CHARCOAL BEFORE THE WAR. III

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While there has been a good deal of interesting work done on the oxidation of charcoal by oxidizing agents at moderate temperatures, its significance is obscure because nobody knows exactly what the material was which was oxidized. At 150° pure and freshly ignited lampblack gives off much carbon dioxide when in contact with aqueous sodium chlorate and a little osmium tetroxide.¹ When heated in an open vessel a very considerable reduction of the chlorate to chloride took place in twenty hours, whereas there was less than one percent as much reduction when the osmium tetroxide was omitted. This experiment is more interesting as showing the catalytic action of osmium tetroxide on chlorate oxidations than as illustrating the properties of charcoal. Since the solution contained mellitic acid, it seems certain that hydrocarbons were being oxidized. Cane sugar charcoal behaved similarly while retort carbon was oxidized very much more slowly.

Hofmann, Schumpelt and Ritter² report that calcium hypochlorite in dilute aqueous solution oxidizes certain charcoals very rapidly, carbon dioxide being evolved. The gas may contain up to 9 percent CO, which they believe is due to the intermediate formation of high-molecular, dark brownish red to black colored, fluorescing carbonyl compounds which decompose to carbon dioxide and carbon monoxide on further oxidation. If black amorphous charcoal in presence of alkali is exposed for a long time to the action of the air at 120°–150°, it is converted into dark brown to red colloids, which change next to formates and oxalates, and finally to oxalates. The different charcoals behave so much alike, except as to initial reaction velocity, that there is no reason to assume any essential difference of chemical constitution.

¹ Hofmann, Ehrhart and Schneider: Ber. deutsch. chem. Ges., 46, 1665 (1913).

² Ber. deutsch. chem. Ges., 46, 2854 (1913).

When charcoals are oxidized by a solution of 25 g NaClO_3 and 0.05 g OsO_4 in 100 g water, the rate of attack decreases in the following order: lampblack, purified bone-black, ignited sugar charcoal, soot, linden charcoal, acetylene black. If these charcoals receive a preliminary treatment with caustic soda at 120° or with a hypochlorite solution, these differences in the rate of attack disappear very largely and this is especially true if the charcoals are washed afterwards with hydrochloric acid and ammonia to remove the mellogen-like substances produced during the etching by caustic soda. Addition of small amounts of acetic acid, primary sodium phosphate, ruthenium chloride, or manganese sulphate increases the catalytic action of osmium tetroxide so remarkably that acetylene black can be oxidized readily without any previous etching, the manganese sulphate being the least effective of the four.

If cane sugar is charred with sulphuric acid, heated to 500° to drive off the acid, extracted with ammonia, and dried at 250° , an activated potassium chlorate mixture in a heat-insulated flask will attack the resulting charcoal so rapidly as to cause foaming. About 70 percent of the theoretical amount of carbon dioxide is obtained and also a mellogen-like, reddish brown product equal in weight to about 35 percent of the charcoal taken. If the solution is boiled, considerable amounts of formic acid are distilled over.

When beechwood charcoal is heated with 25 percent NaClO_3 and 0.05% OsO_4 , the gas consists of 99 percent CO_2 and 0.6 percent CO . When ignited sugar charcoal is heated with the same solution plus 1 percent primary sodium phosphate, the composition of the gas was 93 percent CO_2 , 6 percent CO and 0.5 percent O_2 . It is unfortunate that the nature of the charcoal and the composition of the solution should have been changed simultaneously, because we have no way of telling the relative importance of the two factors. In the experiment with the beechwood charcoal, the gas accounts for practically all the carbon consumed and consequently little or no mellogen or mellitic acid can have been formed.

With the ignited sugar charcoal, the authors state that 5 g mellogen and 2 g mellitic acid were formed. Mellogen can be obtained best by starting with freshly ignited lampblack and boiling it with the activated chlorate solution (30 g KClO_3 to 10 g charcoal) using a reverse cooler, until the charcoal, after being washed, dissolves almost completely in dilute aqueous ammonia. In this operation small amounts of formic acid are formed. If the ammoniacal solution is evaporated to dryness and extracted with hydrochloric acid, a brilliant black residue is obtained which dissolves in ammonia forming a deep blackish brown solution, which is, of course, really a suspension and not a true solution. The material is taken up very slowly by pure water forming a yellowish brown suspension which is precipitated by acids. Alcohol and ether have scarcely any dispersing action. This substance is very like the mellogen of Bartoli and Papasogli.¹ When dried at 100° , the composition is approximately $\text{C}_{10}\text{H}_2\text{O}_3$. The substance can be oxidized easily to mellitic acid by acidified, activated chlorate solution or by hypochlorites.

The Griesheim Elektron Co. makes a calcium hypochlorite containing 75 percent effective chlorine which will give stable concentrated solutions running fifty-three grams of oxygen per liter. The preliminary rate of attack by these solutions is quite different from that by the chlorate solutions. The rate of oxidation decreases in the order: beechwood charcoal, lampblack, acetylene black, soot, linden charcoal, cane sugar charcoal, and charcoal obtained by the interaction of carbon dioxide and magnesium. If one washes these charcoals with hydrochloric acid and with ammonia after the preliminary attack by calcium hypochlorite, and then dries at 140° , all these charcoals are attacked at practically the same rate by hypochlorite. Treatment with concentrated caustic soda at 150° in presence of air has much the same effect. A previously treated acetylene black or linden charcoal reacts at once with hypochlorite solutions containing 40 g oxygen per liter, the solution heating up, and foaming violently.

