The present work was undertaken with a view to study chemisorption of oxygen, chlorine, bromine and iodine, from gaseous as well as dissolved states, on carbons. The adsorbent carbons used were charcoals, prepared by the carbonisation of cane sugar and coconut shells as well as the materials derived from them on outgassing at different temperatures up to 1200°C, and a few samples of commercial carbon blacks.

Chemisorption kinetics of oxygen on an ash-free outgassed sugar charcoal, before and after 38 per cent burn-off in oxygen at 650°C, at 200, 300 and 350°C under oxygen pressure of one atmosphere were studied. The surface area (nitrogen) of the charcoal was 442 m²/g. before the burn-off and 496 m²/g. after the burn-off. The 'active' surface area, as obtained from the amount of oxygen chemisorbed at 350°C assuming one oxygen atom to be fixed per active surface carbon atom occupying area of 8.3 Å², was found to be 16.9 per cent and 20.1 per cent of the total surface area before and after the burn-off, respectively.

The data has been found to follow the Elovich equation. The plots of q versus log t have been found to fit on two straight lines of different slopes indicating two different stages of chemisorption involving two different types of sites.
The rate of chemisorption decreases appreciably in moving from stage 1 to stage 2. The initial rate constant of each stage rises appreciably with rise in temperature and is appreciably higher in the activated sample than in the ordinary sample. Activation energies, obtained from Arrhenius plots, are rather low, varying between 9.9 and 10.7 Kcal. for the first stage and between 11.1 and 12.8 Kcal. for the second stage. The chemisorbed oxygen has been found to come off almost entirely as carbon dioxide and carbon monoxide on evacuating the products at high temperatures. The ratio $\text{CO}_2/\text{CO}$, although remaining invariably $>1$, decreases to some extent with increase in the temperature of chemisorption. The results indicate that Type 1 sites, which are relatively more active, are, in reality, unsaturated sites and that the oxygen chemisorbed at these sites comes off largely as carbon dioxide. This oxygen, however, does not impart acidity to carbons and, therefore, gives rise to what is known in the literature as non-acidic CO$_2$-complex. The oxygen chemisorbed at Type 2 sites comes off largely as carbon monoxide. Nearly half of this oxygen seems to be present as quinonic oxygen, as determined by sodium borohydride reaction.

Heats of combustion of charcoals and carbon blacks coated with varying amounts of different oxygen complexes have been determined and, assuming that formation of these complexes are preceding steps leading towards combustion, heats of formation of the various complexes have been
calculated, applying Hess's Law. The data obtained have been used in evaluating bond energies associated with the various complexes in order to obtain some evidence for various structural models of the complexes about which opinions differ widely at present. The heat of formation of the acidic CO₂-complex has been found to be -77.9 Kcal./mole and this suggests that formation of this complex represents a fairly advanced stage in the process of combustion, the enthalpy change for which is -94.2 Kcal. The bond energies associated with this complex, as calculated from the relevant thermochemical data, amount to -204 Kcal./mole. This permits checking of some of the structural models proposed for this complex.

The heat of formation of the complex capable of evolving carbon monoxide and retained on charcoals and carbon blacks outgassed at 750°C has been found to be -64.2 Kcal./mole. The bond energy associated with this complex works out to be -91.1 Kcal. which lies in between the bond energies associated with C = O bond in quinones (viz., -150 Kcal.) and R-O-R bond in ethers (viz., -47 Kcal).

The heat of formation of non-acidic CO₂-complex, which has been shown by Puri and Sharma to precede the formation of the acidic CO₂-complex, has been found to be -44.3 Kcal. This value, as expected, is appreciably lower than that for the acidic CO₂-complex, viz., -77.9 Kcal. The bond energy
associated with this complex has been calculated to be -170 Kcal. which is not very far from the value obtained on the basis that this complex comes into existence through chemisorption of oxygen at the unsaturated sites present on carbon surfaces.

Chemisorption of oxygen and chlorine, singly as well as jointly, at the optimum temperature of 450°C, and under pressure equal to the atmospheric pressure, on various samples of charcoal and carbon black have been studied. Chemisorption of oxygen generally increases while that of chlorine decreases on outgassing charcoals at increasing temperatures. This appears to be due to creation of unsaturated sites where oxygen and chlorine are chemisorbed in competition with each other and elimination of combined hydrogen which provides suitable sites for chemisorption of chlorine. The chemisorbed oxygen comes off, on outgassing, mostly as carbon dioxide and carbon monoxide and to a small extent as water vapour.

