CHAPTER I

Chemisorption kinetics of oxygen on charcoal and the nature of surface oxygen complexes formed

The kinetics of chemisorption of oxygen on different forms of carbon have been engaging increasing attention in recent years. Lendle (1), using sugar charcoal, in the temperature range 0-350°C, found chemisorption to be rapid during the first 10-20 minutes and to slow down appreciably afterwards. Carpenter and Giddings (2) and Carpenter and Sargent (3), using coals at 65, 85 and 105°C, found the quantity of oxygen sorbed during the first five minutes to be in accordance with the Elovich equation, but afterwards it exceeded the value predicted by the equation. Deitz and McFarlane (4), using high surface area carbon films at temperatures between 100 and 300°C and under oxygen pressure of about 100 millitorr, observed that chemisorption was rapid in the beginning but slowed down afterwards. Allardice (5), using degassed brown coal char at temperatures between 25 and 200°C in the pressure range 160-760 torr observed a rapid initial step, which was found to be a case of reversible adsorption, followed by a slow uptake which was a case of irreversible adsorption. The irreversible adsorption was found to follow the Elovich equation.
Walker, Austin and Tietjen (6) working with highly crystalline natural graphite in the temperature range 335-450°C and pressure of 760 torr studied the chemisorption kinetics by using thermoelectric technique. They found the rate of chemisorption to be independent of the surface coverage; unlike the situation under which the Elovich equation is applicable. Hart, Vastola and Walker (7) studied chemisorption of oxygen in the temperature range 300-625°C under oxygen pressure of 0.5 torr on Graphon—a highly graphitised carbon black—which was previously oxidised to different burn offs in oxygen at 625°C so as to introduce significant amounts of active surface area. By employing spectrometric technique they observed a sharp increase in the saturation amount of oxygen adsorbed at temperatures around 400°C. This suggested converting the presence of two types of active sites. By chemisorbed oxygen, evolved as carbon monoxide and carbon dioxide, into oxygen atoms and assuming that the complex consists of one oxygen atom per active (edge) carbon atom, occupying an area of 8.3 Å², they showed that the total active surface area was about 2-3 per cent of the B.E.T. area. Walker, Bansal and Vastola (8) studied chemisorption of oxygen on Graphon, preoxidised at 625°C to 16.6 per cent weight loss, at 25°C under oxygen pressure range of 0.7 millitorr to 760 torr. The plots of amount of oxygen adsorbed (q) against log of time (t) showed a number of linear regions depending on the oxygen.
pressure. In all five linear regions were found. The limiting amount of oxygen adsorbed in each region was found to be independent of oxygen pressure. These workers (9), later on, extended similar investigations to chemisorption of oxygen on the same sample of Graphon in the temperature range of -78 to 160°C but at a constant oxygen pressure of 100 millitorr. By plotting q against log t as before, they observed, again, five different linear regions. The activation energy did not change within a particular linear region but it changed abruptly in going from one linear region to another. The values of activation energy varied between 3.1 and 12.4 K.cal./mole. Each linear region was considered to correspond to adsorption on a discrete type of sites; thus five different types of sites were postulated.

It appears that very little information is available regarding the nature of the carbon-oxygen complexes formed at different sites or at different temperatures on chemisorption of oxygen under various conditions of temperature and pressure. Walker and coworkers, in their extensive work on Graphon, reported desorption of most of the combined oxygen as carbon monoxide on evacuating the products around 900°C. In their technique, however, even if some oxygen was desorbed as carbon dioxide at a lower temperature, it would have been reduced to carbon monoxide by the carbon itself at the prevailing temperature of 900°C.
The work described in this chapter was undertaken firstly with a view to study chemisorption kinetics of oxygen on an ash-free outgassed charcoal of a relatively large surface area at different temperatures under oxygen pressure of one atmosphere, and secondly to examine the nature of the oxygen complexes formed at different temperatures. For the latter purpose the oxidised products were outgassed at gradually increasing temperatures and the gas evolved (carbon dioxide and carbon monoxide) at any given temperature was removed from the system before the temperature of the furnace was raised by the next 50°C. The oxidised samples were also examined for their base adsorption capacity (10), bromine value (10) and sodium borohydride reaction (11).