¹ Gazz. chim. ital., 11, 468 (1881); 12, 113 (1882); 13, 37 (1883).

With the purest charcoal obtained by reducing carbon dioxide with magnesium, boiling takes place in a few minutes. It follows, therefore, that the differences in the preliminary rates of oxidation of the different charcoals are due to differences in surface conditions. Hofmann considers that the preliminary treatment or etching makes the oxidizing agent more readily adsorbed; but he does not go into any details. With all the etched charcoals the oxidation products are quite similar, very little carbon monoxide being given off and a great deal of carbon dioxide. When the residual charcoal is washed with dilute hydrochloric acid and then with ammonia, large amounts are obtained of the brownish black colloid which was also obtained with the activated chlorate solutions.

When an excess of any charcoal was heated with hypochlorite solution containing 25 g oxygen per liter, the gases had the following compositions:

	CO ₂	CO	O ₂
1. Beechwood charcoal	89.8	9.3	0.3
2. Lampblack	93.4	6.0	0.4
3. Acetylene black	94.5	4.0	1.5

When beechwood charcoal was heated with bleaching powder, the composition of the gas was 92.8 percent CO₂, 5.8 percent CO, 0.2 percent O₂. With the beechwood charcoal and the hypochlorite solution, the amount of CO₂ is only about one-half the theoretical, the balance being used up in forming mellogen and mellitic acid. If the charcoal is not present in excess, some of the mellogen is oxidized to carbon dioxide and mellitic acid. It is interesting to note that there is practically no catalytic decomposition of hypochlorite to chloride and oxygen. Hofmann apparently considers that mellitic acid is formed from pure carbon and he does not refer to the work which contradicts that view.

Acheson graphite is not changed perceptibly after standing for several days in contact with hypochlorite solution. Diamond powder was attacked perceptibly in the course of

fourteen days' treatment with the ten-fold amount of hypochlorite solution containing 43 g. oxygen per liter. The residue consisted of diamond powder, chlorate and carbonate but no hypochlorite. When the diamond powder was washed with hydrochloric acid and then treated with aqueous ammonia, a heavy, white, milky suspension was obtained which ran through a dense double filter and was coagulated by acids to an almost white, amorphous precipitate. The yield was about one percent of the diamond powder and the composition was apparently 86.74 percent carbon and 10.33 percent water. If the undissolved diamond powder was evaporated with aqua regia and again treated with hypochlorite solution, a fresh amount of milky solution could be obtained in the same way as before.

Haber and Bruner¹ found that wood charcoal dissolves in fused caustic at 500°, forming carbonate and hydrogen, while LeBlanc² showed that pure carbon, made by reducing carbon dioxide with sodium, reacts with caustic potash at 650°, setting free three hydrogen atoms per carbon atom, carbonate being formed and potassium volatilizing. At lower temperatures, Millon³ showed that wood charcoal, prepared at 320°, reacts with caustic alkali in presence of air to form a humus-like substance which goes into apparent solution in water. Hofmann, Schumpelt and Ritter⁴ have made experiments at 150–180° because they were anxious to see what were the first products and how far the different charcoals behaved alike.

The first experiments were made with intensely ignited sugar charcoal having a composition of 96.5 percent carbon and 0.6 percent hydrogen. When 15 g charcoal, 20 g purest NaOH, and 40 cc water were heated 40 hours at 160° in presence of CO₂-free air, the resulting aqueous solution was beautifully brown-red with a green fluorescence and, therefore, contained

¹ Zeit. Elektrochemie, 10, 697 (1904).

² Ber. deutsch. chem. Ges., 45, 2309 (1912).

³ Jahresber. Chemie, 1860, 68.

⁴ Ber. deutsch. chem. Ges., 46, 2854 (1913).

Bartoli and Papasogli's compound, $C_{11}H_6O_7$. There were also small amounts of mellitic acid, and oxalic acid corresponding to 1.7 g calcium oxalate. Further treatment of the residual charcoal gave the same products in approximately the same amounts. It is, therefore, not a surface film which reacts. If the air acts longer, the amount of oxalic acid does not increase much but the amount of carbonate does. If water is added continuously to prevent drying, the reaction proceeds more rapidly but the amount of oxalate does not change much. It seems certain, therefore, that oxalate is a preliminary step in the formation of carbonate. Addition of an oxygen carrier, such as one gram ammonium vanadate, increases the rate of formation of carbonate but decreases the recoverable oxalate to about 2 mg and causes the disappearance of the red colloid. If the caustic soda is not made from metallic sodium, it usually contains some vanadate which accounts for Millon and Berthelot not finding oxalate. Above 220° the carbonate is formed so rapidly that the preliminary oxidation stages cannot be isolated. At 120° – 130° considerable amounts of oxalate and of reddish brown oxides are formed and the conversion to carbonate proceeds very slowly. A little formate is obtained at 120° – 150° . In a nitrogen atmosphere, formate and a little carbonate are the only products. The yield of formate is apparently due to oxygen present in the charcoal and Hofmann believes that in the complete absence of oxygen, charcoal and caustic potash would not react at 180° .

