Experimental
EXPERIMENTAL

Materials

Charcoal used mostly in these investigations was prepared by the carbonisation recrystallised cane sugar on the addition of concentrated sulphuric acid, followed by repeated washings with hot distilled water till free of sulphate ions. For some of the experiments, charcoals prepared by the carbonisation of coconut shells, pine wood and cotton stalks (cut into small pieces), in a limited supply of air at 350°, were also used. The chars were well ground and passed through a 400 mesh sieve.

Sugar charcoal was almost free of ash while coconut, pine wood and cotton stalk charcoals were 'deashed' by extracting with hydrofluoric acid. The ash content was thus lowered to about 0.14 per cent.

It has been shown (1) that charcoal, when freshly prepared and not given any treatment, contains a partially oxidised surface. The oxide layer extends further, slowly on exposure to air but rapidly on exposure to oxygen, to about the same limiting value. In order to complete surface oxidation, therefore, charcoals were allowed to remain in contact with oxygen for 12 hours.

These samples are referred to as 'original charcoals' in the text.
A few samples of commercial carbon blacks as received from Mr. M.L. Studebaker of Philips Petroleum Co., U.S.A. were also used in these investigations.

Evacuation of charcoal at different temperatures

The original samples, prepared as above, were outgassed at various temperatures up to 1000° in a resistance tube furnace, the temperature of which could easily be varied by varying the voltage applied to the coil terminals by means of a variac transformer.

About 10 g. charcoal was spread into a thin layer about 10 inches long in the tube furnace. It was kept in position by means of porous copper gauze plugs. The tube was then connected to a vacuum pump capable of giving a vacuum of the order of 3 x 10^-4 cm. of Hg. and its temperature was raised gradually to the required level by applying the appropriate voltage. The gases began to be evolved soon after. The temperature was allowed to rise gradually and before it was raised by another 50° C, complete elimination of the gas at the preceding temperature was ensured. After outgassing at each temperature, the sample was allowed to remain and cool in vacuo to avoid reformation of the complex(es) and was then transferred to a stoppered bottle.

Estimation of surface oxygen complexes

The amounts of surface oxygen and surface hydrogen complexes were determined by evacuating charcoal (1 g., oven dried)
at 1200°, raising the temperature gradually as described above, and analysing the gases evolved. The sample was heated in a platinum boat (4" x 1/2") having a 1 x 1/2" opening on one side. After introducing the sample, the opening was covered by a platinum foil which was held in position by winding a platinum wire over it. This arrangement left small spaces for the gases evolved to escape. The boat was then heated in a resistance tube furnace which was connected to a vacuum pump through weighed calcium chloride U-tubes and a series of Erlenmeyer flask containing a known volume of standard barium hydroxide solution.

The gases evolved were analysed in the following sequence: Water was absorbed in the calcium chloride U-tubes, carbon dioxide was absorbed by barium hydroxide while the rest of the gases were collected over water, an aliquot of which was examined for its CO content in an Orsat Lunge gas analysis apparatus. The amount of total oxygen evolved as water, carbon dioxide and carbon monoxide was in close agreement with oxygen obtained by ultimate analysis of the charcoal.

Determination of base adsorption capacity

Charcoal (1 g.) was mixed with 100 ml. of 0.2 N barium hydroxide solution in a pyrex glass bottle of 250 ml. the suspension capacity, flushed with nitrogen and shaken for 48 hours. The amount of unused alkali was determined by titrating an
 aliquot of the clear supernatant liquid against a standard acid solution. A blank run was also made every time.

This method gave the maximum value for base adsorption which did not increase further on increasing the time of the reaction or the concentration of the alkali used.

