CHAPTER VI

Chemisorption of iodine by charcoals and carbon blacks on interaction with iodine in vapour and dissolved states

A number of studies on interactions of charcoals (1-5), activated carbons (5), carbon blacks (6-10) and graphitised blacks (7) with iodine in vapour (4,6,9) and dissolved states in aqueous (5,8) and non-aqueous (7,8) media have been reported in recent years. Watson and Parkinson (11), from a study of adsorption of iodine from aqueous solutions on a few carbon blacks, indicated possibility of chemisorption and chemical reaction. Puri and Singh (1), working with charcoals and aqueous iodine, observed not only a fairly large amount of adsorption but also appreciable conversion of iodine into hydroiodic acid, the magnitude of the conversion being more in the case of charcoals with acidic reactions. Puri and Bansal (8), later, working with carbon blacks, showed that adsorption of iodine from 0.3 N aqueous solution, using I⁻/I₂ ratio as 14:1, as well as from 0.3 N solutions in chloroform and benzene was almost fully reversible and was proportional to surface area of the black. Hill and Marsh (5), from a study of adsorption of iodine from aqueous solutions of varying iodine concentration and I⁻/I₂ ratio on
activated polyvinylidene chloride carbon and activated coconut charcoal, suggested that the correct isotherm must employ free and not total iodine concentration. Recalculation of Puri and Dansal's data in terms of free iodine concentration by Hill and Marsh gave isotherms very similar in shape to the nitrogen isotherms at 70K on various carbon blacks. Kipling, Sherwood and Shooter (10), and Kipling and Shooter (7), preferred the use of organic solvents in determining isotherms of iodine from solution phase so as to avoid complications caused by the presence of $I^{-}$ and $I_{3}^{-}$ ions in aqueous media. These workers, however, did not recommend the use of such isotherms for estimating surface areas of carbons in view of their findings that the magnitude of adsorption was influenced by the balance of three sets of interactions, namely, interaction of iodine with the surface, interaction of solvent with the surface and interaction of iodine with the solvent. Kipling and Shooter (7) observed a small amount of chemisorption of iodine from organic solvents on heterogeneous surfaces of carbon blacks like Spheron-6, but almost none on homogeneous blacks surfaces of like Graphon (7). The extent of chemisorption from solvents like cyclohexane, carbon tetrachloride, butyl alcohol or ethyl acetate was almost twice as much as from solvents like benzene and toluene. Kipling and Shooter also reported, in another publication (6), chemisorption of iodine from vapour phase on spheron-6. The amount of iodine chemisorbed, in this case, amounted to 20 mg. out of a total
adsorption of 132 mg./g. These workers were of the view that at least two types of sites were involved in the chemisorption of iodine (6) but they could not specify these sites nor suggested any distinction between them. The extent of chemisorption did not appear to correspond to the number of edge atoms of the crystallites although there was some correlation with the concentration of unpaired electrons. Garten and Weiss (12) studied a wider range of carbons and finding that there was no correlation between amount of iodine chemisorbed and the paramagnetism of the carbon, suggested that iodine was taken up by addition at the olefinic double bonds arising out of the quinone groups at sites where they can not participate in resonance. Kipling and Shooter, however, did not accept this view since the concentration of chemisorbed iodine on Sphonon-6 was lower than the probable concentration of quinone groups on this material.

It appears that there is need for further work on interaction of charcoal and carbon black with iodine from vapour as well as solution (aqueous and non-aqueous) phase. The present work was, therefore, undertaken. Sugar and coconut shell charcoals, described in the previous chapters, and six samples of carbon blacks, namely, Philblack-1, Sphonon-4, Sphonon-6, Mogul, ELF-0 and Mogul-A were used in the present investigations. Adsorption of iodine from vapour
phase was studied by passing a current of iodine vapour at the rate of 2 litres/hour on charcoal or carbon black (10 g. over-dried) for specified intervals of time and at specified temperatures varying from 200 to 500°C. There could be no physisorption of iodine under these conditions. The optimum temperature and optimum time for maximum fixation of iodine were ascertained from preliminary experiments on one of the charcoals and one of the carbon blacks and then the same conditions were used for the rest of the samples. The amount of iodine chemisorbed was obtained by heating the product in a current of hydrogen at 500°C and estimating hydrogen iodide evolved. The results were checked in a few cases and were found to be in close agreement with the values obtained by combustion (micro) analysis.