Lampblack behaved like sugar charcoal even after being purified by heating in a current of chlorine and then in a current of hydrogen. Acetylene black is oxidized somewhat more slowly and gives less of the brownish red colloid. There is nothing in all this to show to what extent the decomposition products are those of pure carbon or of hydrocarbons. It is worth noting that since we can get formic, oxalic, and carbonic acids from carbon monoxide or dioxide, there is no apparent theoretical reason why pure carbon should not be oxidized to mellitic acid. The argument against it is merely

that the yield of mellitic acid drops off practically to zero as the charcoal is purified more and more; but it is still possible that changing the conditions of oxidation would enable us to get mellitic acid from a charcoal which yields none under the ordinary treatment. All we can say at present is that the evidence is against the view that mellitic acid is an oxidation product of pure carbon. The electrolytic oxidation of carbon¹ does not introduce any new feature because there is the same uncertainty as to what is oxidized.

While we do not know definitely, whether the colloidal materials obtained by oxidation of the charcoals are or are not oxidation products of pure carbon, there is always the possibility that these substances may play a more or less important part in adsorption under certain circumstances, and, therefore, it is desirable to see what we know in regard to colloidal carbon. Sabbatani² has described the preparation of colloidal carbon and the matter has been taken up in more detail by Thorne.³

"Finely powdered sucrose was added gradually as in Sabbatani's preparation to concentrated sulphuric acid, the proportions being 1 gram of sucrose to 10 cc of acid. . . . When all the sucrose was added, the liquid was allowed to remain for twenty-four hours, and was then poured into four times its volume of cold distilled water. The whole was then filtered to remove the larger particles which were always present to a greater or less degree.

"The filtrates obtained in this way varied in color from yellow to dark reddish brown, which seemed to depend largely on the accidental formation of lumps in the process of preparation. On dialysis through parchment paper, much of the acid diffused out first, but afterwards the outer liquid became yellow owing to the diffusion of other substances. In order to remove the last traces of sulphuric acid very prolonged dialysis

¹ Millot: *Bull. Soc. chim. Paris*, (2) **37**, 337 (1882); *Comptes rendus*, **101**, 432 (1885).

² *Zeit. Kolloidchemie*, **14**, 29 (1914).

³ *Jour. Chem. Soc.*, **109** I, 202 (1916).

was necessary. On examination in an electric field, the particles moved towards the anode, that is, were negatively charged. In the ultra-microscope not many particles were visible; and gold chloride was reduced by the dialyzed filtrate, in some cases in the cold, but sometimes only on heating. On the addition of small quantities of electrolytes (for example, when 0.5 cc of *N*/20 barium nitrate was added to 10 cc of the liquid) a cloudiness appeared, which finally settled to the bottom of the vessel as a brown powder. Even if a considerable quantity of electrolyte was added, no further precipitation occurred, and the substance, which colored the solution brown, remained, presumably in ordinary solution, as it diffused (although slowly) through parchment paper.

"Experiments were made with dehydrating agents other than sulphuric acid. Fuming sulphuric acid and a hot solution of zinc chloride gave results similar to those obtained with sulphuric acid, except that the carbon produced was more compact and less suspended. With phosphoric oxide no action occurred if the mixture of it with the sugar was kept dry, but on addition of a drop either of sulphuric acid or of water a vigorous action took place with the formation of a spongy mass. On adding water and filtering, a liquid was obtained with similar properties to those obtained by the action of sulphuric acid.

"Thus it is clear that although some carbon in the suspended state is produced by the dehydration of sucrose, etc., with excess of concentrated sulphuric acid, its properties are obscured by more complex products of decomposition, the presence of which is obvious from the odor of burnt sugar arising from the solution during the dehydration process or when evaporated to dryness on the water bath. They do not appear to exert a protective action on the carbon.

"When an electric current (0.4-4.0 amperes at 200 volts) is passed through dilute sodium hydroxide solution using carbon electrodes, one of the electrodes being immersed in the solution and the other just touching the surface, the liquid becomes dark owing to the disintegration of the electrodes.

On filtration, most of the particles pass through the filter and, if the sol is then diluted, remain suspended for many months; otherwise a slow deposition of some of the dispersed matter ensues, presumably removing excess of alkali. On varying the positions and signs of the electrodes, it was found that most dispersion occurred when the positive pole just touched the surface of the liquid, thus giving a high current density at its surface; on immersing it further, electrolysis was more vigorous, but little dispersion occurred. With the negative pole touching the surface, an arc was set up between carbon and liquid and the electrode was burnt away, some large particles being formed from its violent disintegration. Only large particles could be obtained by striking an arc between the carbons under the surface. It was also found that almost all the sol originated from the positive pole, for when the other electrode was surrounded by a soaked thimble of parchment paper only the outer liquid became dark. Under ordinary conditions, however, if the current was reversed after it had been flowing for some time, a cloud of dark particles arose from the negative pole immersed in the liquid; this appears to be due to the removal from that pole of particles which were formed from the positive pole and were carried through the liquid and deposited by cataphoretic action.

"Most of the sols were obtained from electrodes of ordinary arc carbons, but similar results were obtained with electrodes of crude gas carbon and of Acheson graphite. A solution of sodium hydroxide containing 2-3 grams per liter is best for the formation of the sol; a more dilute solution does not permit a sufficiently heavy current to pass, while a greater concentration precipitates the sol, and the positive electrode is not so finely broken up. The formation of a sol is noticeable, however; at as low a concentration as 0.4 gram per liter, that is, $N/100$; and although a more concentrated solution is more efficient for the actual preparation, the sol is more stable if diluted soon after formation.