Determination of carboxylic and phenolic oxygen

In order to determine the carboxylic and phenolic groups present on the surface of carbon, the various samples were treated with a solution of diazomethane in dry ether. This treatment resulted in an increase of methoxy contents of carbons, indicating that the treatment has produced methyl esters, methyl ethers or both. As the general aromatic nature of the carbons appears to be well established, it is reasoned that the formation of ester groups involves the methylation of carboxyl groups and the formation of ether groups probably involves the methylation of phenol groups. Treatment of methyl esters and methyl ethers with hydroiodic acid liberates the methyl group as methyl iodide which can be determined quantitatively. The figures for the total methoxy content were obtained this way. Methyl esters are readily hydrolysed by dilute acid but ethers are unaffected. If the methoxy content is determined after hydrolysis, the value represents ether groups, whereas the loss of methoxy content during
hydrolysis represents the ester groups. From the two methoxy determination it is possible to calculate the carboxyl and phenol groups present in the sample.

Preparation of diazomethane: The diazomethane solution in dry ether was prepared by the acetamide method, as described by Vogel (3). The quantity of ether used was such that it gave about 2 per cent solution of diazomethane. The solution was transferred to a flask fitted with a guard tube so as to exclude moisture. As diazomethane decomposes very easily at room temperature the above flask was kept in a refrigerator.

Treatment of charcoal and carbon black with diazomethane: About 0.5 g. of charcoal or carbon black sample was taken in a flask fitted with a guard tube to exclude moisture. Diazomethane solution was added in small quantities and the temperature was kept at about 4°C. The addition of diazomethane solution was continued, till after 24 hours of the addition, the colour of the solution was not discharged. The charcoal sample was filtered, dried at 120°C and cooled in a vacuum desiccator. Part of this treated sample was treated with hydrochloric acid and washed free of chloride ions.

Estimation of methoxy (CH₃O) groups: Estimation of methoxy group was done by Zeisel's method (4) based on the following principles.
A definite amount of the substance (0.1 g.) was weighed out and transferred to the reaction bulb of the apparatus where it was decomposed by refluxing with hydroiodic acid resulting in the liberation of methyl iodide. The liberated methyl iodide was transferred quantitatively (by means of a stream of carbon dioxide gas) to an absorption vessel where it was absorbed in a 20 % aqueous acetic acid containing small amounts of bromine. Iodine monobromide was first formed, which on further oxidation yielded iodic acid, and on subsequent treatment with acidic potassium iodide liberated iodine which was finally estimated by titrating against N/40 sodium thiosulphate solution.

Knowing the volume of standard sodium thiosulphate solution used and the amount of the diazomethane-treated charcoal sample taken, the amount of -OCH₃ per 100 g. of the sample was calculated before as well as after hydrolysis. The amounts of carboxylic and phenolic oxygen were calculated as follows:

Suppose the total methoxy content before hydrolysis = x₁ %
and methoxy content after hydrolysis = x₂ %
then phenolic oxygen = x₂ x 16/31 %
and carboxylic oxygen = (x₁ - x₂) x 32/31 %

The apparatus used and other experimental details were the
same as described by Mann and Saunders (4). The carbon sample (about 0.1 g.) wrapped in a piece of rice paper was used. Blank experiments using A.R. glucose were also performed and the necessary correction applied to the actual experiments.

**Estimation of base adsorption capacity using various alkalies**

The amounts of various alkalies neutralised by various carbons were determined in the same manner as described earlier in the case of barium hydroxide. Charcoal or carbon black (1 g.) was mixed with 100 ml. of 0.2 N alkali solution in a pyrex glass bottle of 250 ml. capacity, flushed with nitrogen, and the suspension shaken for 48 hours. The amount of unused alkali was determined by titrating an aliquot of the clear supernatant liquid against a standard acid solution. The alkalies used were sodium bicarbonate, sodium carbonate, sodium hydroxide and alcoholic sodium hydroxide. CO₂-free distilled water used in all determinations.

**pH titration curves**

To 0.2 g. portions of charcoal, contained in 50 ml. pyrex glass bottles, were added increasing amounts of 0.2 N alkali and the volume made up to 20 ml. by the addition of CO₂-free distilled water. The suspensions were shaken for 48 hours and the pH values determined by Beckmann glass electrode pH meter. The pH
FIG. 1. APPARATUS FOR DETERMINATION OF HYDROGEN UPTAKE BY CARBONS FROM SODIUM BOROHYDRIDE.
values were then plotted against the amount of alkali added. The titration curves using following alkalies were determined: sodium hydroxide, sodium bicarbonate, sodium carbonate, ammonium hydroxide and barium hydroxide.

