The hydroxide ions pass into solution and bring about neutralization of the acids while the positive charges remain on the surface of the charcoal. The amount of acid adsorbed was found to be equivalent to the oxygen of the charcoal.

These workers also observed that acids are not adsorbed by the oxygen-free charcoal obtained on heating the air-activated charcoal in a stream of hydrogen. Bases are adsorbed, instead. The charcoal appeared to behave now as a hydrogen electrode, as represented by the following equation:

$$C_x + H_2 \rightarrow C_x + 2H^+ + 2e^-$$

Hydrogen ions pass into solution while the negative charge remains on the surface.

If activated charcoal was heated in vacuum it adsorbed neither acids nor bases.

Shilov et al. (*122,144*) did not accept the electrochemical theory of Frumkin, as they claimed that some acid was adsorbed even on completely outgassed charcoals in the absence of oxygen. They suggested the presence of surface oxides of definite structures to be responsible for acid-base reactions of carbons. According to them, basic oxides are formed when a charcoal, outgassed in vacuum at high temperatures, is allowed to come into contact with oxygen only after cooling. Acidic surface oxides are formed when a charcoal is heated in oxygen at temperatures between 300° and 500°C. King showed that the optimum temperature for this purpose was 420°C (*124*).

Miller (*145*) criticized the views of both Frumkin and Shilov. He cited a number of facts which could not be explained by either of them. For example, there is no apparent reason why strong alkalies, like sodium hydroxide and potassium hydroxide, are not adsorbed by air-activated charcoal while tetraethyl ammonium hydroxide, an equally strong base, is adsorbed.

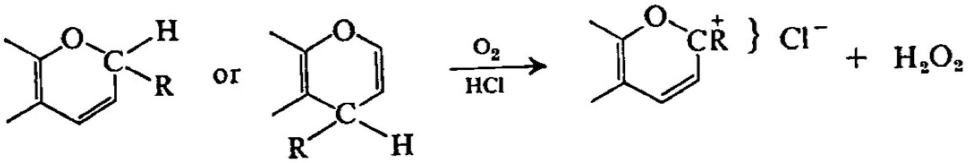
Steenberg (*146*) objected to the basic oxide theory of Shilov et al. because substances of a corresponding nature and stability are not known in bulk. According to him, adsorption of strong acids, e.g., hydrochloric acid, by charcoal activated at high temperatures is due largely to physical forces. The hydronium ions are held close to the surface by primary adsorption forces and the anions are held next to them by secondary electrostatic forces, forming the outer part of a diffuse double layer. The adsorption was found to be largely reversible as the acid could be recovered on shaking with a solvent immiscible in water, such as toluene. The secondarily adsorbed anions could be exchanged for other anions. These observations were confirmed by Straskessko et al. (*147*).

Burstein and Frumkin (*148*), in 1941, suggested the following mechanism for the adsorption of acids in the presence of oxygen to account for the liberation of hydrogen peroxide that they had observed.

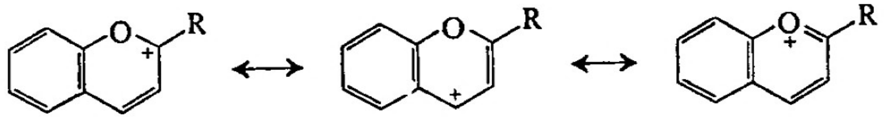
$$C_xO_2 + 2H^+ + 2X^- \rightarrow C_x^{++}X_2^- + H_2O_2$$

The amount of hydrogen peroxide was not equivalent to the amount of acid adsorbed. This was attributed to catalytic decomposition of hydrogen peroxide by the charcoal.

Garten and Weiss (*149*) were of the view that adsorption of acids is partly physical and partly chemical in nature and that the chemical part arises from the presence of chromene groups supposed to be present on the surface of carbons activated in air at high temperatures. According to them, the chromene groups are oxidized in the presence of acids to the corresponding benzpyran and benzo-pyrilium systems. There is also liberation of hydrogen peroxide, as had been reported by Burstein and Frumkin. The following scheme was suggested:



A transfer of the positive charges would be possible:



The existence of chromene groups is only circumstantial. There is no independent proof of their existence. Puri et al. (*22*), and also Weller and Young (*23*), have shown that, unlike adsorption of bases by carbons which is almost irreversible, the adsorption of acids is not only very much less but is also largely reversible. Moreover, charcoals free of oxygen, which are outgassed at 1200°C in vacuum and cooled out of contact with air, are even better acid adsorbents than those which are similarly treated at 800° to 1000°C and retain certain amounts of oxygen. The basic character of carbon, therefore, cannot be attributed to the presence of chromene or any other oxygen-containing group. In this connection Boehm's observation (*150*) that a graphitized carbon black adsorbed acids to an astonishing degree even though no oxygen was present in it seems to be quite significant. Studebaker's explanation (*65*) for the basic character of carbons seems to be more valid. He likened carbons prepared by the various pyrolytic processes to poly-condensed aromatic hydrocarbons which are known to be Lewis bases (electron donors). Such materials are expected to adsorb H^+ in preference to OH^- from water or aqueous solution. This would leave the surrounding liquid in the slurry with excess of OH^- which would give a pH in the alkaline range, as has been actually observed. The chemically combined oxygen, if present, would counteract the basic character in the Lewis sense. This would be true for any oxygen-containing group, although the actual degree of acidity introduced by it would depend upon its nature.

The influence of combined oxygen on basic reactions of carbons, at least, is doubtful. In any case, it is very small in comparison to the influence of combined oxygen on acid reactions of carbons, which will be discussed in detail in the next Section.

F. Functional Groups

Several workers in recent years have attempted to effect more direct analysis of the surface oxide layer by studying specific chemical reactions as well as by employing spectroscopic, potentiometric, and polarographic techniques. As a result of these investigations, the existence of such functional groups as carboxyls, phenols, lactones of fluorescein type (f-lactones), normal lactones, aldehydes, quinones, hydroquinones, and ethereal structures have been postulated. The methods used for the estimation of the various groups, however, have not yielded comparable results; and, what is even more significant, the entire amount of combined oxygen has not been accounted for. The validity of applying organic reactions for identification and estimation of surface groups can be questioned.

According to Boehm et al. (*151*) the functional groups present on graphite crystallites react only slowly and incompletely. The chances for completing the reaction in the case of microcrystalline carbons would be far less, because of the large surface area and, in many cases, the porous structure of these materials. Moreover, the groups on the surface are not likely to behave in the same way as those present in simple organic compounds because of possible association between adjacent groups and steric hindrances. The infrared spectra can also be only of limited help, as has been rightly pointed out (*152*). It is difficult to obtain clear evidence from the spectra because of continued background absorption (*153*) and also the possibility that the various functional groups may not be present as simple, independent, nonassociated structures.

Villars (*154*), in 1947, was among the early workers to initiate research on the surface chemistry of carbons by using a specific chemical reagent.