"The sols thus obtained when subjected to dialysis in a bag or thimble of parchment paper are completely precipitated

if the alkali is entirely removed in this manner; the dialysis can be stopped when just enough alkali is left to render the sol stable. (In this the sol is similar in behavior to a ferric hydroxide sol, which is precipitated if all the acid is dialyzed away from it.) The deposit formed in the dialyzer can be suspended in part by addition of water containing a little alkali.

"The sol showed a very distinct Tyndall cone, and in layers more than a few mm in thickness was black; in very thin layers it was of a brown tint. Under the microscope no particles were seen, but with the ultra-microscope a large number were visible in vigorous Brownian movement. Thus the particles were of a size similar to that of the particles in metallic sols. When exposed to the action of an electric field in the ordinary Y-tube apparatus, the particles in the sols prepared invariably moved towards the anode, that is, they were negatively charged, as are most hydrosols of elements, whether metals or non-metals. If the sol was acidified, no change in the sign of the charge took place.

"The sols were particularly sensitive to electrolytes, so much so that if tap-water was used in preparing them, precipitation of the particles occurred as fast as they were formed. An experiment with a sol containing about 0.3 gram of carbon per liter (by the loss in weight of the electrodes) and $N/40$ barium chloride gave the following results. Ten cc of the sol were used in all cases.

$N/40$ -Barium chloride cc	Result
0.10 } 0.15 } 0.20 } 0.25 } 0.30 } 0.40 }	No precipitate apparent at once; very slight precipitate after a week
0.50 } 0.70 }	No precipitate apparent at once; mostly precipitated after a week
0.80 } 1.00 }	Some aggregates after one hour; completely precipitated in a week
3.00	Some aggregates at once; partly settled in one hour
	Flocculation at once; mostly settled in one hour
	Flocculation at once; mostly settled in twenty minutes

"Thus, taking 0.3 cc as the minimum concentration to effect precipitation of the sol employed, it will be seen that this concentration is one of 0.078 gram of barium chloride (that is, 0.36 millimol.) per liter of sol. This concentration is of the same order as that required to precipitate other suspensoids of similar dispersity and concentration (both of which in the case of sols used in this work were only approximately known). For example, an arsenic trisulphide sol containing 7.54 millimols. per liter required a concentration of 0.691 millimol. per liter of barium chloride to precipitate it.¹ The coagulum from the sol was black, and was only partly dispersed again on prolonged washing with distilled water.

"It was thus seen that the sols formed in this way were typical suspensoids; and it now remained to see whether the particles were pure carbon or a product of oxidation. With this end in view, the sol was made on a considerable scale, and after filtration and keeping was precipitated by barium chloride and the solid collected in order to determine its composition by combustion. The precipitate was washed with distilled water and then with dilute hydrochloric acid to remove the barium carbonate which had gradually accumulated in the mass. On doing this, a yellow liquid passed through the filter; it was apparently not colloidal, as it gave no Tyndall cone and diffused easily through parchment paper. On distilling a portion of the filtrate, the colored substance remained in the non-volatile portion, and on evaporation on the water bath a small quantity of brown residue remained; if sulphuric acid was present during the evaporation, an odor of burnt sugar was noticeable, but there was not sufficient of the substance to permit of its identification.

"The precipitate was washed with dilute hydrochloric acid until the filtrate gave no precipitate with dilute sulphuric acid; on finally washing with distilled water, some of the colloid passed through the filter paper, so it was washed with very dilute hydrochloric acid until the filtrate ceased to be

¹ Freundlich: *Zeit. phys. Chem.*, **44**, 144 (1903).

yellow. It was then dried in the air for a week, ground, and kept for a similar period in a vacuum desiccator.

"On burning it in oxygen in the ordinary apparatus for organic combustion, the following results were obtained:

	I	II	Mean values
Carbon	65.73	67.50	66.61
Hydrogen	2.07	1.93	1.99
Residue	15.85	14.66	15.25
	83.65	84.09	83.85
	16.35	15.91	16.15
Difference	100.00	100.00	100.00

The 'residue' remains unburnt even when heated to bright redness in pure oxygen, and on examination it was found to consist mostly of silica with a trace of iron. Thus it is probably derived from impurities in the arc carbons used to make the sol. The difference is presumably oxygen.

"When the results are calculated on the basis of percentage of combustible material they agree fairly well with those obtained by Söhngen,¹ who obtained C = 81.2, H = 0.85 and O = 18 percent, while the mean results in this work are C = 78.59, H = 2.35, O = 19.05 percent. It is clear that very considerable oxidation occurs during the disintegration of the electrodes, as organic compounds occur in the washings, and possibly in the above product. The results of analysis of the latter may point to the existence of a carbohydrate, or more likely to water firmly retained by the carbon; the latter seems probable in view of the washing of the precipitate until free from colored soluble matter, but in any case organic matter is present in the sol and seems necessary for a stable dispersion.

"The carbon formed by the reduction of carbon dioxide with magnesium was prepared, and the crude product treated with dilute hydrochloric acid to remove magnesium oxide and carbonate. On powdering it and adding it to water, no perma-

¹ Chem. Weekblad, II, 593 (1914).

nent suspension was noted after some months, neither did the addition of alkali to the water cause a colloidal solution to be formed. Silicon, when prepared in this way, readily forms a suspension.¹

"When acetylene reacts with chlorine, a fine soot is produced. It was found to be impossible to produce it in water by simultaneously bubbling the two gases through the liquid. If produced by spontaneous combustion of the gases, it was difficult to moisten it and no suspension ensued.