Estimation of carboxylic groups on treatment with calcium acetate

The procedure employed was the same as described by Donnet et al. (5). Calcium acetate (12.6 g.) was dissolved in water and the volume made up to 1 litre. Hundred ml. of this calcium acetate solution was added to 0.5 g. of charcoal and refluxed for 24 hours. The supernatant liquid was taken in a flask and the charcoal was washed thrice with small quantities of distilled water and each time the supernatant liquid was collected in the flask. The entire volume was then titrated against standard sodium hydroxide solution using phenolphthalein as indicator. The amount of acetic acid liberated was taken as equivalent of carboxylic groups present.

Reduction with sodium borohydride

The apparatus used for measuring the hydrogen uptake from sodium borohydride by carbons was a modification of the hydrogenation micro apparatus described by Ogg and Copper (6) and is shown in Fig. 1. E is the reaction flask (50 ml.) which is connected to the manometer M through a
replaceable joint and stop cock $S_1$. B is a graduated burette which forms one limb of the manometer and in which the gases are measured. The manometer $M$ and flask $E$ are also connected to a vacuum pump and a pure nitrogen supply unit, through a stop cock $S_2$ and three way stop cock $S$ as shown in the figure. The flask $E$ has an opening on one side in which a rubber stopple, $R$, is fixed. The solutions could be introduced into the flask, $E$, through rubber stopple by means of a hypodermic syringe.

A known weight of the carbon sample (0.5 g.) was taken in the flask, $E$. The level of the mercury in $B$ was raised by raising the reservoir till the level of mercury was up to the stop cock $S_1$, and stop cock $S_1$ closed. Stop cock $S_2$ was then opened and the apparatus connected to the vacuum pump. The apparatus was then subjected to evacuation along with the carbon sample for 15 minutes. The vacuum pump was then disconnected and the evacuated apparatus was filled with pure nitrogen. Stop cock $S_1$ was opened and some nitrogen was also allowed to enter $B$ so that after adjustment of the mercury level in both the limbs of manometer $M$ to the atmospheric pressure, the level of mercury was within the graduated part of $B$. Ten ml. of sodium borohydride solution made in $0.1\ N$ sodium hydroxide was introduced into the flask with a hypodermic syringe through rubber stopple $R$. The suspension was stirred for 30 minutes with the help of a magnetic stirrer after which time the unused sodium borohydride
was decomposed by adding 30 ml. of 1 N sulphuric acid. The volume of gases evolved was measured by manipulating the manometer. The volume of hydrogen liberated was calculated after making correction for the volume of solutions added. A blank experiment was also performed. From the two experiments the quantity of hydrogen consumed by the carbon sample was calculated. This hydrogen is supposed to be used for the reduction of quinone groups. Knowing the amount of hydrogen taken up by the carbon sample, the amount of quinonic oxygen could be calculated.

**Treatments of carbons with various oxidising solutions and gases**

The charcoal and carbon black samples were treated with oxidising solutions and gases in the manner described below. The conditions of the various treatments given below were worked out in preliminary experiments for getting maximum fixation of oxygen.

(i) **Treatment with potassium persulphate** :- Carbon sample (in 1 g. portions) was mixed with 200 ml. of nearly saturated solution of potassium persulphate in 2 N sulphuric acid and the suspension shaken for 24 hours. The carbon was filtered, washed with hot distilled water till free of sulphate ions, and dried.
(ii) **Treatment with chlorine water**: Carbon sample (in 1 g. portions) was mixed with 100 ml. of 0.05 N chlorine water and the suspension shaken for 24 hours. The clear supernatent liquid was siphoned off, and a fresh lot of 100 ml. of the same chlorine water was added and the suspension shaken for another 24 hours. This was repeated 5 times. The carbon was washed with hot distilled water till free of chloride ions, filtered and dried.

(iii) **Treatment with hydrogen peroxide**: Carbon sample (in 1 g. portions) was mixed with 100 ml. of 3 N H₂O₂ and the suspension shaken for 24 hours. The carbon was washed, filtered and dried.