Adsorption isotherms (55°C) of iodine from aqueous solutions of varying I⁻/I₂ ratio, as well as from solutions in benzene and chloroform were also determined. The product, at the end of each isotherm, was washed with 0.1 N Na₂S₂O₃ to recover and estimate physically adsorbed iodine, as suggested by Kipling and Shooter (7). The residual iodine which could not be recovered by this procedure was obtained by heating the final product in a current of hydrogen and estimating hydrogen iodide evolved. The details of the various procedures are given in the experimental portion of the thesis.
The effects of temperature and time on the extent of chemisorption of iodine and formation of hydrogen iodide, using original sugar charcoal and spheron-4, are shown in Figs. 1 and 2, respectively. It is seen that 300°C is the optimum temperature for maximum fixation of iodine as well as for the formation of hydrogen iodide and that 5 hours treatment is necessary for completion of each reaction. The steep fall in the extent of chemisorption of iodine at temperatures exceeding 300°C appears to be due to instability of the carbon-iodine complex at higher temperatures. It may be recalled that fall in the extent of chemisorption of bromine was observed at temperatures close to 500°C (Chapter V, Fig. 1).

The amounts of iodine fixed and hydrogen iodide evolved on treating the various samples of charcoal and carbon black with iodine vapour under the optimum conditions specified above are recorded in Table I. It is seen, in the first instance, that only 2.5 per cent of initial hydrogen and not more than 8 per cent of content of a charcoaled carbon black can be changed into hydrogen iodide under the experimental conditions. The treatment with bromine vapour at 500°C, as shown in the previous chapter (cf. Table I, page 137), results in the conversion of about 50-75 per cent of hydrogen into hydrogen bromide. The
FIG. 1. EFFECT OF TEMPERATURE ON THE CHEMISORPTION OF IODINE AND FORMATION OF HYDROIODIC ACID ON TREATING ORIGINAL SUGAR CHARCOAL AND SPHERON-4 WITH IODINE FOR 5 HOURS.
FIG. 2. EFFECT OF TIME ON THE CHEMISORPTION OF IODINE AND FORMATION OF HYDROIODIC ACID ON TREATING ORIGINAL SUGAR CHARCOAL AND SPHERON-4 WITH IODINE AT 300°C.

- △ △ IODINE CHEMISORBED, ORIGINAL SUGAR CHARCOAL
- ○ ○ H₂ FORMED, ORIGINAL SUGAR CHARCOAL
- ▲ ▲ IODINE CHEMISORBED, SPHERON-4
- ● ● H₂ FORMED, SPHERON-4
Table I

Reaction of charcoal and carbon black with iodine at 300°C

<table>
<thead>
<tr>
<th>Description of the sample</th>
<th>Initial *</th>
<th>HI (free) *</th>
<th>Iodine fixed *</th>
<th>Hydrogen content *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar charcoal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original</td>
<td>3380</td>
<td>168</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>Outgassed at 400°</td>
<td>3000</td>
<td>58</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>&quot; 700°</td>
<td>2580</td>
<td>52</td>
<td>233</td>
<td></td>
</tr>
<tr>
<td>&quot; 1100°</td>
<td>1080</td>
<td>21</td>
<td>224</td>
<td></td>
</tr>
<tr>
<td>Coconut shell charcoal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original</td>
<td>2230</td>
<td>108</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Outgassed at 400°</td>
<td>2140</td>
<td>56</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>&quot; 700°</td>
<td>1010</td>
<td>48</td>
<td>231</td>
<td></td>
</tr>
<tr>
<td>&quot; 1100°</td>
<td>640</td>
<td>12</td>
<td>221</td>
<td></td>
</tr>
<tr>
<td>Carbon blacks</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Philblack-I</td>
<td>290</td>
<td>22</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Spheron-4</td>
<td>410</td>
<td>28</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Spheron-C</td>
<td>250</td>
<td>21</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Mogul</td>
<td>301</td>
<td>20</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>ELF-0</td>
<td>380</td>
<td>21</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Philblack-I, outgassed at 700°</td>
<td>175</td>
<td>14</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>Mogul, outgassed at 700°</td>
<td>221</td>
<td>15</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>ELF-0, outgassed at 700°</td>
<td>301</td>
<td>15</td>
<td>65</td>
<td></td>
</tr>
</tbody>
</table>
discrepancy is probably due to lower temperature of 300°C used in the case of treatment with iodine vapour and higher energy of activation of hydrogen-iodine reaction. The amount of iodine fixed on a given sample is also seen to be considerably less than that of bromine. This is particularly so in the case of the original and 400°C-outgassed charcoals in which hydrogen content was high. However, the differences narrow down considerably as the hydrogen content falls down on outgassing at increasing temperatures. It appears that hydrogen in charcoal or carbon black can not be substituted by iodine at 300°C so effectively as by bromine at 500°C. In this connection it may also be noted that whereas fixation of chlorine or bromine on charcoals decreases (cf. Tables II, III, IV, V of Chapter III and Table I of Chapter V), that of iodine increases on outgassing charcoals at increasing temperatures. This anomaly also arises from very low substitution of hydrogen by iodine at 300°C, the optimum temperature for maximum fixation of iodine.