By reacting a few carbon blacks with Grignard reagent (methyl magnesium iodide) and measuring the methane evolved, he showed that about 20% of the combined oxygen could be accounted for partly as carboxylic and partly as phenolic groups.

$$R{-}COOH + CH_3MgI \rightarrow R{-}COOMgI + CH_4$$
$$R{-}OH + CH_3MgI \rightarrow R{-}OMgI + CH_4$$

Some of the Grignard reagent was consumed without evolution of methane. This indicated the possibility for the presence of other groups such as aldehydes, ketones, or quinones. The rest of the combined oxygen, representing as much as 75% of the total, was inert. This was considered to be ether oxygen. Smith and Schaeffer (*155*) used fast-moving electrons to desorb the surface oxide layer; and, from a study of the emission spectra, obtained evidence for the presence of OH, CO, COOH, and CHO groups. Hofmann and Ohlerich (*156*) used diazomethane for differentiating between carboxylic and phenolic groups in sugar charcoal containing 16.5% of oxygen. This substance is known to react with carboxylic acids to form methyl esters which are easily hydrolyzed by dilute hydrochloric acid,

$$R{-}COOH + CH_2N_2 \rightarrow R{-}COOCH_3 + N_2$$
$$R{-}COOCH_3 + HCl \rightarrow R{-}COCl + CH_3OH$$

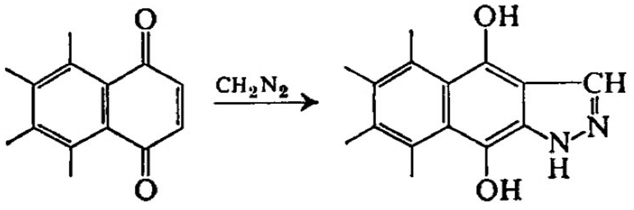
and with phenols forming ethers which are stable to hydrolysis,

$$R{-}OH + CH_2N_2 \rightarrow ROCH_3 + N_2$$

Studebaker et al. (*157*) employed the diazomethane reaction to estimate carboxylic and phenolic groups in a number of carbon blacks. His results indicated that for every 3.2 atoms of oxygen found in carboxylic groups one atom of oxygen was present in phenolic groups. Furnace blacks contained 5%; channel blacks, 9%; and color blacks, 8–19% of their total oxygen as carboxyl groups.

1. Quinones

During the reaction with diazomethane, the nitrogen content of the samples was found to increase. This indicated the possibility of 1,4-quinone groups with which diazomethane can give an addition reaction, forming pyrazoline rings:



The indication was not conclusive as diazomethane can add itself to other double bonds as well. The idea was substantiated, however, by carrying out the sodium borohydride reaction which, as shown by Lindberg and Paju (*158*), reduces quinones quantitatively to hydroquinones. One hydrogen atom adds itself to the sample for each quinone-type oxygen. The idea was also confirmed by catalytic hydrogenation, using Adams reduced platinum oxide as catalyst. The analysis of twelve carbon blacks indicated that nearly 18% of the total oxygen was present in 1,4-quinone form (*157*).

The existence of quinone groups has been supported on the basis of some other reactions as well. Garten and Weiss (*159*) observed that certain oxygen-containing carbons, which adsorbed no alkali, could take up appreciable amounts of alkali after electrolytic reduction. This was attributed to the reduction of quinones, originally present on the surface, into hydroquinones. Puri and Bedi (*160*) observed similar effects in oxygen-containing charcoals and Puri and Bansal (*114*), in oxygen-containing carbon blacks. These workers reduced their carbons in a current of hydrogen gas at 160°C for 8 hr. Assuming the increase in surface acidity to be due to reduction of quinones that were originally present into hydroquinones, the quinonic oxygen could be easily calculated (1,000 mEq increase ≡ 16 g quinone type oxygen). The values obtained in a few carbon blacks (*114*) which had been examined by Studebaker (*157*) by the sodium borohydride method were, however, appreciably low. This is probably because hydroquinone groups cannot be completely titrated by alkalies in an aqueous medium due to excessive hydrolysis.

If the surface quinone groups are converted only partially into hydroquinone groups by treating the charcoal with hydrogen at 160°C for a shorter duration, say for 2 or 3 hr, the resulting product may behave, like quinhydrone, as a reversible hydrogen electrode. The potential (E_h) of this electrode should be expressed by the equation,

$$E_h = E_0 - \frac{RT}{F}\log_e\left[\frac{1}{\mathrm{H}^+}\right]$$

$$= E_0 + 0.0591\ \mathrm{pH}\ (\text{at } 25°\mathrm{C})$$

where E_0 is the characteristic constant potential of the system and the other symbols have the usual significance. This view was checked by working with sugar charcoal which had been outgassed at 500°C (to eliminate most of the acidic complex), and then treated with hydrogen at 160°C for a couple of hours. A series of buffer solutions of pH values varying from 1 to 8 were prepared; and the E_h values, with respect to a calomel electrode, were determined after adding a pinch of charcoal in one case and a pinch of quinhydrone in another, in the usual manner.

The plot of E_h against pH is shown in Fig. 4 for both sets of experiments. The two curves are almost identical. The treated charcoal evidently behaves as a reversible hydrogen electrode. When some other charcoal was taken—one which had not been treated in hydrogen in this manner—the E_h value was not even stabilized and it continued to vary within a wide range.

Rivin (*116*) also reported an increase in active hydrogen, as measured on treatment with lithium aluminum hydride, after chemical reduction of his carbon blacks with the same reagent at elevated temperatures. This was taken as due to the reduction of quinone and lactone structures originally present on the carbons.

Further evidence for the presence of quinone groups has been offered by Hallum and Drushel (*161*), principally by infrared and polarographic techniques. In their studies of infrared spectra, for example, they observed that after methylation with diazomethane, a distinct absorption band appeared at 1750-1700 cm^{-1}, together with a weak absorption band at 1240 cm^{-1}, which was not shown initially by the carbon black. As the first band is associated generally with normal carbonyl groups and the latter

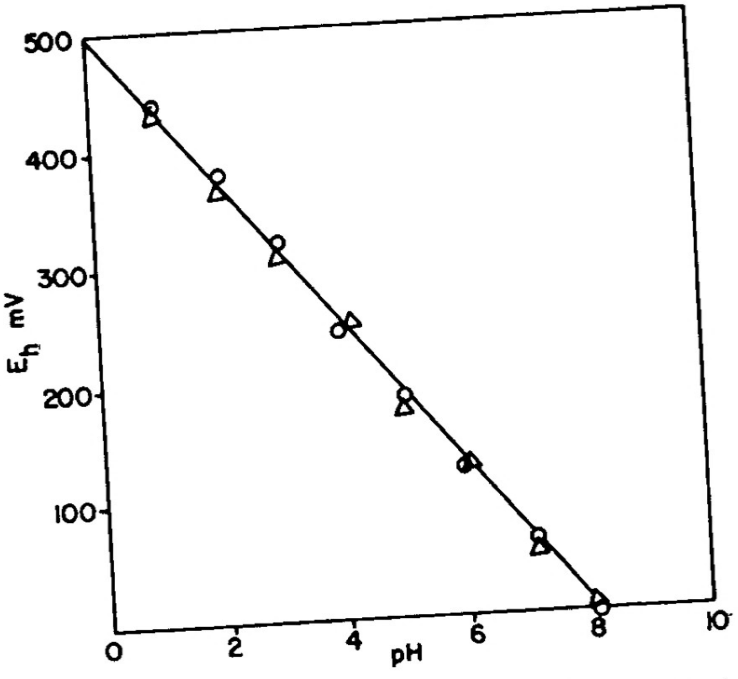
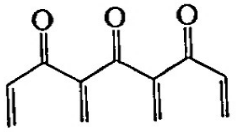
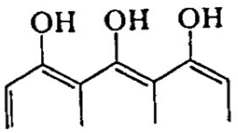


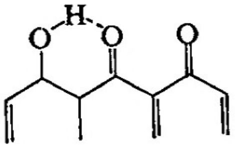
Fig. 4. Plot of E_h against pH (O—O, using quinhydrone electrode and △—△, using charcoal sample degassed at 500°C and treated with hydrogen at 160°C).

with methoxy groups, it was concluded that originally carbonyl groups had been chelated to phenolic hydroxyl groups through hydrogen bonding.