(iv) **Treatment with potassium permanganate**: Carbon sample (in 1 g. portions) was mixed with 100 ml. of 0.1 N potassium permanganate solution containing excess of sulphuric acid and the suspension shaken for 24 hours. The carbon was washed and filtered. It was then treated with a hot concentrated solution of ferrous ammonium sulphate in order to remove any MnO₂ formed during the reaction (7). The carbon was then washed free of sulphate ions, filtered and dried.

All the above treatments were given at room temperature.

(v) **Treatment with oxygen**: Pure and dry oxygen was led (at 2 l/hr.) over 10 g. carbon placed in a rotating pyrex glass tube of 3/4" bore heated in a silica tube furnace maintained at 400° for 4 hours. The charcoal was allowed to cool in the atmosphere of oxygen.
(vi) Treatment with nitrogen dioxide: - Treatment with nitrogen dioxide was given in the same way as with oxygen. After treatment the carbon was washed with hot distilled water, filtered and dried.

(vii) Treatment with superheated steam: - Steam prepared in an autoclave was passed through a pre-heater maintained at 1000° and then led over 10 g. charcoal placed in a rotating silica tube heated in a furnace maintained at 1000° for 4 hours.

After each treatment the carbon was dried and stored in an atmosphere of nitrogen.

determination of bromine value: Charcoal (1 g. oven-dried) was shaken mechanically with bromine solution (200 ml.) in 500 ml. stoppered pyrex glass bottles, wrapped in thick black papers, for 24 hours (necessary for the attainment of the end point) after which the suspension was filtered and the charcoal repeatedly washed with distilled water. The filtrate and washings were made up to a known volume and an aliquot was analysed for free bromine by adding potassium iodide and titrating the liberated iodine with sodium thiosulphate solution, and then for hydrobromic acid by titration against standard sodium hydroxide.

A blank was also run every time, there being no noticeable change in the composition of the solution in the absence of
FIG. 2. MODIFIED M. BAIN'S QUARTZ SPRING BALANCE.
charcoal. None of the charcoals liberated hydrobromic acid from the solution of potassium bromide in the absence of bromine.

Treatment with nitric acid

Charcoal (10 g.) was heated with a certain amount of nitric acid (varying from 10 ml. to 300 ml. i.e. from 1 ml./g. to 30 ml./g.) in a pyrex beaker of 500 ml. capacity over a low bunsen flame. When all but about 10 ml. of the acid had evaporated, the contents were transferred over a filter paper and the charcoal washed with hot distilled water till the leachate was free of nitrate ions. The charcoal was dried first in air and then in an air oven at 110°, outgassed at 150°, and then stored in an atmosphere of nitrogen.

Vapour adsorption isotherms

Quartz fibre spring technique was employed for the vapour adsorption determinations. The sorption balance used was a modified form of McBains quartz spring balance and is shown in Fig.2. It consists of a long double walled tube A (adsorption chamber) having a removable top from which a glass rod R having a hook H at the lower end passes into the inner tube (about 30 cm. long and 4.5 cm. in diameter). From this hook quartz spring could be suspended. The inner tube has some holes in its sides which allow the vapours to pass to and from the outer tube.
freely but at the same time do not allow the pressure to change suddenly in the inner tube. The outer tube is connected to a large removeable glass bulb B, a small removeable glass tube T containing the liquid through a stop cock S₁ and a manometer M as shown in Fig. 2. Manometer M has a stop cock S₂ at the top of one limb as shown in the figure. When stop cock S₂ is open the mercury remains at the same level in both limbs whatever be the pressure in the apparatus. But when S₂ is closed, after subjecting the whole apparatus to vacuum, any pressure change in the apparatus is recorded in the manometer. The function of bulb B is to allow more space for the vapour, so that when sorption is taking place, the pressure does not change appreciably. The apparatus is connected to a vacuum line through stop cock S₃. The whole apparatus was placed in an air thermostat maintained at 30°C. The thermostat had a glass window on the front side so that the readings of the manometer and the quartz spring could be taken by means of a cathetometer placed in front of the thermostat. The air thermostat also had an opening in its side from which the stop cocks etc. could be manipulated by hand.