Sugar charcoal, outgassed at 1100°C in vacuum of the order of $10^{-4}$ mm. of mercury to remove most of the volatile impurities, was used in these investigations. This sample was essentially free of oxygen and contained 1.08 per cent of hydrogen which, however, could not be removed unless the temperature of evacuation was raised above 1600°C. This would have caused considerable graphitisation and loss of surface and, therefore, was not attempted.

The nitrogen surface area of the sample was 442 m²/g. The active surface area, as obtained from the amount of oxygen chemisorbed at 350°C, assuming one oxygen atom to be fixed per active carbon atom occupying area of 8.3 Å² (12), was found
to be 75.1 m²/g., i.e. about 16.9 per cent of the total surface. The charcoal was also subjected to a burn off of 38 per cent in oxygen at 650°C when the nitrogen surface area increased to 496 m²/g. whereas the active surface area increased to 100.1 m²/g. i.e. about 20.1 per cent of the total surface.

Results and Discussion

The amounts of oxygen chemisorbed (q) on 1100°C outgassed sugar charcoal at 200, 300 and 350°C are plotted against time (t) in Fig. 1 before any burn off and in Fig. 2 after 38 per cent burn off. The rate of chemisorption, evidently, goes on decreasing with increase in surface coverage. The reaction appears to approach the end point after about 450 minutes. The maximum amount of oxygen chemisorbed at 200°C on the outgassed charcoal before any burn off is seen to be close to that reported on brown coal char (5). Higher temperatures had not been tried on brown coal char.

The magnitude of the chemisorption during any given interval of time or at the end point of the reaction is seen to increase with temperature. Taking total active surface area as equal to that obtained from the amount of oxygen chemisorbed
FIG. 1. RATE OF CHEMISORPTION OF OXYGEN ON 1100°-OUTGASSED SUGAR CHARCOAL AT DIFFERENT TEMPERATURES BEFORE BURN OFF.
FIG. 2. RATE OF CHEMISORPTION OF OXYGEN ON 1100°C-OUTGASSED SUGAR CHARCOAL AT DIFFERENT TEMPERATURES AFTER 38 PERCENT BURN OFF.

AMOUNT (g) OF OXYGEN CHEMISORBED (mg/g) vs TIME (t) IN MINUTES

- 350°C
- 300°C
- 200°C
at 350°C in the manner discussed above, it can be shown that the fraction of the active surface covered at 200 and 300°C amounts to about 54 per cent and 82 per cent before as well as after the burn off. The increase in the amount of chemisorption of oxygen by the charcoal after 38 per cent burn off at each temperature, as can be seen on comparison of Figs. 1 and 2, therefore, appears to be due to introduction of new active surface area.

The Elovich equation, although empirical, has found wide applications in kinetic studies of chemisorption processes. According to this equation

\[ \frac{dq}{dt} = ae^{-\alpha q} \]  

...(i)

where \( a \) and \( \alpha \) are constants. In the integrated form, the equation may be put as:

\[ q = 2.3/\alpha \log (a \cdot t + 1) \]  

...(ii)

This indicates that a plot of \( q \) versus \( \log t \) should be a straight line.

The applicability of the equation was checked by plotting \( q \), the amount of oxygen chemisorbed against \( \log t \), as shown in Figs. 3 and 4. It is seen that the points fit on two straight lines of different slopes. This indicates that two different types of sites are involved in the process. In this connection, it may be noted that Walker, Bansal and Vastola (8) while studying chemisorption of oxygen on Graphon, of 16.6 per cent burn off, at room temperature but at increasing pressures found the Elovich
FIG. 3. $\varphi - \log t$ PLOTS FOR CHEMISORPTION OF OXYGEN ON 1100-OUTGASSED SUGAR CHARCOAL AT DIFFERENT TEMPERATURES BEFORE BURN OFF.
FIG. 4. $\tau - \log t$ PLOTS FOR CHEMISORPTION OF OXYGEN ON 1100°C-OUTGASSED SUGAR CHARCOAL AT DIFFERENT TEMPERATURES AFTER 38 PERCENT BURN OFF.
plots of their data at low pressures to fall on 5 different lines, indicating 5 different kinetic stages and the presence of 5 different sites. However, by plotting the data obtained at increasing pressures of oxygen, the number of such lines decreased and at a pressure of 760 torr there were only two lines of different slopes. This was explained as due to chemisorption at higher pressures being so rapid that the earlier stages pass almost instantaneously during the interval between the exposure of the carbon to oxygen and the first measurement. Similar observations were reported (9) during measurements at low oxygen pressures but at increasing temperatures. Since our experiments were carried out at oxygen pressure equal to the prevailing atmospheric pressure and at temperatures above 200°C, only two kinetic stages would be expected on analogy with the results obtained with Graphon. This is seen to be actually the case. Thus chemisorption of oxygen on charcoal appears to follow the same trends as reported for Graphon.