"Carbon, prepared by the dehydration of sucrose by sulphuric acid, was treated with excess of the acid in order to dehydrate, if possible, the intermediate compounds formed. The mass was then washed with water until free from acid, but it did not form a suspension either in water or alkali; a brownish yellow solution was observed after some time in the alkali used, while in the aqueous liquid a fungus began to grow showing that organic compounds were still present. Similarly, if the carbon was heated to a red heat either in air or in chlorine, the residue gave no sol with water or alkali.

"On examination of pieces of an Acheson graphite electrode, it was found that although they were more difficult to disintegrate when used in place of arc carbons in the electrolytic method, a similar sol was obtained. A finely powdered portion could not be dispersed in water or alkali, but floated on the surface. However, on the addition of a few crystals of tannic acid to either solution, the powder was immediately dispersed to give a violet sol which had almost the same properties as those obtained by the electrolytic method. The precise action of the tannic acid has not yet been determined, but it may have a surface-tension effect, thus permitting the particles to be made wet, or it may exert a protective influence on the carbon particles.

"Animal charcoal was extracted with concentrated hydrochloric acid to remove inorganic salts, and then well washed with water and dried. The powder thus obtained did not form a suspension in water, alkali, or tannic acid. When some

¹ Astfalk and Gutbier: *Zeit. Kolloidchemie*, **15**, 23 (1914).

of it was treated with about twenty times its weight of concentrated sulphuric acid, a brown liquid was obtained. On dilution with water to ten times the volume, almost the whole was precipitated in brownish black flocks, which when filtered and washed were suspended, but only for a short time, both in alkali and in tannic acid. Patterson¹ has obtained the sulphuric acid solution, and regards it as evidence that organic matter is still left in animal charcoal, and to this he attributes the superior adsorptive power of such charcoal over other varieties of carbon. Comparing these results with the others obtained in this work, they seem to confirm the supposition of the existence of organic matter in the charcoal."

Herzog² shows that animal charcoal adsorbs sugars from aqueous solution and that a reversible equilibrium is reached which can be expressed by the equation $x/m = kC^n$, where x is the amount of sugar adsorbed by m grams of charcoal, and C is the concentration of the unadsorbed sugar, while k and n are constants. Starting with 100 cc of solutions and 5 grams of animal charcoal, the following values were obtained for k and n with different sugars:

Sugar	k	n
Dextrose	0.766	0.474
Laevulose	0.338	0.539
Galactose	1.016	0.694
Sucrose	0.106?	0.127
Maltose	1.142	0.133
Lactose	1.138	0.135

Rona and Michaelis³ point out that the adsorption of sugar by charcoal may be entirely inhibited by the presence of a sufficient quantity of another substance, such as acetone or acetic acid, which is adsorbed more powerfully than the sugar. The practical value of this observation lies in the fact that a dilute solution of sugar to which 10 percent of acetic

¹ Jour. Soc. Chem. Ind., 22, 609 (1903).

² Zeit. physiol. Chem., 60, 79 (1909).

³ Biochem. Zeit., 16, 489 (1896).

acid or acetone has been added, may be decolorized by shaking with 5 percent of charcoal without any loss of sugar. This applies both to dextrose and to sucrose, and the charcoal has no inverting action on the latter sugar. The presence of albumin does not influence the adsorption of sugar or acetone by charcoal.

On the other hand, Clark¹ found that a bad decolorization with animal charcoal is always obtained when fruit sugar and salts are present in considerable quantity showing that these substances interfere with the adsorption of the coloring matter. This is in line with some of the earlier observations by Anthon.²

"A molasses containing 109 parts of non-sugars to 100 parts of sugar was filtered through bone-black and then washed with water. A large part of the non-sugars was removed. A red infusion of Pernambuco wood was passed through bone-black until the charcoal took up no more color. The bone-black was washed with water until the water came off colorless. On treatment with clear sugar solution a red color was obtained. After the charcoal was washed until the sugar solution came off colorless a nearly saturated soda solution took out large amounts of color. When this latter removed no more color a solution of potassium carbonate took out some and after this caustic potash removed color. Anthon questions the necessity of using bone-black at all. Its adsorption of organic substances is very slight in presence of free alkalies and its adsorption of lime is limited to a few percent of the weight of the charcoal. On the other hand there is a distinct loss of sugar."

Bauer³ found that both hydrochloric acid and acetic acid decrease the adsorption of sugar by charcoal without interfering with the removal of the color.

Glassner and Suida⁴ made experiments with a large num-

¹ Jour. Soc. Chem. Ind., 32, 262 (1913).

² Chem. Centralblatt, (2) 13, 1003 (1868).

³ Jour. Soc. Chem. Ind., 7, 636 (1888).