The amounts of iodine fixed by addition at the unsaturated sites, as obtained from fall in bromine value, are given in Table II. It is seen that most of the iodine, except in the original sugar and coconut shell charcoals, is fixed by addition at these sites. The rest of the iodine may be taken as fixed in substitution for hydrogen, as before,
Table II

Amount of iodine fixed in relation to surface unsaturation by various samples of charcoal and carbon black on treatment with iodine at 300°C

<table>
<thead>
<tr>
<th>Description of the sample</th>
<th>Surface unsaturation (milliequivalents of bromine/100 g.)</th>
<th>Break up of chemisorbed iodine (milliequivalents/100 g.)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>* Before treatment</td>
<td>* After treatment</td>
<td>* Total iodine fixed</td>
</tr>
<tr>
<td>Sugar charcoal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original</td>
<td>31</td>
<td>nil</td>
<td>142</td>
</tr>
<tr>
<td>Outgassed at 400°C</td>
<td>271</td>
<td>157</td>
<td>165</td>
</tr>
<tr>
<td>&quot; 700</td>
<td>376</td>
<td>163</td>
<td>233</td>
</tr>
<tr>
<td>&quot; 1100</td>
<td>389</td>
<td>164</td>
<td>224</td>
</tr>
<tr>
<td>Coconut shell charcoal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original</td>
<td>38</td>
<td>10</td>
<td>102</td>
</tr>
<tr>
<td>Outgassed at 400°C</td>
<td>201</td>
<td>98</td>
<td>126</td>
</tr>
<tr>
<td>&quot; 700</td>
<td>289</td>
<td>81</td>
<td>231</td>
</tr>
<tr>
<td>&quot; 1100</td>
<td>291</td>
<td>69</td>
<td>221</td>
</tr>
</tbody>
</table>

Table continued on next page
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<th></th>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Philblack-I</td>
<td>35</td>
<td>nil</td>
<td>46</td>
<td>35</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Spheron-4</td>
<td>59</td>
<td>10</td>
<td>59</td>
<td>49</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Spheron- C</td>
<td>60</td>
<td>10</td>
<td>60</td>
<td>50</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Mogul</td>
<td>10</td>
<td>nil</td>
<td>15</td>
<td>10</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>ELF-0</td>
<td>19</td>
<td>nil</td>
<td>18</td>
<td>12</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Philblack-I, outgassed at 700°</td>
<td>72</td>
<td>nil</td>
<td>71</td>
<td>71</td>
<td>nil</td>
<td></td>
</tr>
<tr>
<td>Mogul, outgassed at 700°</td>
<td>78</td>
<td>nil</td>
<td>77</td>
<td>77</td>
<td>nil</td>
<td></td>
</tr>
<tr>
<td>ELF-0, outgassed at 700°</td>
<td>67</td>
<td>nil</td>
<td>65</td>
<td>65</td>
<td>nil</td>
<td></td>
</tr>
</tbody>
</table>
The view of Kipling and Shooter (7) that there are at least two types of sites where chemisorption of iodine takes place seems to be substantiated. In fact, the present work indicates that there are also two distinct types of mechanisms by which iodine is chemisorbed on charcoals and carbon blacks. It also appears reasonable to conclude that double bond sites constitute one type and the edge carbon atoms associated with hydrogen constitute the second type of sites concerned in chemisorption of iodine.