Ground glass joints were used in the apparatus. For the lubrication of joints and stop cocks Dow Corning high vacuum grease was used.

Quartz spring: Quartz springs used were supplied by M/s. Thermal Syndicate Limited, England. These springs had a maximum
load capacity of 0.4 g. and a stretch of about 15 cm./g. These springs were carefully recalibrated before used and were found to give uniform stretch with increase in weight. The stretch of the two springs used in these investigations was found to be 15.4 cm. and 15.1 cm. per gram, respectively.

Vacuum line: The vacuum line consisted of an oil vacuum pump and a mercury diffusion pump. A Mcleod gauge was also used in order to measure the pressures in the apparatus. A vacuum of the order of 10^-6 cm. of Hg. could be achieved.

Procedure: The given sample was dried at 110°C and allowed to cool in a vacuum desiccator. A known weight (0.2 g.) of the sample was weighed in a small boat K made from thin platinum foil weighing about 0.35 g. which could be suspended from the quartz spring by means of a hook made from thin platinum wire. The quartz spring was then suspended from the hook H, the platinum boat suspended from it and lowered into tube A and top of the tube again placed in position.

Stop cocks S3 and S2 were then opened and the apparatus was subjected to vacuum by using mercury diffusion pump in the usual manner. The sample was evaporated at 150°C by heating tube A by means of a resistance wire furnace (not shown in figure) for one hour. S2 and S3 were then closed. The length of the spring was noted by means of the cathetometer. S1 was opened briefly to
allow some vapour of the liquid in T to pass in the apparatus. S1 was then closed and the increase in the length of the spring was noted after every 20 minutes till no further increase was observed. The equilibrium pressure was then read on the manometer. The vapour pressure was successively increased and the increase in the length of quartz spring noted, till the saturation vapour pressure was reached. The time required for the equilibrium at each pressure was about 4 hours.

Knowing the increase in length of the spring at a particular equilibrium pressure, the weight of the adsorbed vapour could be easily calculated. Thus knowing the weight of vapour adsorbed by a known weight of corson, the percentage adsorption could be calculated.

Water, methanol and benzene used in these investigations were of extra pure quality. Water was distilled thrice before it was used. Methanol and benzene used were of B.D.H. 'Analar' grade and were further purified by fractional distillation and well dried in the usual manner before use.

**Determination of heats of immersion**

Heats of immersion were determined by using an isothermal phase change calorimeter described by Dainton et al (8). In the calorimeter, diphenyl ether was used as the dilatometric fluid. The calorimeter is very sensitive and has special advantages in
the case of experiments where the magnitude of heat evolved is small. The calorimeter is illustrated in Fig.3 and has the following essential parts.

**Mixing vessel:** The central tube R, shown in Fig.3 was the mixing vessel and could accommodate a sealed glass bulb G of about 3/4" diameter (containing the adsorbent) together with 50 ml. of the adsorbate. The vessel R could be covered with a stopper S, which fitted in its top. This was made from a standard taper joint. The hollow stopper was evacuated to reduce the flow of heat from the vessel to its surroundings. A glass stirrer passed through the centre of the stopper and carried small glass blades at its lower end. The same stirrer was used to break the bulb. The stopper was fitted with a mercury seal (P) to avoid the contact of the reactants with the atmosphere and also to avoid the evaporation of volatile adsorbates during the reaction.

**Diphenyl ether jacket:** The tube D, which surrounded the mixing vessel R, contained the dilatometric fluid (diphenyl ether). The dilatometric fluid was supported above the level by a column of mercury as shown in Fig.3. At its base the diphenyl ether jacket was connected to a glass spiral which was further connected to capillary C which also contained mercury. Capillary C was joined to a three way stop cock T, which in one direction connected the capillary C to the reservoir of mercury M and in the other direction to the horizontal calibrated capillary
H of a uniform bore.