The rate of chemisorption is seen to decrease appreciably in moving from stage 1 to stage 2. The sites of type 2, therefore, appear to be less active than those of type 1.
By expressing the Elovich equation as:

\[ q = 2.3/\alpha \left( \log (t + t_0) - \log t_0 \right) \quad \text{(iii)} \]

where \( t_0 \) is another constant equal to \( 1/a^\alpha \), and by ignoring \( t_0 \) in those cases in which the plot of \( q \) against \( \log t \) is linear, Allardice (5) obtained the value of \( \alpha \) from the slope of the curve for his data on brown coal char. Walker, Bansal and Vastola (9) also used the same procedure for obtaining \( \alpha \) from their data on Graphon.

The values of \( \alpha \), calculated from the slopes of the linear plots in Figs. 3 and 4, are given in Table I. These are seen to be independent of temperature, as expected. The values, however, are lower, roughly half as small as those for brown charcoal (5) for the same pressure and temperature, but slightly higher than those for Graphon (9). Substituting the value of \( \alpha \) and various values of \( q \) and \( t \) in equation (ii), the initial rate constant 'a' at different temperatures was evaluated. The results, included in Table I, show that the initial rate constant rises appreciably with rise in temperature and, at a given temperature, it is more in the case of the activated sample obtained on 38 per cent burn off than in the ordinary sample without the burn off. However, the values are much lower than those reported for brown coal char (5) under similar conditions although appreciably higher than
Table I

Parameters in the Elovich equation for chemisorption of oxygen on 1100°-
outgassed sugar charcoal at different temperatures before and after
38 per cent burn off

<table>
<thead>
<tr>
<th>Temperature of treatment °C</th>
<th>Before burn off</th>
<th>After 38 per cent burn off</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First kinetic stage</td>
<td>Second kinetic stage</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>α</td>
</tr>
<tr>
<td></td>
<td>(mg./g.)</td>
<td><em>(mg./g.)</em></td>
</tr>
<tr>
<td></td>
<td>per min.</td>
<td><em>(per min.)</em></td>
</tr>
<tr>
<td>200</td>
<td>1.99</td>
<td>0.60</td>
</tr>
<tr>
<td>300</td>
<td>13.10</td>
<td>0.58</td>
</tr>
<tr>
<td>350</td>
<td>35.12</td>
<td>0.57</td>
</tr>
</tbody>
</table>
those reported for Graphon (9).

Activation energies of the chemisorption process on the two types of sites were obtained from Arrhenius plots (i.e., plot of log a against 1/T), as had been done by previous workers (5,9). The values for sites I and II were found to be 10.7 and 12.8 Kcal. respectively, before activation and 9.9 and 11.1 Kcal. after activation. These are of the same order as those reported by previous workers on Graphon (9) and brown coal char (6). Such low values have been explained (5) on the basis that oxygen is first physically adsorbed and then migrates along the surface to active sites where chemical interaction occurs. Since activation energy in the present investigations does not undergo any significant change after 38 per cent burn off of the sample, it appears that the mechanism of chemisorption, before as well as after 38 per cent burn off, is essentially the same.

Nature of the oxygen complexes formed

It was thought of interest to determine the form of disposition of the combined oxygen and to study a few characteristic properties of the oxidised carbon with a view to get some information regarding the nature of the oxygen complexes formed. For this purpose, the products obtained after completion of chemisorption at each temperature and, in some cases, after completion of the first kinetic stage and before the commencement of the second stage were examined. These
were allowed to cool in the reactor in an atmosphere of nitrogen and then transferred rapidly to small bottles flushed with nitrogen and stored in the same atmosphere till required for use in various experiments.