The amount of oxygen chemisorbed on carbon blacks has been found to be a function of surface area and initial oxygen status of the black - the lower the initial oxygen status per unit surface the greater the chemisorption. After chemisorption, the final oxygen content per unit surface, in most cases, appears to correspond to 0.01 milli g.atoms/m² of surface. The chemisorption of chlorine, however, does not show any such relation with surface area.
It has been shown that oxygen and chlorine are chemisorbed simultaneously whenever a charcoal or carbon black is exposed to a combined atmosphere of oxygen and chlorine at 450°C. The extent of chemisorption of each gas increases with increase in its partial pressure in the mixture. At equal partial pressures, the extent of chemisorption of oxygen is more than that of chlorine. It has also been found that the total uptake of oxygen and chlorine from oxygen-chlorine mixture of any proportion, on a given sample of charcoal or carbon black, is invariably higher than the uptake of oxygen and chlorine alone on exposure to pure oxygen or pure chlorine. This shows that apart from certain common sites where oxygen and chlorine might be competing with each other for fixation there may be some other sites as well where chemisorption of oxygen and chlorine might be taking place independently of each other. Further examination indicates that the common sites referred to above are the unsaturated ethylenic double bond sites and that, apart from these sites, oxygen is fixed also at certain other sites where formation of phenolic, quinonic and acidic CO₂-complex is possible and chlorine at those sites where substitution of combined hydrogen is possible.

The fixation of oxygen enhances sorption of water vapour on charcoal appreciably at all relative vapour pressures. This appears to be due to interaction of water vapour at the oxyge-containing sites, probably due to a mechanism involving
hydrogen bonding. The fixation of chlorine, on the other hand, causes only a small increase in the sorption of water vapour at lower relative vapour pressures and a decrease at higher relative vapour pressures. This indicates alteration in the size-distribution of capillary pores in charcoal, resulting in an increase in the number of smaller capillary pores and a decrease in the number of larger capillary pores.

Interaction of charcoals and carbon blacks with aqueous chlorine at ordinary temperature has been investigated. The chlorine solution (\(~0.05\, N\)) was renewed after every 24 hours of contact and this was continued for 12 days. It is observed that the interaction involves chemisorption of oxygen as well as chlorine. The total uptake of oxygen increases while that of chlorine decreases as charcoal is outgassed at increasing temperatures.

Interaction of charcoals or carbon blacks with \(\text{H}_2\text{O}_2\)-HCl mixture in the presence of acetic acid involves not only chemisorption of chlorine, as has been considered hitherto, but simultaneously that of oxygen as well. The uptake of oxygen, in fact, has been found to be higher than that of chlorine in the case of carbon blacks as well as charcoals outgassed at high temperatures. The oxygen chemisorbed during the interaction with aqueous chlorine has been found to come off very largely and that during the interaction with \(\text{H}_2\text{O}_2\)-HCl mixture almost entirely as carbon dioxide. The \(\text{CO}_2\)-complex
formed is acidic in case of the original charcoals as well as carbon blacks, like ELF-0, which had not been subjected to high temperature-treatment during their preparation. The complex, however, is partly non-acidic in case of the charcoals outgassed at high temperatures as well as carbon blacks, like Philblack-A, Philblack-E, Statex-B, Spheron-4 etc., which had been subjected to high temperature-treatment in the course of their preparation. It appears that heating at high temperatures results in decreasing the number of active centres where fixation of oxygen can take place as acidic CO₂-complex and in creating unsaturated sites where fixation of oxygen can take place as non-acidic CO₂-complex.

The results indicate again that chlorine is fixed partly by addition at the unsaturated sites and partly in substitution of combined hydrogen.

Interaction of carbons with bromine vapour has been found to involve formation of hydrogen bromide as well as chemisorption of the halogen, the optimum temperature being 500°C. In the case of charcoals, the amount of hydrogen bromide formed is considerably in excess of the amount of bromine fixed indicating that only a small fraction of the hydrogen eliminated during the process can be substituted by bromine. This may be due to inaccessibility of bromine to some of the hydrogen-containing sites located within the minute
capillary pores of charcoal. In the case of carbon blacks which are essentially non porous, however, the amount of hydrogen bromide formed is fairly close to the amount of bromine fixed. There is evidence to show that bromine is fixed by addition as well as substitution processes and that whereas the former process predominates in charcoals, the latter predominates in carbon blacks.