⁴ Liebig's Ann., 357, 95 (1907).

ber of organic dyes and found that "the vegetable charcoals (wood, sugar) do not take up appreciable amounts of dyes. Charcoals having a high ash content (sodium and sponge charcoal) behave similarly. Soot has a distinct adsorbing power for basic dyes but takes only the slightest amounts of acid dyes out of solution with the exception of the following dyes which have a peculiar physical condition in aqueous solution: fast red A, fast red A acid, alizarin yellow GGW, alizarin yellow RW. These results with soot are in harmony with those previously found by Lehmann. Glue and wool charcoals also have very slight adsorbing powers for all dyes. A very different behavior was observed with the charcoals obtained from Merck: bone-black, blood charcoal and animal charcoal. If one compares the composition of the different charcoals with the adsorbing power for dyes, it appears that the vegetable charcoals, which decolorize badly, contain no nitrogen or only traces, while the animal charcoals are relatively rich in nitrogen. This cannot be the sole cause of the difference because certain animal charcoals, such as glue charcoal, have a relatively low ash content and high nitrogen content; but are bad decolorizers, while soot which contains relatively little nitrogen or ash can take up appreciable amounts, at any rate of the basic dyes. Also, the best decolorizing animal charcoal has the lowest nitrogen and hydrogen content and the highest ash content of the good animal charcoals. It is, therefore, probable that the nature of the ash is important and the way in which the nitrogen is bound.

"The addition of sodium chloride and tri-calcium phosphate has relatively little beneficial effect with blood charcoal but more with soot which does not adsorb well.

"When basic dyes (chlorides) are taken up by blood charcoal the chloride remains in the solution, which, however, does not become acid. The amount of the color bases which can be extracted by alcohol or ether is very much less than clings to the amount of chloride in the decolorizing solutions. It seems certain, therefore, that a large part of the color bases is held by the charcoal very firmly. It is easier to wash the

dye out of soot than out of blood charcoal. Experiments show that there has been no appreciable oxidation of the dyes.

"It seems probable that the high decolorizing power of some of the animal charcoal is due to the presence of polymeric cyanimide derivatives, such as melam, melamine, etc. As a matter of fact, it appears that the best animal charcoal which was tested came from a Prussian Blue manufacture, and, therefore undoubtedly contained cyanogen in some form. Platinized asbestos has practically no decolorizing action on any of the dye solutions studied.

"Heating charcoal with potassium carbonate increases the adsorption power for crystal violet and crystal ponceau. This is apparently due chiefly to the formation of cyanide compounds because the increase in adsorbing power is much less when the charcoal is heated with potassium carbonate in an atmosphere of CO_2 ."

Knecht¹ also harks back to the effect of nitrogen, showing that decreasing the percentage of nitrogen in an animal charcoal decreases its adsorption of acid dyes like crystal scarlet. The decrease in the percentage of nitrogen has practically no effect on the adsorption of a basic dye like methylene blue. If, on the other hand, purified animal charcoal be heated with aluminum powder or zinc dust and then treated successively with hydrochloric and hydrofluoric acids to remove impurities, the adsorbing power for methylene blue is decreased very much while that for crystal scarlet is decreased to a much lesser extent (probably owing to unavoidable loss of nitrogen). This seems to be pretty strong evidence that the impurities in the charcoal are very important. Knecht agrees with Patterson and with Glassner and Suida that the decolorizing action of animal charcoal is due to the presence of organic compounds which are stable at a red heat. He believes that absolutely pure, amorphous carbon probably has no decolorizing action either for acid or basic dyes. Knecht also claims that the adsorption by animal charcoal of iodine dissolved in

¹ Jour. Soc. Chem. Ind., 26, 949 (1907); 28, 700 (1909).

a potassium iodide solution depends on the amount of fixed nitrogen in the charcoal.

Rosenthaler and Türk¹ have studied the adsorption of various pharmaceutical substances from their solutions when treated under standard conditions with different kinds of charcoal. These charcoals may be divided, according to their adsorbent powers, into strongly adsorbent: bone, flesh, and "vegetable blood" charcoals, in the above order; and weakly adsorbent or non-adsorbent: blood, lime-wood, and sponge charcoals. For the same kind of charcoal, the adsorption of any substance varies with the solvent which is employed. The adsorption is by far the strongest in aqueous solutions, it is less with ethyl alcohol, methyl alcohol, ethyl acetate, acetone, and least of all with chloroform solutions. The speed of adsorption depends on the same factors as influence the amount of adsorption, being the greatest in the case of bone charcoal and aqueous solutions. The quantity of substance adsorbed by a given quantity of charcoal is relatively less for concentrated solutions than for dilute solutions. All the circumstances which favor adsorption act in a similar degree in resisting the re-extraction of the adsorbed substance. The decolorizing power of the charcoal is dependent on its adsorbing power. As regards the use of charcoal for decolorizing purposes, they state that the charcoal must be carefully purified before use and the quantity of charcoal employed should be as small as possible. It is not necessary to heat the liquid with the charcoal; several hours' contact at the ordinary temperature will suffice. The decolorization should not, for preference, be effected on an aqueous solution, because the loss of substance by adsorption is at a maximum in that solvent the solution should be as concentrated as possible. Easily oxidizable substances should not be decolorized by animal charcoal, because this charcoal has a powerful oxidizing action; the oxidation of alkaloids is retarded by treating them in the form of salts. Blood charcoal has the strongest oxidizing action, lime-wood charcoal has hardly any. Bone and

¹ Arch. Pharm., 244, 517; Jour. Soc. Chem. Ind., 25, 1172 (1906).

flesh charcoals can be employed in the determination of caffeine without loss of alkaloid, but in the determination of sugars, etc., in wine and other liquids, charcoal should not be used unless it has proved that no loss by adsorption takes place under the conditions of the experiment. The close interdependence of the decolorizing and adsorbing properties of charcoals suggests that the decolorization is due to adsorption of the coloring matters. The fact that successful results can be obtained in practice depends first on the circumstance that the amount of coloring matter is generally only a fraction of the total substance in solution, and secondly, on a selective adsorption, according to which the quantity adsorbed is generally proportional to the molecular weight, most coloring matters being substances of high molecular weight."