The amounts of carbon dioxide and carbon monoxide evolved at gradually increasing temperatures, by pumping out the gas evolved at any given temperature before raising the temperature of the furnace by the next 50°C, as mentioned before, are recorded in Table II. It is seen, in the first instance, that the value of oxygen as obtained directly in the chemisorption experiments agrees very well with that obtained as carbon monoxide and carbon dioxide in the evacuation experiments. It is seen, further, that the pattern of disposition of chemisorbed oxygen as carbon dioxide and carbon monoxide does not undergo much change after activation of the charcoal.

The ratio \( \frac{\text{CO}_2}{\text{CO}} \) is seen to be invariably \( > 1 \) at each temperature of chemisorption. However, the ratio decreases significantly with increasing temperature. These results indicate that although the complexes capable of evolving carbon dioxide and carbon monoxide are formed at all temperatures between 200 and 350°C, those capable of evolving carbon dioxide are formed more readily at lower temperatures and those capable of evolving carbon monoxide are formed more readily at higher temperatures.

The results of outgassing four samples in which chemisorption of oxygen was interrupted after completion of the first kinetic stage, given in Table III,
Chemisorption of oxygen on 1100°-outgassed sugar charcoal at different temperatures before and after 38 per cent burn off

<table>
<thead>
<tr>
<th>Temperature of treatment °C</th>
<th>* Amount of oxygen chemisorbed (mg./g.) before burn off</th>
<th>* Amount of oxygen chemisorbed (mg./g.) after 38 per cent burn off</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>* Obtained directly * Obtained by evacuation at 1100°C as:</td>
<td>* Obtained directly * Obtained by evacuation at 1100°C as:</td>
</tr>
<tr>
<td></td>
<td>* from chemisorption measurements * Total</td>
<td>* from chemisorption measurements * Total</td>
</tr>
<tr>
<td></td>
<td>* CO₂ * CO * Total</td>
<td>* CO₂ * CO * Total</td>
</tr>
<tr>
<td>200</td>
<td>12.5 8.2 3.9 12.1</td>
<td>17.9 10.9 6.9 17.8</td>
</tr>
<tr>
<td>300</td>
<td>20.2 12.0 8.6 20.6</td>
<td>25.4 14.6 10.6 25.2</td>
</tr>
<tr>
<td>350</td>
<td>24.0 13.2 10.9 24.1</td>
<td>32.0 16.8 15.4 32.2</td>
</tr>
</tbody>
</table>
### Table III

Disposition of chemisorbed oxygen at the first kinetic stage

<table>
<thead>
<tr>
<th>Temperature of treatment °C</th>
<th><em>Amount of oxygen chemisorbed (mg./g.)</em> before burn off</th>
<th><em>Amount of oxygen chemisorbed (mg./g.)</em> after 38 per cent burn off</th>
<th><em>Obtained directly</em> from chemisorption at 1200°C as</th>
<th><em>Obtained by evacuation</em> from chemisorption at 1200°C as</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>* Obtained directly* measurements</td>
<td>* CO₂ *</td>
<td>* CO *</td>
<td>* Total *</td>
</tr>
<tr>
<td>200</td>
<td>7.0 *</td>
<td>6.9</td>
<td>0.2</td>
<td>7.1</td>
</tr>
<tr>
<td>300</td>
<td>8.8</td>
<td>8.7</td>
<td>0.3</td>
<td>9.0</td>
</tr>
</tbody>
</table>
show that type I sites are involved largely in the formation of the complex or complexes capable of evolving carbon dioxide. Type II sites, therefore, by elimination, should be involved largely in the formation of the complex or complexes capable of evolving carbon monoxide.

The complexes which evolve carbon dioxide are generally considered to be acidic in nature and to have structures described variously as lactonic (13,14), carboxylic (11,14) or merely as an oxide film in which two oxygen atoms are linked per active surface carbon atom (15). Puri (16) has shown recently the possibility of formation of another complex, particularly in the case of outgassed carbons, which comes off as carbon dioxide but is non-acidic in nature. This complex, believed to be formed by chemisorption of oxygen at the unsaturated sites, as measured by bromine value (10), however, has a transitory existence, as on exhaustive treatment, either in oxygen gas at 400°C (17) or in oxidising solutions (18), it gradually changes into acidic CO₂-complex with appreciable gasification of the carbon. In the present case there was no sign of development of any acidity in any of the samples. The pH values in aqueous suspensions remained close to 7.4 as before and barium hydroxide values remained zero. This rules out formation of lactonic, carboxylic or any other acidic structure. It appears highly probable that the
CO₂-complex in the present case is formed through addition of oxygen at the unsaturated sites, a tentative mechanism for which had been suggested (16) as under:

\[
\begin{array}{c}
\text{C} \\
\text{C}
\end{array}
+ \text{O}_2 \rightarrow \begin{array}{c}
\text{C} \\
\text{C}
\end{array}
\]