Carbon-bromine surface complex has been found to be less stable than the corresponding carbon-chlorine surface complex. On refluxing the products with a concentrated solution (2.5 N) of sodium hydroxide, nearly 20-40 per cent of the combined bromine, depending upon the nature of the sample used, could be recovered as bromide ion. On evacuating the products at gradually increasing temperatures, the evolution of bromine as hydrogen bromide, presumably by combination with the residual hydrogen contained in the products, commences in small amounts at 200°C and becomes appreciable at 600°C. The entire amount of bromine, however, can not be recovered even on raising the temperature to 1200°C. Nearly 10 per cent by weight of the combined bromine in the case of charcoals and 45 per cent in the case of carbon blacks, which were deficient in hydrogen, remained intact even on prolonged evacuation at 1200°C.

The fixation of bromine alters the shape of water vapour adsorption isotherms (35°C), shifting it upward at lower
relative vapour pressures and downward at higher relative vapour pressures. This appears to be due to narrowing down of capillary pores as a result of which there is increase in the number of smaller capillary pores and decrease in the number of larger capillary pores. There is no evidence for any chemical or quasi-chemical interaction between water vapour and brominated sites on the carbon surface. The narrowing down of capillary pores was checked by studying methanol adsorption isotherms (35°C). Methanol molecules, being larger than water molecules, could find even smaller access to micro-capillary pores, and the effect increased with increasing fixation of bromine.

Interaction of charcoals and carbon blacks with iodine vapour at different temperatures results in the formation of hydrogen iodide and chemisorption of iodine. The optimum temperature for the maximum fixation of iodine is 300°C. The value starts decreasing sharply if the temperature is raised above 300°C, due to instability of the carbon-iodine surface complex. The amount of iodine fixed, on a given sample, has been found to be considerably less than that of either bromine or chlorine. The amount of combined hydrogen changing into hydrogen iodide represents only 2-5 per cent of the total in the case of charcoals and up to 8 per cent in the case of carbon blacks. These values are considerably lower than those observed in the formation of hydrogen bromide during the interaction with bromine vapour. The reason appears to
lie in the higher activation energy of hydrogen-iodine reaction and also smaller accessibility of iodine to some of the hydrogen-containing sites.

There is evidence to show that iodine is fixed largely by addition at the unsaturated sites and only to a small extent by substitution for hydrogen. The amount fixed, however, is so small that it cannot even cover up all the unsaturated sites available in a given sample. The view of some workers that the unsaturated sites for fixation of iodine arise from the presence of quinonic oxygen at sites where they cannot participate in resonance is not substantiated since the amount of iodine chemisorbed on 700°-outgassed charcoals, which retain appreciable amounts of quinonic oxygen, is of the same order as on 1100°-outgassed charcoals, which are essentially free of oxygen.

Interaction with dissolved iodine in water, chloroform and benzene solutions results in physisorption (i.e., reversible adsorption) as well as chemisorption. The optimum concentration of the solution for maximum total adsorption has been found to be 0.3 N in every solvent. The optimum $I^-/I_2$ ratio in the case of aqueous solutions has been found to be 3:1. The time of contact has been found to be about 3 days in the case of aqueous solutions.
and about 15 days in the case of chloroform and benzene solutions. The extent of reversible adsorption on a given sample varies with the nature of the solvent, depending upon the intensity of interaction of iodine with the solvent itself. This interaction is much weaker in the case of chloroform and therefore the magnitude of physisorption on a given sample of charcoal or carbon black is much more from chloroform solution than that from water or benzene solution. The extent of physisorption, from a given solution, seems to be a function of surface area, more so in the case of carbon blacks than in the case of charcoals.

The extent of chemisorption of iodine on a given charcoal or carbon black, however, seems to be almost independent of the nature of the solvent used.

The carbon-iodine surface complex is not as stable as the corresponding carbon-bromine or carbon-chlorine surface complex. A much larger fraction of the combined iodine than that of the combined bromine or chlorine can be recovered as iodide ion on refluxing with a concentrated solution (2.5 N) of sodium hydroxide. Also unlike combined bromine or chlorine, the combined iodine can be recovered considerably even in the elementary state and to a relatively small extent as hydrogen iodide on evacuating the products at gradually increasing temperatures. The process of elimination in this manner gets almost completed
even at such a low temperature as $500^\circ$ C.

The fixation of iodine produces a considerable narrowing down of capillary pores as indicated by adsorption isotherms of water vapour ($35^\circ$C) on charcoals before and after fixation of iodine.