Since adsorption is selective, we may have three extreme cases with a salt in aqueous solution. The charcoal may have strong selective adsorption for the salt itself, or for one of the hydrolysis products, the free base or the free acid. All three cases are known. Liebermann¹ showed that with barium formate, sodium and lead acetates, calcium glycollate, zinc lactate, ammonium oxalate and potassium sodium tartrate solutions, bone-black removed the basic constituents to a greater extent than the acid ones, thus leaving the solution acid. Calcium and barium benzoates are adsorbed without change, as is also the case with sodium chloride, nitrate and sulphate. From a solution of aniline benzoate, charcoal takes out more benzoic acid than aniline while with aniline acetate, more aniline is removed than acetic acid.²

The decomposition of salts as a result of selective adsorption was studied many years ago by Weppen.³ He found that bone-black would easily remove all traces of the metal from ammoniacal solutions of copper, zinc, silver, and lead, that lead oxide is taken out of an alkaline lead plumbite solution, and that the acids are removed from potassium antimoniate and

¹ Sitzungsber. Akad. Wiss. Wien, **75**, II, 331 (1878).

² Freundlich and Masius: "Van Bemmelen Gedenkboek," 100 (1910).

³ Liebig's Ann., **55**, 241 (1845); **59**, 354 (1846).

sodium tungstate solutions. Mercuric iodide was adsorbed quantitatively from a solution in ammonium iodide and arsenic sulphide from a solution in ammonium sulphide. In presence of ammonia, some barium hydroxide is taken out of a barium chloride solution. From ferrous sulphate and mercuric chloride solutions basic sulphates are adsorbed. Chevalier¹ found that charcoal takes lead oxide out of lead nitrate or acetate dissolved in water, alcohol or acetic acid. More is taken from a hot than a cold solution.

Charcoal takes out ferric chloride without decomposition from solutions in pure acetone and in ethyl acetate;² but takes out chiefly the iron from solutions in water or 95 percent alcohol. Exposure to sunlight increases the hydrolysis.

In addition to causing hydrolysis and dissociation, charcoal may also reduce salts. Heintz³ reports on a case of this sort: "I believed that bone-black, when washed carefully and then ignited would not precipitate platinum chloride. To my surprise, I found recently that platinum is actually precipitated from its solution by charcoal. If one takes bone-black which has been boiled thoroughly with hydrochloric acid and with water and then ignited, and lets it stand in contact with a platinum chloride solution, one notices after awhile that the color of the solution is distinctly lighter. If the solution is boiled for a few minutes with the charcoal the color becomes very much less; but the liquid takes on a reddish shade. If sufficient charcoal is present and if the boiling is kept up the solution becomes entirely colorless, containing hydrochloric acid but no platinum. It is not surprising that platinum chloride is precipitated by bone-black. It has long been known that organic dyes, many colorless organic substances, and certain colored and colorless organic substances are precipitated by charcoal. It is perhaps new, however, that bone-black decomposes a boiling platinum chloride solution chemically. It seems improbable that the reduction is due to char-

¹ *Comptes rendus*, **19**, 1279 (1845).

² Oeschner de Coninck: *Comptes rendus*, **130**, 1627; **131**, 275 (1900).

³ Liebig's *Ann.*, **187**, 227 (1877).

coal itself. Since charcoal, no matter how highly heated, always contains hydrogen it is probable that hydrogen causes the reduction since it is known that platinum chloride is easily reduced by hydrogen with formation of hydrochloric acid.

"On the other hand the reduction of platinum chloride by a simultaneous action of carbon and water is not impossible; but in this case carbon dioxide or carbon monoxide must be formed in addition to platinum and hydrochloric acid. An experiment showed, however, that neither of these gases was formed. In this experiment platinum chloride was not used; I took ferric chloride since I had found that its aqueous solution is reduced at the boiling point to ferrous chloride by freshly ignited bone-black. If one takes a solution of pure ferric chloride which gives no trace of Prussian Blue with potassium ferricyanide and boils it with purified and freshly ignited bone-black, the filtered solution gives a tremendous precipitate of Prussian Blue. One can see that reduction has taken place, because the intense yellow color of the solution decreases very much when boiled with bone-black. If an air current free from carbon dioxide is passed through the boiling liquid and then through a mixture of calcium chloride and ammonia, no clouding takes place in the latter solution. The same result is obtained if the air current is passed previously over glowing copper oxide. During the reduction of ferric chloride to ferrous chloride by charcoal there is, therefore, formed neither carbon dioxide, carbon monoxide nor any other gas containing carbon. The charcoal used was free from heavy metals and even iron was present only in extraordinarily small amount.

"The marked reducing action of bone-black is, therefore, to be ascribed to hydrogen which is always present even in charcoal which has been raised to a white heat. The ferric chloride may give rise to a complicated carbon compound just as we know that potassium permanganate converts charcoal into mellitic acid. In this case the reaction should take place both in alkaline and in acid solution. As a matter of fact if one filters the ferric chloride solution which has been boiled

with charcoal, precipitates the iron with ammonia, washes, and evaporates both the filtrate and the solution, both residues contain traces of carbonaceous matter. While the formation of a small amount of organic substances certainly occurs when ferric chloride solution acts on ignited bone-black, the amount of this substance is so very small that one must seek another cause for the considerable amount of ferrous chloride formed. It is practically certain, therefore, that the greater part of the reduction is due to the hydrogen in the charcoal."