This view receives support from almost an equivalent decrease in bromine value (Table IV) in all samples after surface oxidation. Since this complex is formed mostly at type I sites, as indicated earlier in this paper, it appears that these sites, which are relatively more active, are, in reality, the unsaturated sites as measured by bromine value (10).

It is interesting to note that since according to the mechanism of the formation of this complex, as mentioned above, one oxygen atom is fixed per active surface carbon atom, the calculation of active surface area based on the assumption of one oxygen atom per active carbon atom as suggested by Walker et al. (12) and as adopted in this paper also is not vitiated by any means.

As regards the nature of the complex that comes off as carbon monoxide, the possibilities are for the formation of some of phenolic, quinonic, ethereal or other yet unidentified groups. Since there is no change in acidity of carbons,
### Table IV

$\text{CO}_2$-evolved, base adsorption capacity and bromine values of $1100^\circ$-outgassed sugar charcoal after treatment with oxygen at different temperatures before and after 38 per cent burn off.

<table>
<thead>
<tr>
<th>Temperature of treatment (°C)</th>
<th><em>$\text{CO}_2$ evolved on the product</em> (m.e./100 g.)</th>
<th><em>Base adsorption capacity of the product</em> (m.e./100 g.)</th>
<th><em>Amount of non-acidic $\text{CO}_2$-complex formed</em> m.e./100 g.</th>
<th><em>Surface unsaturation (milliatoms of bromine/100 g.) Before treatment</em>*</th>
<th><em>Surface unsaturation (milliatoms of bromine/100 g.) After treatment</em>**</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>52</td>
<td>nil</td>
<td>52</td>
<td>391</td>
<td>336</td>
</tr>
<tr>
<td>300</td>
<td>75</td>
<td>nil</td>
<td>75</td>
<td>391</td>
<td>315</td>
</tr>
<tr>
<td>350</td>
<td>83</td>
<td>nil</td>
<td>83</td>
<td>391</td>
<td>307</td>
</tr>
<tr>
<td><strong>Before burn off</strong></td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>200</td>
<td>68</td>
<td>nil</td>
<td>68</td>
<td>405</td>
<td>335</td>
</tr>
<tr>
<td>300</td>
<td>92</td>
<td>nil</td>
<td>92</td>
<td>405</td>
<td>311</td>
</tr>
<tr>
<td>350</td>
<td>105</td>
<td>nil</td>
<td>105</td>
<td>405</td>
<td>298</td>
</tr>
<tr>
<td><strong>After 38 per cent burn off</strong></td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>
as already mentioned, the formation of phenols may be ruled out. The amounts of quinonic oxygen, as obtained from the uptake of hydrogen in sodium borohydride reaction (11), are recorded in Table V. These are seen to constitute only about half of the oxygen evolved as carbon monoxide. The rest of the oxygen fixed at type II sites may be present in some other form.
### Table V

**Breakup of chemisorbed oxygen evolved as CO on treatment of 1100°-outgassed sugar charcoal with oxygen at different temperatures before and after 38 per cent burn off**

<table>
<thead>
<tr>
<th>Temperature of Treatment°C</th>
<th>Before burn off</th>
<th>After 38 per cent burn off</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxygen evolved as CO-complex (mg./g.)</td>
<td>Quinonic (mg./g.)</td>
</tr>
<tr>
<td></td>
<td>(mg./g.)</td>
<td>(mg./g.)</td>
</tr>
<tr>
<td>200</td>
<td>3.9</td>
<td>2.0</td>
</tr>
<tr>
<td>300</td>
<td>8.6</td>
<td>4.4</td>
</tr>
<tr>
<td>350</td>
<td>10.9</td>
<td>5.5</td>
</tr>
</tbody>
</table>
REFERENCES


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