As regards the genesis of the double bond sites it may be noted that the results do not support the view of Garten and Weiss that these arise from the presence of quinonic oxygen, since there is hardly any difference in the extent of chemisorption of iodine on 700°-outgassed sugar charcoal, which contained 4.6 per cent of oxygen, and 1100°-outgassed sugar charcoal, which was essentially free from oxygen. It may be recalled that according to Puri et al. (13,14), the unsaturation arises from the elimination of CO₂-complex which commences on outgassing at about 400°C and gets completed at temperatures around 700°C. This explains why the amounts of iodine chemisorbed on 700° and 1100° outgassed charcoals are of about the same order.
The experiments were then conducted with iodine dissolved in water. Charcoal or carbon black (1 g. oven-dried) was mixed with 100 ml. of solution in every case. The effect of using different $I^-/I_2$ ratio was studied first. The results obtained in the case of a few samples of charcoal and carbon black are plotted in Fig. 3. It is seen that the extent of adsorption decreases with increase in the ratio but tends to acquire a constant value when the ratio is 14:1 or more, as has been reported and discussed previously by Puri and Bansal (8). The $I^-/I_2$ ratio for maximum adsorption was found to be 3:1. The effect of concentration of iodine, keeping the ratio $I^-/I_2$ as 3:1, on the extent of adsorption on a few samples of charcoal and carbon black, is shown in Fig. 4. It is seen that maximum values are obtained with 0.3 N solution and that there is hardly any change on raising the concentration thereafter. The effect of time of contact, using 0.3 N solution, is shown in Fig. 5. It appears that 70 hours of contact is sufficient to get the ultimate value in all cases, although in some cases even 30 hours of contact is sufficient for the purpose.

The effects of concentration of iodine solution in benzene and time of contact on the extent of adsorption, using some of the carbons, are shown in Figs. 6 and 7, respectively. It is seen, again, that 0.3 N solution of iodine is the
FIG. 3. ADSORPTION OF IODINE BY CHARCOAL AND CARBON BLACK FROM AQUEOUS SOLUTIONS (0.3N) WITH DIFFERENT 3:4 RATIOS.

TIME OF CONTACT = 70 HOURS

- ▲ ORIGINAL SUGAR CHARCOAL
- ○ 700°-OUTGASSED SUGAR CHARCOAL
- ■ MOGUL-A
- • 700°-OUTGASSED MOGUL-A

IODINE ADSORBED (MILLIATOMS/g)

0 5 10 15 20
3:4 RATIO

FIG. 4. EFFECT OF CONCENTRATION ON ADSORPTION OF IODINE BY CHARCOAL AND CARBON BLACK FROM AQUEOUS SOLUTION 3:4 = 3:1.

TIME OF CONTACT = 70 HOURS

- ▲ ORIGINAL SUGAR CHARCOAL
- ○ 700°-OUTGASSED SUGAR CHARCOAL
- ■ MOGUL-A
- • 700°-OUTGASSED MOGUL-A

IODINE ADSORBED (MILLIATOMS/g)

0 0.1 0.2 0.3 0.4 0.5 N
NORMALITY OF IODINE SOLUTION
FIG. 5. EFFECT OF TIME OF CONTACT ON ADSORPTION OF IODINE BY CHARCOAL AND CARBON BLACK FROM AQUEOUS SOLUTION (0.3N I$_2$ 3:1)

- △△△ ORIGINAL SUGAR CHARCOAL
- ○○○ 700° OUTGASSSED SUGAR CHARCOAL
- ××× MOGUL-A
- ••• 700° OUTGASSSED MOGUL-A

IODINE ADSORBED (MILLIATOMS/g.)

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140

TIME (HOURS)
FIG. 6. EFFECT OF CONCENTRATION ON ADSORPTION OF IODINE BY ORIGINAL CHARCOALS FROM BENZENE SOLUTION.
FIG. 7. EFFECT OF TIME OF CONTACT ON ADSORPTION OF IODINE BY ORIGINAL CHARCOALS FROM BENZENE SOLUTION (0.3N).

- ORIGINAL SUGAR CHARCOAL
- ORIGINAL COCONUT SHELL CHARCOAL

IODE ASOBERED (MILLIATOMS/2)

0 5 10 15 20
TIME IN DAYS
optimum concentration for maximum adsorption. The process, however, now seems to be very slow as the value continues to rise with the time of contact and attains the final value after 15 days.

The results of similar experiments on the same carbon using iodine solutions in chloroform are plotted in Figs.8 and 9. It is seen that in this case too, the use of 0.3 N solution and 15 days of contact are required for getting maximum values.