These observations were confirmed by a polarographic analysis of carbon blacks suspended in dimethyl formamide, using tetra-*n*-butylammonium iodide as the supporting electrolyte. Half-wave potentials, characteristic of quinones, appeared at the cathode and disappeared on treatment with lithium aluminum hydride. Half-wave potentials, characteristic of hydroquinones, appeared at the anode and disappeared on treatment with hydrogen peroxide or diazomethane. These workers proposed the following models for the structures investigated by them:







Donnet and Henrich (*91*) also observed a similar half-wave potential in the cathodic polarogram of an oxidized carbon black. The wave disappeared on treatment with isobutyronitrile which is known to react with quinones. Cole and Dannenberg (*162*), quoted by Studebaker (*65*), employing infra-red techniques, observed an absorption band near $6.3\ \mu$. This was believed to be a conjugate chelate of beta-substituted ketonic groups and phenolic hydroxyl groups, probably the same structure as reported by Hallum and Drushell. Kiselev and co-workers (*95*) also reported evidence from infrared absorption spectra, for the interaction between hydroxyl and carbonyl groups.

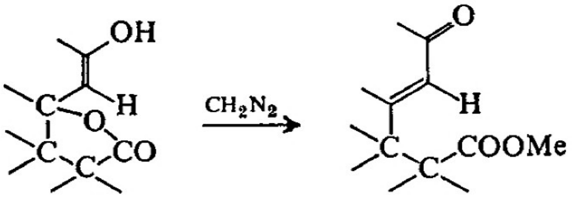
The evidence for the presence of simple quinones, or quinones in association with phenols through hydrogen bonding, seems to be fairly convincing. There is little doubt that these groups constitute a part of the combined oxygen, evolved as carbon monoxide on evacuation at high temperatures. Reduction with sodium borohydride, as developed by Studebaker, seems to provide a satisfactory method for the estimation of oxygen present as quinones.

2. Acidic surface oxides

The presence of acidic surface oxides has been implied since the time it became known that oxygen-containing carbons can neutralize appreciable amounts of alkalies irreversibly. Some of the earlier determinations were made under arbitrarily fixed conditions with respect to the concentration of the alkali solution employed and the time of contact allowed. Weller and Young (*23*), for example, allowed their carbons to remain in contact with 0.03*N* solution of sodium hydroxide for 30 min. The work reported in comparatively recent years aims at maximum neutralization effected by taking an excess of the alkali and prolonging the time of contact. It is now well known (*22,101,159*) that if a suspension of charcoal or carbon black is agitated with a moderate excess of a strong alkali, preferably in an atmosphere of nitrogen, for a sufficiently long time, extending to two or three days, it is possible to obtain maximum and reproducible values. The process can be quickened on heating the suspensions, under reflux, for about eight hours (*114*). As carbon surfaces are generally contaminated with adsorbed gases, chiefly carbon dioxide and water vapor, it is always desirable to remove these impurities before making determinations. The best method for this is to outgas the carbon under examination in high vacuum at 150°C before equilibrating with alkalies. At this temperature, the surface oxides remain unaffected.

It is now well realized that the so-called base adsorption by carbons represents to a very large extent the amount of alkali cations exchanged for hydrogen ions furnished by the acidic functional groups present on the surface. Kruyt and de Kadt (*136,163*) suggested that carboxyl groups were responsible for acidic behavior of carbons and that these groups were developed when carbons were heated in oxygen or air at 400°C. Schweitzer and Goodrich (*164*) also attributed acidity of carbon blacks to these groups. Hofmann and Ohlerich (*156*) as well as Studebaker et al. (*157*), as already mentioned, on reacting their carbons with diazomethane and hydrolyzing the products with a mineral acid, suggested the presence of two types of acidic groups: Carboxylic groups to account for the hydrolyzed fraction; and phenolic groups to account for the nonhydrolyzed fraction of the products.

Garten and Weiss (*90*), however, on the basis of the shapes of the titration curves of sugar carbons obtained earlier by Villars (*165*) and of a series of carbon blacks obtained by themselves, questioned the existence of acidic groups of such strength as carboxylic. They were of the view that the acidity was of phenolic character. In order to account for the reaction of diazomethane to form esters which can be hydrolyzed, they proposed the presence of lactones of the fluorescein type (f-lactones). These lactones can also react with diazomethane and be changed into the quinnoid form.



But because acidity measured by the diazomethane reaction as phenols and f-lactones accounted for only a part of the acidity measured by sodium hydroxide, it was suggested that the rest of the acidity was due to a group which could react with alkali but not with diazomethane. This was considered to be a normal lactone group. According to Garten and Weiss, therefore, acidity of carbons is primarily due to three functional groups: (1) phenols, (2) f-lactones, and (3) *n*-lactones. They sought evidence for their views from the infrared spectra of Carbolac—a carbon black with a high oxygen content (*152*). An absorption band appeared at 1600 cm^{-1} which could be attributed to a carbonyl group chelated to a phenolic hydroxyl group through hydrogen bonding, as reported also by other workers (*153,166*). There was another absorption band at 1760 cm^{-1}. This was attributed to the presence of a carbonyl group belonging to a lactone because this disappeared when the sodium salt was formed.

Bruin and Vander Plas (*167*) attempted to identify lactones in carbon blacks by reacting them with hydrogen bromide dissolved in glacial acetic acid. If lactones were present, bromocarboxylic acid should have resulted. They observed an increase in bromine content, but there was no corresponding increase in the carboxyl content as determined by titrating with sodium bicarbonate (*101*) or treatment with calcium acetate (*91,100*).

Studebaker (*168*) carried out potentiometric titrations of a number of carbon blacks in ethylenediamine (nonaqueous medium) using 0.1*N* sodium aminoethoxide as the titrant. Antimony electrodes were used as indicating and reference electrodes. The acidity values were appreciably higher than those obtained on titrating with sodium hydroxide in an aqueous medium. The channel black, Spheron-9 and the color blacks, Elf-0 and Mogul, which have high oxygen contents, showed two breaks in their titration curves. The first break indicated neutralization of an acid stronger than a phenol and more comparable to the acid strength of a carboxyl group, while the second break was comparable in strength to a phenolic group. These carbons were referred to as "acid carbons." The furnace blacks, which are low in oxygen content, showed only a single break which corresponded in acid strength to the second break observed in "acid carbons." The values obtained from the second break were in agreement with active hydrogen obtained on treatment with Grignard reagent.

Combining these results with those obtained on reduction with sodium borohydride, Studebaker showed that approximately one phenolic group was present for each quinone group, a situation which had been indicated previously from infrared (*161*) and polargraphic techniques (*91,161*).

As hydroxyquinones are known to be strong acids, this was taken as the explanation for the sharp inflection at the second break. Although there was a good correlation between the acidity found at the second break and the active hydrogen, this was not so in the acidity found at the first break in carbons of high oxygen content. It was concluded, therefore, that the stronger acid group cannot be a carboxyl group. It might be a lactone of some type, although certain other results did not fit in well with the f-lactone structure of Garten and Weiss (*151*).

Rivin (*116*) combined acidimetry and vacuum pyrolysis techniques to determine the distribution of functional groups on various types of carbon blacks. He measured total acidity by reacting with strongly basic lithium aluminum hydride in diethylsorbitol, as well as by equilibration with aqueous sodium hydroxide under nitrogen. The two values were usually in close agreement with each other. The carboxylic acidity was determined separately by titrating against sodium bicarbonate (*101*) or on heating with calcium acetate (*91,100*) and estimating the liberated acetic acid. Subtracting this from the total gave phenolic acidity. The carboxyl values subtracted from the carbon dioxide evolved in vacuum pyrolysis at 1300°C gave lactones (which were taken as neutral), while the phenol values subtracted from the carbon monoxide evolved gave quinones. The sum of the neutral lactones and quinones was confirmed by chemical reduction of carbons with lithium aluminum hydride at 120°–130°C and measuring the increase in active hydrogen produced by treating the product with the same reagent at ordinary temperatures, as had been done before the chemical reduction.