**Vacuum jacket:** Diphenyl ether jacket D was completely surrounded by another jacket V, which was evacuated to minimise the conduction of heat between the vessel D and the outer water bath W. This helped to maintain the temperature of diphenyl ether at 26.9°C without any significant change in the state of diphenyl ether from liquid to solid or vice versa and hence minimised the drift of the position of mercury meniscus in the calibrated capillary H.

**Temperature control:** Maintenance of the temperature of the calorimeter better than ± 0.001°C is necessary to measure the heat change during the wetting of the adsorbent accurately. To achieve this the water thermostat was enclosed in an air thermostat, made from 'cellotex' sheets, the temperature of which was maintained at 26.9 ± 0.01°C. As the temperature of water and air thermostats was maintained at 26.9°C, the fluctuations of the temperature were reduced to less than ± 0.001°C. The water thermostat was provided with an efficient stirrer and a 500-watt heater fed from 30 volts potential by means of a variac. The vacuum jacket, surrounding the diphenyl ether jacket further reduced the fluctuation of temperature. Hence it was possible to control the drift rate in capillary to about 0.001 cm. per minute, which represent a change of 0.005 calories.

**Filling of the calorimeter with diphenyl ether:** Diphenyl ether was repeatedly crystallised for purification and then
300 ml. (approx.) was taken and distilled under vacuum into the inverted calorimeter. When the calorimeter was inverted later, the diphenyl ether column was sealed with mercury under vacuum. The capillary C the stop cock T and the calibrated capillary H were then sealed to the calorimeter. A rigid brass stand (not shown in the figure) was used to hold the calorimeter in position.

Selection and calibration of capillary H: The capillary H was sealed and its uniformity tested by measuring the length of a known weight of mercury in different parts of the capillary. The amount of mercury per cm. length of the uniform capillary was then calculated.

Weight of mercury thread = 2.1435 g.
Mean length of mercury thread = 8.06 cm.
Amount of mercury thread per cm length = 0.2659 g.

Procedure: The reaction vessel was cleaned and dried by means of a tissue paper and flushed with nitrogen. About 40 ml. of liquid at 26.9° was put into it. Then a sealed glass bulb containing a known weight of the adsorbent (-3g.) was put in it. Reaction vessel was then covered with the stopper with mercury seal in such a way that the sharp end of the stirrer rested gently on the glass bulb. The temperature of the thermostat was then controlled to get a uniform drift rate. This took about 4 hours. During this period the contents of the reaction vessel attained the temperature of the bath.
FIG. 4. DISPLACEMENT OF MERCURY MINISCUS WITH TIME, FOR NEUTRALIZATION.
REACTION OF NaOH AND HCl.
When the desired uniform drift rate was obtained, the bulb was broken by tapping it gently with the stirrer and stirring was gently done by revolving the stirrer in a horizontal plane, which gave an efficient stirring without producing any measureable heat due to stirring. The equilibrium between solid and liquid diphenyl ether was disturbed due to heat change occurring during reaction and it resulted in volume change of the fluid.

Before breaking the bulb, the drift rate was noted for 30 minutes at intervals of 5 minutes. After breaking the bulb the reading of the mercury meniscus in the calibrated capillary was taken after every two minutes till the initial drift rate was again obtained. The heat change could be determined graphically in terms of the shift of mercury meniscus in the capillary in centimeters, as illustrated in figure 4. The heat change in terms of calories could be obtained from the calibration factor of the capillary.

**Standardisation of the apparatus**: The calibration factor of the calorimeter may be defined as the amount of mercury displaced when one calorie of heat is either evolved or absorbed. The calibration factors calculated by various workers have a wide range of values (8-10).

So it was found necessary to standardise the calorimeter by determining the amount of heat evolved in neutralisation...
of a strong base (N/2 sodium hydroxide) by a strong acid (N/2 hydrochloric acid). Four experiments were performed. The heat change determination in one of the experiments is described in Table I. The heat evolved is graphically measured as illustrated in Fig. 4.

Heat of bulb breaking: Heat of bulb breaking is a source of error in such determinations as suggested by Bartell and Suggitt (14). Seven determinations were done by breaking empty bulbs. The mean value of the heat of bulb breaking was found to be 0.2 cals. A suitable correction was applied in all the subsequent determinations.