The total amount of iodine uptake by the various samples of charcoal and carbon black using solutions in water, chloroform and benzene under the optimum conditions mentioned above, and its break up into physisorption and chemisorption are given in Table III. In the case of aqueous solutions, some of the iodine was hydrolysed to hydroiodic acid also. These values are given in a separate column.

Considering the results from aqueous solutions, in the first instance, it is seen that the extent of adsorption on a given sample of charcoal or carbon black increases on outgassing the carbon at increasing temperatures and that most of the increase is due to increase in chemisorption rather than due to increase in physisorption.

The amount of iodine physically adsorbed in most cases from solution in chloroform is higher than that from
FIG. 8. EFFECT OF CONCENTRATION ON ADSORPTION OF IODINE BY ORIGINAL CHARCOALS FROM CHLOROFORM SOLUTION.

- O - - - O - ORIGINAL SUGAR CHARCOAL
- △ - - - △ - ORIGINAL COCONUT SHELL CHARCOAL

IODINE ABSORBED (MILLIATOMS/g)

NORMALITY OF IODINE SOLUTION

0 0.1 0.2 0.3 0.4 0.5

0 1 2 3
FIG. 9. EFFECT OF TIME OF CONTACT ON ADSORPTION OF IODINE BY ORIGINAL CHARCOALS FROM CHLOROFORM SOLUTION.

- ORIGINAL SUGAR CHARCOAL
- ORIGINAL COCONUT SHELL CHARCOAL

IODINE ADSORBED (MILLIATOMS/g)

TIME IN DAYS
Table III

Interaction of charcoals and carbon blacks of different surface areas with iodine solutions in water, chloroform and benzene.

<table>
<thead>
<tr>
<th>Description of the sample</th>
<th>Amount of iodine formed</th>
<th>Amount adsorbed</th>
<th>Amount adsorbed</th>
<th>Total Amount adsorbed</th>
<th>Amount chemisorbed</th>
<th>Amount physisorbed</th>
<th>Total Amount physisorbed</th>
<th>Surface area (nitrogen)</th>
<th>Surface area</th>
<th>Amount iodine from vapour phase</th>
<th>Amount iodine from aqueous solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar charcoal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Original</td>
<td>1.70</td>
<td>2.95</td>
<td>2.20</td>
<td>0.75</td>
<td>3.05</td>
<td>2.35</td>
<td>0.70</td>
<td>1.90</td>
<td>1.20</td>
<td>0.70</td>
<td>1.42</td>
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<tr>
<td>Outgassed at 400°</td>
<td>0.70</td>
<td>3.05</td>
<td>1.85</td>
<td>1.20</td>
<td>3.40</td>
<td>2.30</td>
<td>1.10</td>
<td>2.20</td>
<td>1.10</td>
<td>1.10</td>
<td>1.65</td>
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<tr>
<td>&quot; &quot; 700 nil</td>
<td>4.10</td>
<td>1.80</td>
<td>2.30</td>
<td>4.50</td>
<td>2.30</td>
<td>2.20</td>
<td>3.55</td>
<td>1.35</td>
<td>2.20</td>
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<td></td>
<td></td>
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<tr>
<td>Original</td>
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<td>2.85</td>
<td>2.05</td>
<td>0.80</td>
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<td>1.95</td>
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<td>0.90</td>
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<td>0.95</td>
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<td>1.60</td>
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<td>1.05</td>
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Table III continued