Puri and co-workers tried to correlate the capacity of charcoal to neutralize alkalies with the amount of carbon dioxide evolved from it when it was outgassed at high temperatures (CO_2 complex). They examined a large number of samples of charcoal before as well as after outgassing them at various temperatures (*107,112,113*). The amounts of sodium hydroxide or barium hydroxide neutralized in each case were found to be almost equivalent to the CO_2 complex. Some of the charcoals outgassed at 1200°C were given extensive treatment in a current of oxygen at 400°C (*22*). A few original charcoals were treated with various oxidizing solutions, such as potassium persulfate, bromate, nitrate, and iodate (*104*), aqueous chlorine (*97*) and hydrogen peroxide (*169*). It was found that in these samples also the amount of alkali neutralized was close to the amount of CO_2 complex. As the amount of the complex decreased on outgassing the oxidized samples at increasing temperatures, the capacity for the base adsorption decreased correspondingly. When the entire amount of the complex was eliminated on outgassing at around 700°C, the carbon lost completely the property to neutralize alkali even though it still retained an appreciable amount of oxygen. A few of the data obtained by these workers have been summarized in Table I with a view to illustrate these findings (*206*).

This work was later extended to a number of commercial carbon blacks representing furnace, channel, and color blacks (*114*). The values for sodium hydroxide and barium hydroxide were found to be close to each other as well as to the amount of the CO_2 complex contained in each sample. The acidity decreased as the samples were outgassed at increasing temperatures and the decrease at a particular temperature was equivalent to the loss suffered in the CO_2 complex. Some of these results are also included in Table I. It will be seen that the samples outgassed in the 700°–800°C temperature range retain appreciable amounts of oxygen, evolved as carbon monoxide and water vapor, but they cannot neutralize alkalies at all.

A sample of sugar charcoal outgassed at 1200°C and three samples of carbon blacks, one representing each type, were treated with hot concentrated nitric acid (*92,114*). This resulted in the loss of 25–40% carbon and at the same time the addition of an appreciable amount of oxygen, about 85–90% of which was found to come off as carbon dioxide on evacuation. The base-adsorption capacity increased tremendously in each case in proportion to the amount of CO_2 complex formed. In the case of charcoal outgassed at 1200°C, for instance, the base-adsorption capacity increased from zero to about 1200 mEq/100 g and so did the CO_2 complex. As the complex was eliminated gradually on evacuation at increasing temperatures, the base-adsorption capacity decreased correspondingly.

Some of the original charcoals were heated under reflux with suspensions of calcium carbonate and barium sulfide (*170*). Carbon dioxide was evolved in the first case and hydrogen sulfide in the second. The amount of each gas evolved at the end point was almost equivalent to the amount of CO_2 complex. At the same time an equivalent amount of calcium in the first case and that of barium in the second case was found to be associated with the carbon after the completion of the reaction. Titrations with aqueous ammonia gave lower values, which were only 50–60% of the CO_2 complex, obviously due to the weaker nature of the base.

Dry ammonia was passed over charcoal or carbon black at room temperature under controlled conditions (*171*), so as not to allow the temperature to rise unduly because the thermal effect involved in neutralizing the complex might cause partial elimination of the complex itself.

TABLE I

Neutralization of Different Bases by Various Samples of Charcoal and Carbon Black in Relation to CO_2 Complex

Description	Amounts of different bases neutralized, mEq/100 g				CO_2 complex on outgassing, mEq/100 g
Description 1	$Ba(OH)_2$ 2	NaOH 3	Gaseous ammonia 4	*n*-Butyl amine 5	6
Sugar charcoal original	655	643	670	682	669
Treated with $K_2S_2O_8$	970	985	898	—	975
Treated with aqueous chlorine	902	888	825	879	881
Treated with H_2O_2	810	795	790	802	819
Outgassed at 300°C	361	366	347	361	359
400°C	215	209	198	202	206
500°C	166	163	159	161	160
600°C	45	43	38	48	48
750°C	Nil	Nil	Nil	Nil	Nil
1000°C	Nil	Nil	Nil	Nil	Nil
Outgassed at 1000°C, treated with HNO_3	1184	1166	955	—	1163
Coconut charcoal original	374	376	338	381	384
Treated with $K_2S_2O_8$	749	757	698	704	741
Treated with aqueous chlorine	678	668	624	659	686
Treated with H_2O_2	612	618	—	614	—
Outgassed at 300°C	308	316	302	327	314
400°C	56	51	49	57	59
500°C	3	2	Nil	3	8
600°C	Nil	Nil	Nil	Nil	Nil
750°C	Nil	Nil	Nil	Nil	Nil
1000°C	Nil	Nil	Nil	Nil	Nil
Outgassed at 1000°C, treated with HNO_3	621	612	584	602	617
Spheron–6 original	29	28	18	30	34
Treated with HNO_3	253	258	240	250	257
Mogul original	139	135	—	123	137
Outgassed at 200°C	138	133	—	—	137
400°C	82	79	69	70	83
700°C	22	22	—	18	18
Treated with HNO_3	529	534	492	524	524
Mogul–A original	113	115	—	—	115
Outgassed at 400°C	59	62	—	61	59
500°C	24	18	—	19	24
700°C	Nil	Nil	—	Nil	Nil

The amount of ammonia adsorbed and recovered on boiling the product with sodium hydroxide was found to be closer to the amount of the CO_2 complex or that of sodium hydroxide or barium hydroxide neutralized, as shown in Table I (column 4). It may be mentioned that in these experiments besides hydrolyzable ammonia, a certain amount of nonhydrolyzable ammonia was fixed as well. This latter fraction could not be recovered on boiling with either sodium hydroxide or dilute hydrochloric acid. The reaction with ammonia at elevated temperatures caused a decrease in the amount of hydrolyzable ammonia, evidently due to elimination of the CO_2 complex by the sweeping action of the gas. But there was an increase in the amount of nonhydrolyzable ammonia, as shown in Table II. Fixation of ammonia in nonhydrolyzable form by oxygen-containing charcoal or carbon black on treatment with the gas at various temperatures was reported earlier by Hofmann and Ohlerich (*156*), Boehm et al. (*151*), Emmett (*67*), and Studebaker (*172*) as well. It has not been possible to attribute fixation of nonhydrolyzable ammonia to any specific functional group so far.

Adsorption of simple aliphatic amines on activated charcoal, presumably of low oxygen content, as studied by Phelps and Peters (*173*), Kipling (*174*), and Bodfors and Inge Ehrlen (*175*) appeared to be largely physical in nature, taking place through undissociated molecules in which the nature of the surface was not of much significance. Adsorption of methylamine on oxygen-containing carbon blacks, as studied by Anderson and Emmett (*176*), on the other hand, appeared to be largely influenced by the nature of the surface; and the amount adsorbed in excess of a monolayer was attributed to the polarity of the molecules and their ability to form hydrogen bonds with the constituents of the oxygen complex.