Measurement of adsorption from binary solutions

All adsorption measurements were carried out at 30°C. The procedure essentially consisted of adding a known weight of the solution of known concentration to a known weight of the adsorbent and determining the change in concentration after attainment of the adsorption equilibrium. Generally, about 0.25g. of the adsorbent, which had previously been dried for at least two hours at 150°C, was mixed with about 5g. of the appropriate solution. All the weighings were carried out using test tubes which were then sealed off. The sealed tubes were then placed in a thermostated shaker maintained at 30 ± 0.1°C and left there for about 24 hours for the attainment of equilibrium. Preliminary experiments had shown that shaking for this period was more than sufficient.
Table I

Drift of mercury miniscus on the calibrated capillary
in the neutralisation reaction of NaOH and HCl

Amount of N/2 NaOH taken in the sealed bulb = 7.9105 g.

Density of N/2 NaOH = 1.02 g/ml.

Volume of N/2 NaOH = 7.755 ml.

Amount of N/2 HCl taken in the calorimeter = 50 ml.

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>Drift (cm.)</th>
<th>Time (Minutes)</th>
<th>Drift (cm.)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>24.25</td>
<td>35</td>
<td>33.30</td>
</tr>
<tr>
<td>5</td>
<td>24.25</td>
<td>40</td>
<td>33.50</td>
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<tr>
<td>10</td>
<td>24.25</td>
<td>50</td>
<td>33.70</td>
</tr>
<tr>
<td>15 (bulb broken)</td>
<td>28.80</td>
<td>60</td>
<td>33.75</td>
</tr>
<tr>
<td>20</td>
<td>31.20</td>
<td>70</td>
<td>33.80</td>
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<tr>
<td>25</td>
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<tr>
<td>30</td>
<td>32.90</td>
<td>90</td>
<td>33.80</td>
</tr>
</tbody>
</table>

Drift rate = 0.00 cm.

Displacement in the position of mercury miniscus determined graphically = 9.55 cm.

...Continued next page....
Calculations:

Heat of neutralisation of this reaction $= -13.36 \text{ Kcal.mole}^{-1}$

i.e.

1000 ml. of N NaOH on neutralisation should liberate $= 13.36 \text{ Kcal.}$

7.755 ml. of N/2 NaOH should evolve $= \frac{13.36 \times 7.755}{2 \times 1000} = 0.0519 \text{ Kcal.}$

$= 51.9 \text{ cals.}$

It is obvious that

9.55 cm. of displacement corresponds to $= 51.9 \text{ cals.}$

1 cm. of displacement corresponds to $= \frac{56.8}{9.55} = 5.434 \text{ cal/cm.}$

Result of another similar experiment $= 5.317 \text{ cal/cm.}$

Mean of the two experiments $= 5.375 \text{ cal/cm.}$

Amount of mercury in one cm length of the capillary $= 0.2659 \text{ g.}$

Weight of the mercury displaced by one calorie heat change $= \frac{0.2659}{5.375} = 0.0493 \text{ g.}$
The change in concentration brought about by adsorption was determined interferometrically. A I.T.R. laboratory interferometer supplied by M/s. Stankoimport, Moscow, was used for this purpose. The instrument was calibrated first with solutions of known concentrations.

After shaking for the required period the tubes were then removed from the shaker, centrifuged and the seals broken. A small amount of the supernatant liquid was placed in one compartment of the interferometer cell. In the other compartment was placed a portion of the original solution. From the interferometer reading and the calibration curves, the concentration change could be calculated.

The two main sources of error in such determinations are the evaporation of the solvent and the presence of impurities either in the solvent or solute or in the cell of the interferometer. Solvent may evaporate during weighing, sealing or during transfer of the solution from the tubes to the cell. To prevent these losses, the tubes were always kept corked during weighing as well as during sealing. The tubes were also cooled in liquid air before sealing. A special cell with ground stoppers was used to avoid any loss due to evaporation from the cell itself. Solvents used in these investigations were of extra pure quality and were well dried in the usual manner before use. Charcoals were refluxed with water before use in order to remove any impurities.
REFERENCES