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<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon blacks</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Philblack-I</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td>nil</td>
<td>1.15</td>
<td>0.95</td>
<td>0.70</td>
<td>1.25</td>
<td>1.15</td>
<td>0.10</td>
<td>0.65</td>
<td>0.45</td>
<td>0.20</td>
<td>-</td>
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<td>1.25</td>
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<td>0.25</td>
<td>1.35</td>
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<td>0.71</td>
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<tr>
<td>Original</td>
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<td>2.15</td>
<td>2.05</td>
<td>0.10</td>
<td>2.20</td>
<td>2.10</td>
<td>0.10</td>
<td>1.25</td>
<td>1.15</td>
<td>0.10</td>
<td>0.15</td>
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<td>2.50</td>
<td>2.10</td>
<td>0.40</td>
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<td>1.10</td>
<td>0.30</td>
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<td>304</td>
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<td>&quot; * 700</td>
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<td>2.70</td>
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<td>0.50</td>
<td>1.80</td>
<td>1.16</td>
<td>0.70</td>
<td>0.77</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original</td>
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<td>1.50</td>
<td>1.40</td>
<td>0.10</td>
<td>1.55</td>
<td>1.45</td>
<td>0.10</td>
<td>1.05</td>
<td>0.95</td>
<td>0.10</td>
<td>0.18</td>
<td></td>
<td>177</td>
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<td>Outgassed at 400°</td>
<td>0.05</td>
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<td>1.40</td>
<td>0.25</td>
<td>1.75</td>
<td>1.45</td>
<td>0.30</td>
<td>1.20</td>
<td>0.90</td>
<td>0.30</td>
<td>-</td>
<td>174</td>
<td></td>
</tr>
<tr>
<td>&quot; * 700</td>
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<td>2.01</td>
<td>1.45</td>
<td>0.50</td>
<td>1.90</td>
<td>1.40</td>
<td>0.50</td>
<td>1.45</td>
<td>0.90</td>
<td>0.55</td>
<td>0.65</td>
<td>173</td>
<td></td>
</tr>
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</table>
solution in water or benzene. This appears to be due to much lower solute-solvent interaction in chloroform than in water (due to the presence of iodide ion) or in benzene (in which iodine is more soluble than in chloroform) (7).

The nitrogen surface areas of the various samples are recorded in the last column of Table III. It is seen that although surface areas of sugar and coconut shell charcoals do not undergo any noticeable change on outgassing at various temperatures, the extent of physisorption from aqueous phase, generally, tends to decrease with increase in the temperature of outgassing. In such cases, therefore, the extent of physisorption of iodine cannot serve as a reliable index of surface area. The conversion of a part of iodine into hydroiodic acid in this case also complicates the issue. The values of physisorption from solutions in chloroform and to some extent those from solutions in benzene, however, do not undergo much change on evacuation. The amounts of iodine physically adsorbed from chloroform and benzene solutions on the various samples of charcoal and carbon black are plotted against respective surface areas in Fig. 10. It is seen that the points fit around a straight line, more so in the case of solutions in chloroform.

The extent of chemisorption of iodine on a given charcoal or carbon black is seen to increase on outgassing
FIG. 10. PHYSISORPTION OF IODINE FROM SOLUTIONS IN CHLOROFORM AND BENZENE ON CHARCOALS AND CARBON BLACKS IN RELATION TO THEIR SURFACE AREA.
at increasing temperatures. This is to be expected on account of creation of additional unsaturated sites, as expected in view of the results obtained with iodine vapour, as already discussed. It is significant to note that the amount of iodine chemisorbed on a given charcoal or carbon black, original or outgassed, is of the same order from each solvent. This gives strong indication of the fact that chemisorption is taking place at specified sites and that it proceeds, more or less equally, from all solvents irrespective of their nature.

The amounts of iodine chemisorbed on the same carbons from vapour phase at 300°C, given in Table I and reproduced in a separate column in Table III for the sake of ready reference, are seen to be higher than the corresponding values obtained from the various solvents used. This may be, partly at least, due to the higher temperature of 300°C used during the interaction with iodine vapour, since chemisorption processes, like most chemical reactions, are, generally, of activated type. It may be noted, however, that even the maximum value of chemisorption of iodine falls short of the total unsaturation available (cf. Table II, col. 2) for such fixations in a given sample.

Stability of carbon-iodine complex

The carbon-iodine surface complex does not appear to be as stable as the corresponding carbon-bromine or carbon-chlorine surface complex. A considerable fraction of the
combined iodine could be recovered as iodide ion on refluxing with sodium hydroxide solutions of increasing concentrations, as shown in Table IV. The maximum fraction of iodine recovered using 2.5 N sodium hydroxide is seen to be of the order of 80 per cent in the original charcoal, but only about 40 per cent in the outgassed charcoals. This shows that iodine fixed at the unsaturated sites, which predominates in outgassed samples, is more firmly held than that fixed by substitution process which predominates in the original samples (cf. Table II, col. 5). The results with carbon blacks point to similar conclusions.

The amounts of iodine recovered on heating some of the products in vacuum at increasing temperatures are recorded in Table V. It is seen that unlike combined bromine and chlorine which do not come off in the elementary state to any appreciable extent, the combined iodine comes off very largely in the elementary state and to a relatively small extent as hydrogen iodide. The process of elimination of combined iodine commences even at 200°C and gets almost completed at 500°C.