TABLE II

Reaction of Original Sugar Charcoal with Dry Ammonia

Temperature, °C	Ammonia adsorbed and recovered on treatment with HCl, mEq/100 g	Ammonia adsorbed but not recovered, mEq/100 g
35	498	156
200	301	194
300	232	265
400	179	298

The work of Puri, Talwar, and Sandle (*177*) on adsorption of *n*-butyl-, dimethyl-, diethyl-, and triethylamines in aqueous solution by a series of charcoals and carbon blacks indicated that the process was a neutralizing reaction involving the acidic sites provided by the CO_2 complex. The *n*-butylamine values were close to the CO_2 complex (see Table I, column 5). The values of the secondary and tertiary amines were low, however, and the longer the hydrocarbon chain, or the larger the number of chains, the lower was the value (Table III). The discrepancies appeared to arise from orientation and steric effects. Assuming that the basic amino (NH_2) group is oriented towards the acid sites provided by the CO_2 complex, it could be shown with the help of models that the single hydrocarbon chain as in *n*-butylamine, which projects vertically and sharply out of the middle of the pyramidal nitrogen atom, would not cover any noticeable portion of the carbon surface. The existence of two or three hydrocarbon chains, as in secondary and tertiary amines, which project sideways, would cover a portion of the surface, and thus some of the acidic CO_2 complex sites would not be available for neutralization. The relative proportions of the sites rendered unavailable in this manner will evidently be greater in tertiary than in secondary amines; among the latter the effect will be larger in diethylamine than in dimethylamine.

Assuming that there is no steric effect in *n*-butylamine and that in the other amines the effect varies as the diameter of the molecule, that is, the distance between extreme hydrogen atoms of the alkyl radicals attached to the nitrogen atom, it follows that the ratio of the adsorbability of *n*-butylamine to that of any other amine varies inversely as the ratio of their molecular diameters. The ratios of the molecular diameters of dimethyl-,

TABLE III

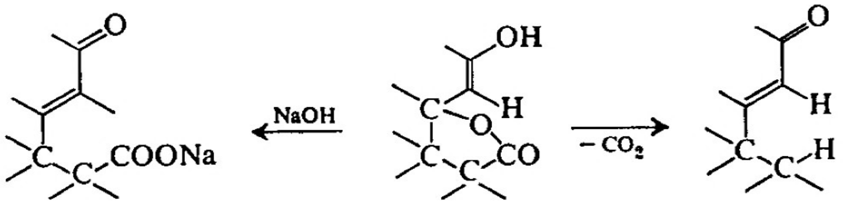
Amines Neutralized by Original Sugar Charcoal

CO_2 Complex = 669 mEq/100 g

Amine	Amount neutralized, mEq/100 g	Ratio diameters: $\frac{n\text{-butylamine}}{\text{given amine}}$	Amount neutralized (calculated), mEq/100 g
n-Butylamine	682	1.00	682
Dimethylamine	509	0.75	652
Diethylamine	406	0.57	712
Triethylamine	312	0.43	725

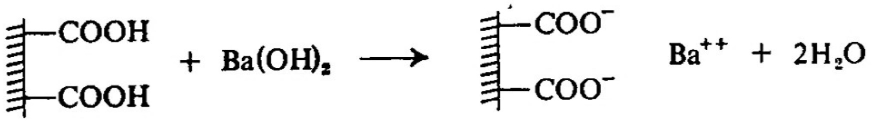
diethyl-, and triethylamines to that of *n*-butylamine, as obtained from the models, are included in Table III. The adsorbabilities of the various amines by original sugar charcoal, when corrected for steric effects on the considerations advanced here, are seen to be closer to one another and also to the CO_2 complex (see Table III).

The observations like those just discussed give strong indications that in charcoals as well as in carbon blacks the same surface group which is involved in the liberation of carbon dioxide is also involved in the neutralizing of alkalies. This cannot be a carboxyl group because no significant correlation between acidity and active (Grignard) hydrogen has been found. This cannot be a lactone group either, because according to the following mechanism of its reaction and decomposition (*90*),

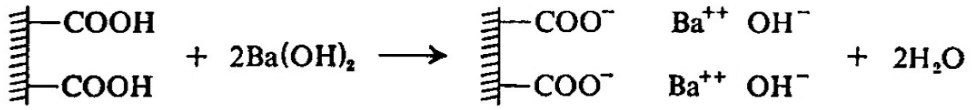


for every equivalent of alkali neutralized, one mole of carbon dioxide (and not one equivalent, as actually observed) should have been evolved. This objection is equally valid for the existence of carboxyl groups.

Boehm (*150*) has argued that there can be two ways of neutralizing a base like barium hydroxide and proposed



$$\begin{matrix}-COOH\\ \\-COOH\end{matrix} + Ba(OH)_2 \longrightarrow \begin{matrix}-COO^-\\ \\-COO^-\end{matrix} \quad Ba^{++} + 2H_2O \qquad (1)$$

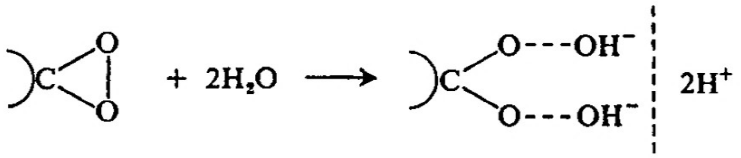


$$\begin{matrix}-COOH\\ \\-COOH\end{matrix} + 2Ba(OH)_2 \longrightarrow \begin{matrix}-COO^- & Ba^{++}\ OH^-\\ & \\-COO^- & Ba^{++}\ OH^-\end{matrix} + 2H_2O \qquad (2)$$

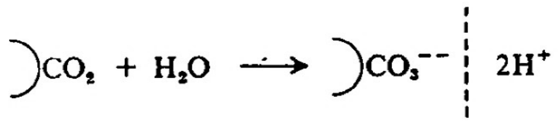
If the carboxyl or lactone groups are close together, neutralization is equivalent, as represented by the first equation. If these are not adjacent, neutralization is equimolecular, as represented by the second equation. A barium ion is bound by each acid group, the extra positive charge on the surface being balanced by one hydroxide ion. With bases that have univalent cations, such as sodium hydroxide, only equivalent neutralization as represented by the first equation is possible, irrespective of whether or not the carboxyl or lactone groups are adjacent to one another. Boehm actually observed higher neutralization values—almost twice as high—with barium hydroxide than with sodium hydroxide. In our experience so far with charcoals or carbon blacks, however, we have never observed any significant difference between values for barium hydroxide and for sodium hydroxide when determined under similar conditions.

The possibility for the existence of certain types of lactone structures which would hydrolyze to give a carboxyl group and a phenolic hydroxyl group, each capable of stoichiometric ionic absorption, cannot be ruled out. Alternatively, it looks probable that the acidic complex consists of two oxygen atoms attached to each "active" carbon atom lying at the edges of the basal planes or other "active sites" on the surface; and thus the system behaves, for practical purposes, as a layer of "frozen" carbon dioxide.

The ionization of such a complex in water, analogous to ionization of acid complexes as reported in the literature (*38*), may be represented as



or



The hydrogen ions are directed towards the liquid phase while the equivalent negative charge is left on the carbon surface.

This mechanism receives support from the facts (*a*) that equivalent amounts of various alkalies are neutralized by a carbon (see Table I); and (*b*) that an equivalent amount of oxygen is added to the charcoal after partial or complete neutralization of the acidity by any alkali. According to this mechanism 16 grams of oxygen should be added for every two equivalents of alkali neutralized by charcoal, irrespective of the nature of the alkali. The results presented in Table IV amply support this view.

It has been shown (*178*) that metal cations which displace surface hydrogen ions when carbons are treated with alkalies can be exchanged fairly readily with other cations, as in clays, permutites and zeolites, in the usual column operations. The displacing powers of different cations decrease in the following order

$$H^+ > Al^{+++} > Ba^{++} > Ca^{++} > Mg^{++} > Na^+$$

which is the same as in the well-known lyotropic series.

