamic equilibrium value, but tended always to become richer in monoxide. This was ascribed to a primary decomposition into dioxide of continually decreasing velocity, followed by reduction of the dioxide at the diamond surface. The ratio CO : CO_2 is conditioned by the relative velocities of the two reactions.

4. The reduction of carbon dioxide was studied, and found to be of the same retarded type observed for primary carbon dioxide liberation and for oxygen sorption. The temperature coefficient increased as the reaction proceeded. Starting with 15×10^{-3} cm. pressure, the energies calculated from the times of $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ decomposition were 45, 50, and 54 kg.-cals. The reaction proceeded principally through the mechanism $CO_2 +$

C(solid) ⟶ 2CO(gas). A little monoxide was retained as adsorbed film. Gaseous carbon monoxide reacted very slightly with diamond at 830°.

5. The similarities to and differences from the corresponding graphite systems have been indicated. From previous work on hydrogen–graphite systems and the present work, two types of active centres are suggested—one due to material of variable C–C distances, and one to differences in accessibility of surface available for physical sorption, and of internal surfaces.

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