Adsorption isotherms of water vapour

The water vapour adsorption isotherms (35°C) on 700°C-outgassed sugar charcoal, before and after fixation of different amounts of iodine, are plotted in Fig.11. The
FIG. II. WATER VAPOUR ADSORPTION ISOTHERMS (35°C) ON 700°C-OUTGASSED SUGAR CHARCOAL BEFORE AND AFTER FIXATION OF VARYING AMOUNTS OF IODINE.

1. BEFORE FIXATION OF IODINE
2. AFTER FIXATION OF IODINE: 1.96 MILLIATOMS/100G
3. " " " : 191 "
4. " " " : 233 "

RELATIVE VAPOUR PRESSURE

AMOUNT OF WATER ADSORBED (g/100g)

RELATIVE VAPOUR PRESSURE
Table IV

Iodine fixed by charcoal and carbon black on treatment with iodine at 300° C and recovered as iodide ion on refluxing with sodium hydroxide solutions of increasing concentrations

<table>
<thead>
<tr>
<th>Description of the sample</th>
<th>Iodine fixed (milligrams/100 g.)</th>
<th>Iodine recovered as I⁻ ion (milligrams/100 g.) on refluxing with sodium hydroxide solution *1.5 N *2.5 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar charcoal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original</td>
<td>142</td>
<td>40</td>
</tr>
<tr>
<td>Outgassed at 700°</td>
<td>233</td>
<td>38</td>
</tr>
<tr>
<td>&quot; 1100</td>
<td>234</td>
<td>31</td>
</tr>
<tr>
<td>Coconut shell charcoal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original</td>
<td>102</td>
<td>51</td>
</tr>
<tr>
<td>Outgassed at 700°</td>
<td>231</td>
<td>35</td>
</tr>
<tr>
<td>Outgassed at 1100</td>
<td>221</td>
<td>38</td>
</tr>
<tr>
<td>Carbon blacks</td>
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<td></td>
</tr>
<tr>
<td>Philblack-I</td>
<td>46</td>
<td>7</td>
</tr>
<tr>
<td>Spheron-4</td>
<td>59</td>
<td>8</td>
</tr>
<tr>
<td>Spheron-C</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>Mogul</td>
<td>35</td>
<td>nil</td>
</tr>
</tbody>
</table>
Table V

Decomposition of carbon-iodine surface complex, formed on treatment of charcoals with iodine at 300°, on heating in vacuum at different temperatures

<table>
<thead>
<tr>
<th>Description of the sample</th>
<th>Iodine (milli- atoms/100 g.)</th>
<th>Amount of iodine (milli- atoms/100 g.) described as free iodine or as hydrogen iodide on degassing at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fixed</td>
<td>200</td>
</tr>
<tr>
<td>(milli- atoms/100 g.) free</td>
<td>As</td>
<td>As</td>
</tr>
<tr>
<td>HI</td>
<td>Total</td>
<td>free</td>
</tr>
<tr>
<td>I₂</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

Sugar charcoal

| Original | 142 | 15 | 11 | 26 | 40 | 10 | 50 | 66 | 35 | 101 | 104 | 40 | 144 |
| Outgassed at 700° | 233 | 5 | 5 | 10 | 38 | 10 | 48 | 90 | 21 | 118 | 200 | 29 | 229 |
| " 1100 | 224 | 11 | nil | 11 | 34 | 5 | 39 | 99 | 5 | 104 | 211 | 16 | 227 |

Coconut shell charcoal

| Original | 102 | 10 | 19 | 29 | 20 | 18 | 38 | 45 | 24 | 69 | 74 | 30 | 104 |
| Outgassed at 700° | 231 | 8 | nil | 8 | 26 | 10 | 36 | 100 | 21 | 121 | 206 | 22 | 228 |
| " 1100 | 221 | 6 | nil | 6 | 36 | 5 | 41 | 110 | 10 | 120 | 209 | 13 | 222 |

* Values are cumulative
effect of fixation of iodine in narrowing down of capillary pores is seen to be even greater than that of fixation of bromine. This is to be expected in view of the larger molecular diameter of iodine.

The effect is seen to increase with increase in the amount of iodine fixed.
REFERENCES