TABLE IV

Increase in Oxygen Content of Sugar Charcoal After Different Neutralizations

Nature and amount of metal cations introduced in exchange for H^+ ions, mEq/100 g		Increase in oxygen content, mg/g	
		Experimental	Theoretical
Li^+	121	10.7	9.7
	230	19.1	18.4
	439	34.8	35.1
Na^+	114	9.0	9.1
	220	18.2	17.6
	448	36.3	35.8
Ba^{++}	133	10.9	10.6
	426	34.4	34.0
Ca^{++}	145	11.8	11.6
	441	33.8	35.3

Charcoal of high acidity and, therefore, of high cation exchange capacity (around 1000 mEq/100 g) can be prepared by oxidizing chars obtained from easily available raw materials. This charcoal with Na^+ in the exchange position can be used for the removal of Ca^{++} from water, as in the usual water-softening operations; that with H^+ can be used for removing free alkali from water, and that with Ca^{++} for raising the calcium status of irrigation waters (*179*). The column, in each case, can be regenerated by leaching with a suitable solution. The possibility of using charcoal with H^+ or Ca^{++} in order to lower excessive alkalinity in soils and that with K^+ or NH_4^+ to lower excessive acidity in soils has also been indicated (*179*).

3. pH titration curves

The presence of strongly acidic groups on the surface of activated carbons and carbon blacks was questioned by some workers (*154,159*) on the ground that the titration curves with strong alkalies were flat, without a break and did not resemble those of strong acids. In 1957 Puri and coworkers (*170*) reported titration curves of sugar and coconut charcoals using barium hydroxide as the titrant. Some of these are reproduced in Fig. 5. The resemblance of these curves in the case of carbons of high acidity with a titration curve of carbonic acid in the same figure is fairly close. The points of inflection are quite sharp. However, as the acidity decreases with increase in the temperature of evacuation and approaches a

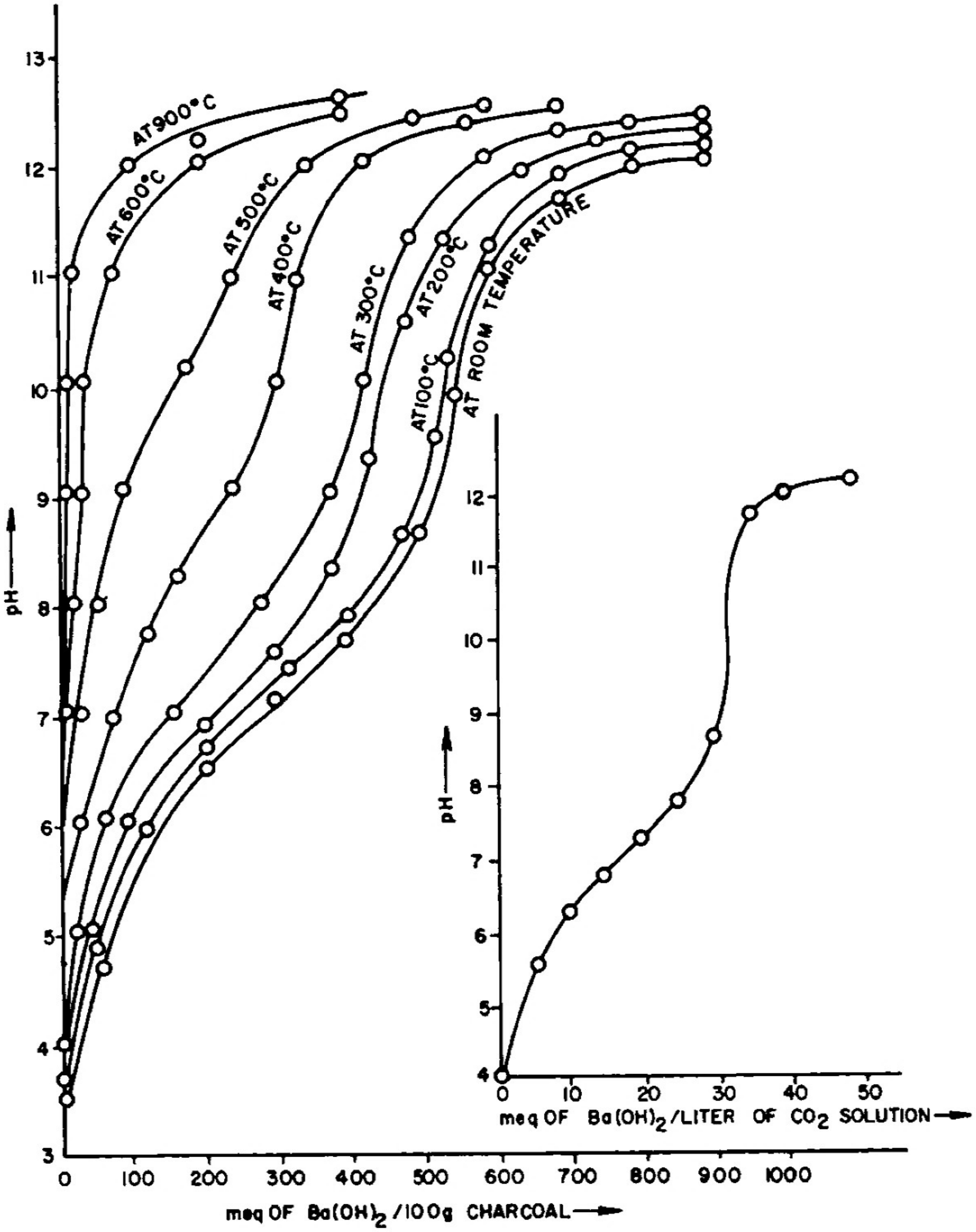


Fig. 5. Titration curves of sugar charcoal outgassed at different temperatures, and of carbon dioxide with barium hydroxide.

value close to that of the carbons used by other workers (*169*) i.e., about 50 mEq/100 g, the curves become flat, and the points of break are not easily detected.

The titration curves of Elf–0, Mogul, and Mogul A with acidities around 70, 115, and 138 mEq/100 g, respectively, which were obtained by Puri and Bansal (*114*), using barium hydroxide as the titrant, are shown in Fig. 6. The end points, though not very sharp, can be located without

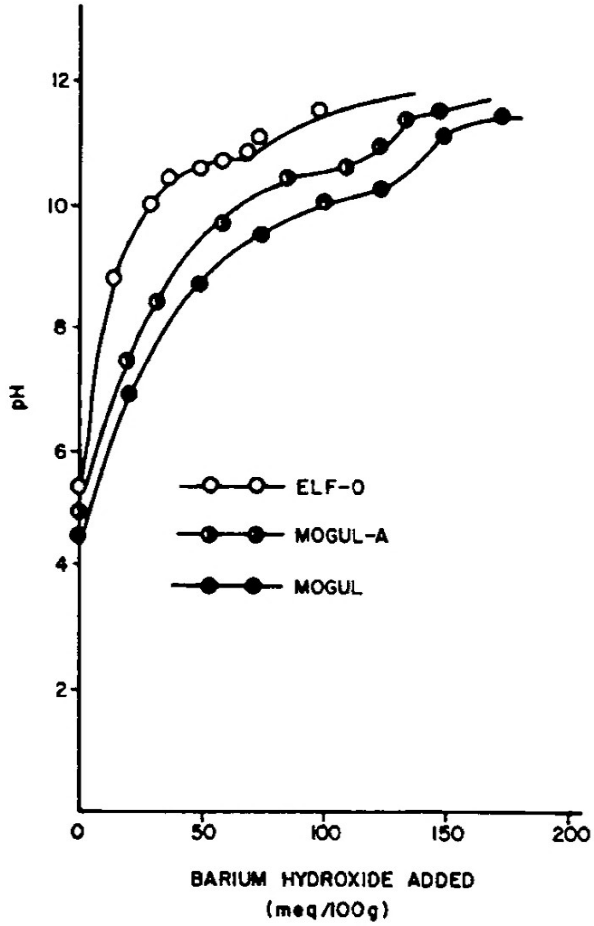


Fig. 6. Titration curves of various carbon blacks with barium hydroxide.

much difficulty. The acidity values, determined at the break points, were fairly close to those obtained by direct titrations. The titration curves, evidently, do not resemble those of carbonic or a carboxylic acid, in fact, these indicate the presence of much weaker acid groups, of strength comparable to that of a phenol. The pK values, taken as pH values at half neutralizations, can be shown to lie between 9 and 10.

On the other hand, the titration curve of Mogul, after oxidation with nitric acid (*114*), with surface acidity as high as 530 mEq/100 g, shown in Fig. 7, suggests the presence of acid groups of strength similar to carbonic or even a carboxylic acid. The pK value is now about 5.5. The oxidized Mogul was subjected to partial evacuations to eliminate increasing amounts of the CO_2 complex. The titration curves of the residual products are also included in Fig. 7. The titration curve of the original Mogul on a similar scale has also been reproduced in this figure.

The gradual decrease in the strength of the acid with decrease in the amount of CO_2 complex is quite evident. But it would be too much of a strain to believe that in each case a different acid with a different dissociation

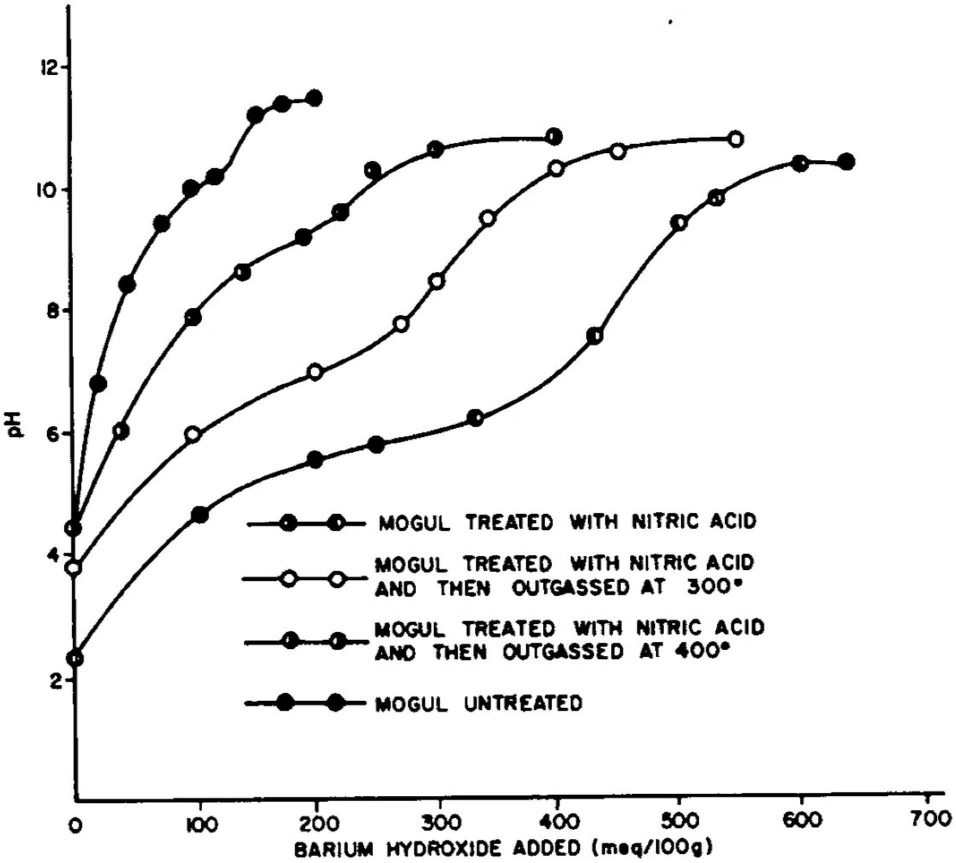


Fig. 7. Titration curves of Mogul with barium hydroxide.

constant is being titrated. In view of the equivalence between carbon dioxide evolved and alkali neutralized in every case, it appears more reasonable to conclude that it is the same CO_2 complex which is responsible for surface acidity in every case. It appears that as the concentration of this complex at the surface increases there is a much greater amount of surface ionization, which gives rise to a higher concentration of hydrogen ions to a unit of surface, and that this results in a stronger acid character of the carbon.

Puri and Bansal have also argued (*114*) that it may not be safe to stretch the analogy between ionization at the surface and ionization in solution too far, as some workers appear to have done (*159,90*) as it may lead to unnecessary confusion and unsatisfactory interpretation. For example, the hydrogen ion concentration in a solution of a weak acid varies with the concentration (c) of the acid in accordance with the equation

$$C_{H^+} \approx \sqrt{Kc}$$

where K is the dissociation constant of the acid. This equation does not seem to be valid for the variation in hydrogen ion concentration of a carbon suspension in water with variation in the concentration of the acidity. The acidity of Mogul, for instance, after treatment with nitric acid, increased from 115 to 530 mEq/100 g, indicating roughly a fourfold increase; but the hydrogen ion concentration of the suspension rose nearly 100 times, as the pH value of the suspension decreased from about 4.3 to 2.3 (see Fig. 7). It appears that the dissociation constant of the acidic complex itself changes with change in the surface coverage.

4. Selective neutralization technique

Boehm et al. (*101*) employed a selective neutralization technique to estimate what they described as various acidic surface oxides of varying strengths. The carbons used by them were extensively oxidized charcoals and carbon blacks. The bases employed for successive neutralizations were sodium bicarbonate, sodium carbonate, sodium hydroxide and sodium ethoxide. The strongly acidic groups neutralized by sodium bicarbonate were taken as carboxylic groups, while those neutralized by sodium carbonate but not by sodium bicarbonate were taken as lactones. The weakly acidic groups neutralized by sodium hydroxide but not by sodium carbonate were taken as phenols. The reaction with sodium ethoxide was not considered to be true neutralization because it did not involve exchange of H^+ by Na^+. The groups responsible for reaction with sodium ethoxide but not with sodium hydroxide were supposed to be carbonyl groups.

Some corroborating evidence for the various groups, postulated by Boehm et al., was obtained by comparing them with other independent reactions. The carboxyl groups, for example, were checked by reacting the carbons with calcium acetate and estimating the amount of acetic acid set free, as well as by carrying out certain characteristic reactions of acyl chlorides obtained by treating the carbons with thionyl chloride. The acidic groups neutralized by sodium hydroxide could be methylated. Some of the methoxy groups could be hydrolyzed on refluxing with dilute hydrochloric acid. These were taken as carboxyl and lactone groups and their values were found to be equivalent to those obtained by the neutralization of sodium carbonate. The methoxy groups which were resistant to hydrolysis were taken as phenols, the values tallied with those obtained by taking the difference between neutralization of sodium hydroxide and of sodium carbonate. The oxygen contents of the various acid groups put together accounted for only about 50% of the total combined oxygen. The rest of the oxygen was found to be evolved mainly as carbon monoxide.

The validity of the selective neutralization technique in determining acidic groups of varying strengths is open to question, because even if

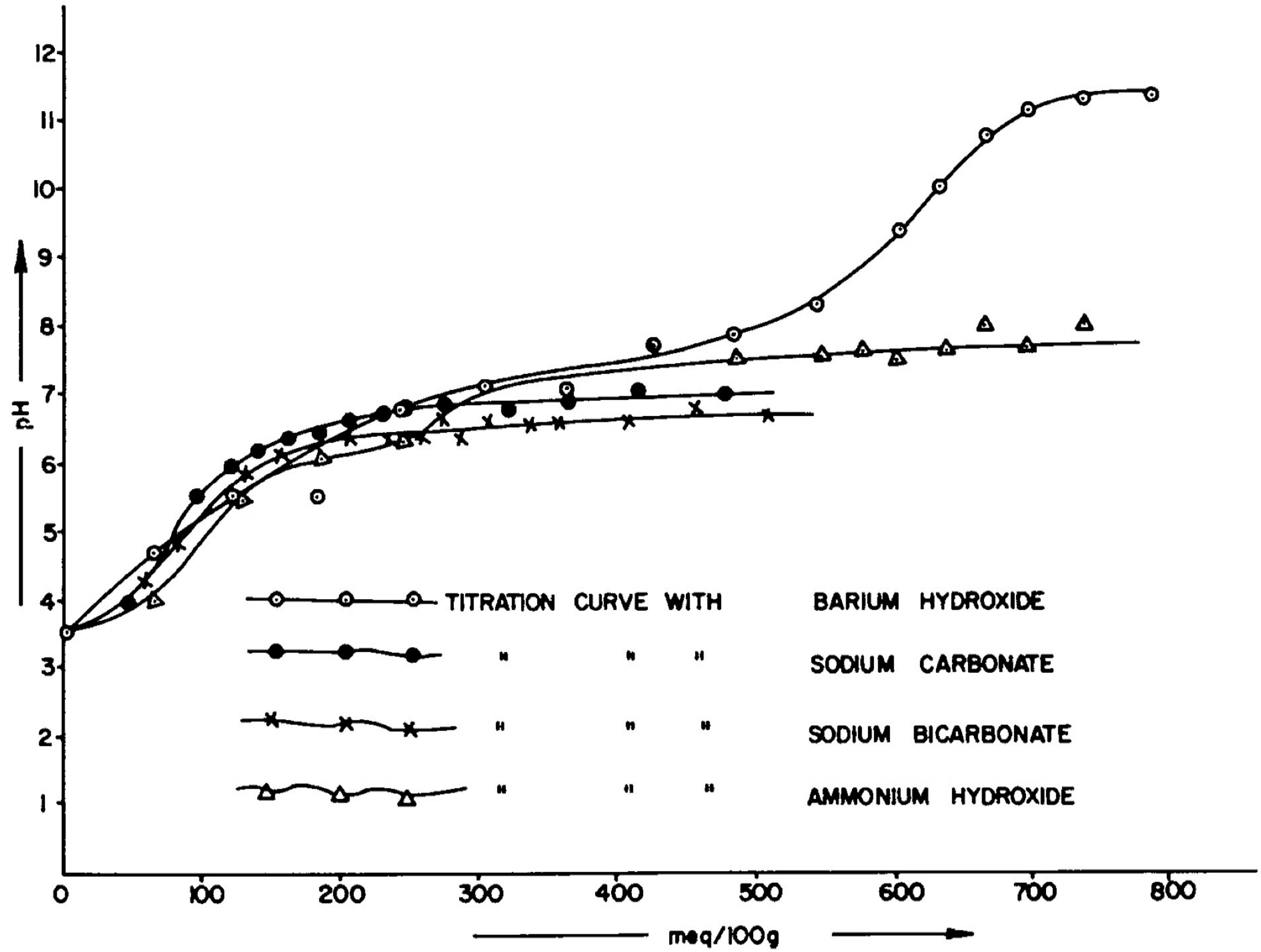


Fig. 8. Titration curves of sugar charcoal with alkalies of different strengths.

one and the same acid group is present, the amounts of alkalies of varying strengths will be neutralized to different extents. This is true even for a soluble acid, like acetic acid. A weak acid can be neutralized completely only at an appreciably high pH value on account of hydrolysis. When treated against a *weak* alkali, like sodium bicarbonate, the neutralization is only partial because it cannot be pushed beyond the pH value of the alkali itself. Titration with sodium carbonate would yield a higher value, as it would be able to push neutralization up to a higher pH level. Complete neutralization, however, would be possible only by using a much *stronger* alkali, like sodium hydroxide or barium hydroxide.

The pH-titration curves of a sugar charcoal, having a total acidity of about 700 mEq/100 g, with sodium bicarbonate, sodium carbonate, ammonium hydroxide, and barium hydroxide are shown in Fig. 8, to substantiate the points mentioned. Titrations with ammonium hydroxide and barium hydroxide show fairly sharp end points. The amounts of sodium bicarbonate and sodium carbonate neutralized, which correspond to the points where the titration curves just tend to become asymptotic, and those of ammonium hydroxide and barium hydroxide, as read from the points of inflection, are recorded in Table V, along with the value of CO_2 complex. Evidently titration with barium hydroxide alone measures total acidity.

Carboxyl groups have also been estimated by some workers (*101,157*) by heating carbons with calcium acetate and measuring the amount of acetic acid set free. The values obtained by Puri and Sharma (*180*) by following the same technique with some of their carbons are recorded in Table VI, along with the values obtained on titrating with sodium bicarbonate. The agreement is not good. This is to be expected because in the first case the surface complex is competing for the base, calcium hydroxide, with acetic acid, while in the second case the complex is competing for the base, sodium hydroxide, with carbonic acid. As carbonic acid is

TABLE V

Neutralization of Alkalies of Different Strength as Obtained from Titration Curves (mEq/100 g)

Charcoal	Sodium bicarbonate	Sodium carbonate	Ammonium hydroxide	Barium hydroxide	CO_2 complex
Sugar charcoal, original	204	270	295	650	669
Coconut charcoal, original	115	166	179	372	384

TABLE VI

Carboxylic Oxygen as Obtained by Different Methods (mEq/100 g)

Carbon used	Treatment with calcium acetate	Titration with sodium bicarbonate	Diazomethane reaction
Sugar charcoal, original	188	204	51
Outgassed at 300°C	57	65	9
Outgassed at 400°C	11	13	6
Coconut charcoal, original	43	71	37
Outgassed at 300°C	25	32	15
Spheron-9	4	10	13
Mogul	35	50	49

relatively a weaker acid, the values with sodium bicarbonate are expected to be a bit higher on the basis of the well-known laws governing acid-base reactions. The values obtained from the hydrolyzable methoxy group produced on treatment with diazomethane (*157*) are also included in Table VI. These results do not agree with the other two values.

It would appear from the preceding resumé that the present position with regard to acidic surface oxides is not quite satisfactory. The procedures for the estimation of functional groups have not yet been established and the various structures and mechanisms that have been proposed are not yet outside the realm of speculation. The author believes that any satisfactory theory will have to take into account the close equivalence between acidity, as measured by titrating against strong alkalies in aqueous solution, and carbon dioxide evolved on vacuum pyrolysis under controlled conditions. It may be noted that the equivalence between these quantities indicates that phenolic acidity is not measured by alkalies in aqueous solution, because phenolic hydroxyl groups are expected to evolve carbon monoxide—not carbon dioxide—on thermal pyrolysis.

Other workers (*90,101,157*), however, include phenolic acidity also in the acidity obtained by titrations in aqueous medium. The only direct evidence for the existence of phenols lies in the formation of ethers that are resistant to hydrolysis, when treated with diazomethane. As discussed previously the evidence from a differential neutralization technique is at least doubtful. Puri and Sharma (*180*) are of the view that groups of such weak acidity as phenols cannot be titrated completely in an aqueous medium on account of excessive hydrolysis. In this connection it may be recalled that Studebaker (*168*) using nonaqueous potentiometric titrations, on several carbon blacks, obtained acidity values 50–60% higher than