Avery¹ came to quite a different conclusion.

"Charcoal is used largely for the precipitation of gold from its solutions in the extraction of this metal from its ores by the 'chlorine' or the 'cyanide' process. In the former case, the solution of gold chloride, is heated, and filtered through tubs filled with wood charcoal. The precipitation is rapid and complete. The charcoal with which the solution first comes into contact soon becomes covered with a beautiful, tough yellow deposit of metallic gold; as the solution becomes more dilute no deposit is visible on the charcoal; but the ash left on incineration is colored pink by the finely-divided metal. In the cyanide process, the filtration through charcoal takes place in the cold. The solutions are much more dilute with respect to their gold content, a longer column of charcoal is used, and no metallic deposit appears. After the charcoal has been in use for some time, the precipitation of gold takes place less actively, but it can be renewed by heating the charcoal to redness in absence of air and replacing in the filters. It has also been noticed that if a current of electricity is passed for a short time through a filter, so arranged that the charcoal is the cathode the gold is afterwards precipitated for some time by the charcoal so treated, even more readily than by freshly-burnt material. The reaction that takes place during this reduction does not appear to have been satisfactorily investigated, although it has been noticed and various suggestions made regarding it. The reducing action of lampblack, animal charcoal, bone-black, and coke, on various metallic salts has

¹ Jour. Soc. Chem. Ind., 27, 255 (1908).

been described by several investigators, who have attributed the action to impurities in the carbon, to occluded hydrogen, or to the mechanical attraction of carbon for the dissolved salts. In most cases no quantitative work has been attempted. Weppen¹ found that the greater part of the acid was present in the free state after the reduction of the salt, and that it was very difficult to recover the last portions of the acid. König,² working with purified charcoal, found that carbon dioxide was formed. He assumed the reaction to be in accordance with an equation which, expressed in modern form, would be, $4\text{AuCl}_3 + 6\text{H}_2\text{O} + 3\text{C} = 4\text{Au} + 12\text{HCl} + 3\text{CO}_2$; but in his experiment he found only $\frac{1}{20}$ of this theoretical amount of carbon dioxide. He concluded that this fraction only of the reduction of gold chloride was due to the charcoal, the rest being due probably to physically adsorbed gases.

"Attempts were made to prepare charcoal free from all occluded reducing gases, so that the part played by the charcoal alone might be determined. Sugar was first heated to a high temperature in absence of oxygen, but it was found that the light porous mass so obtained was less suitable for manipulation than wood charcoal, and, moreover, that even after prolonged heating it still contained appreciable quantities of hydrocarbons. Ordinary wood charcoal was used, crushed to small size, treated with acids to dissolve out mineral matter, heated in chlorine to decompose hydrocarbons, and then in nitrogen to get rid of the chlorine. It was found that even after prolonged heating in nitrogen, traces of chlorine were still present. Finally a very pure form of charcoal was obtained from coconut shell. This was strongly heated in closed clay crucibles for some hours, then boiled with nitric acid for 5 or 6 hours, and washed thoroughly till the washings were nearly free from acid—the washing taking several days. It was then dried in the air, crushed and sieved, collecting the particles between 1 and 3 mm diameter. These were dried first in a desiccator over strong sulphuric acid, then over phosphorus pentoxide,

¹ Liebig's Ann., **55**, 241 (1845).

² Chem. News, **45**, 215.

and finally heated to redness in a closed platinum crucible and cooled in a desiccator over phosphorus pentoxide. The crucible was heated in a muffle in an oxidizing atmosphere to avoid the possibility of adsorption of hydrogen or other reducing gases from the furnace. This charcoal was examined, first by heating it for one or two hours in a current of pure nitrogen and finding its loss of weight. It was then heated in a current of oxygen and the amount of water formed, determined. From this the amount of hydrogen still present in the charcoal was calculated. The weight lost when heated in nitrogen was found to be due to water and carbon dioxide: The gas current was carried through another combustion furnace containing copper oxide, but no hydrogen, hydrocarbons, or carbon monoxide were found present.

"The results of the analysis of the charcoal were as follows:

	Heated in nitrogen Loss Percent	Combustion in oxygen	
		Water formed, calcu- lated as hydrogen Percent	Ash Percent
No. 1	5.0 ¹	0.16	0.26
No. 2	0.1	0.25	0.23
No. 3	0.5	0.15	0.20

"The results show that the amount of adsorbed gases in this charcoal is very small—the loss in nitrogen and amount of hydrogen found on combustion (0.25 percent at most), being due to a large extent probably, to moisture still present. In the subsequent work the charcoal is regarded as pure, the small amount of reducing agent other than carbon, possibly present being ignored." This charcoal was heated in nitrogen to remove other occluded gases and was then added to the gold chloride solution. By taking special precautions to remove

¹ No. 1 was dried over phosphoric anhydride but not ignited in platinum crucibles. Nos. 2 and 3 were dried, ignited and cooled over phosphoric anhydride before analysis.

all the carbon dioxide formed, it was found that the reaction apparently proceeded according to the equation $4\text{AuCl}_3 + 6\text{H}_2\text{O} + 3\text{C} = 4\text{Au} + 12\text{HCl} + 3\text{CO}_2$."

In view of the fact that carbon monoxide will reduce gold chloride solutions, and in view of the fact that carbon is known to react with oxygen slowly, there is no reason why charcoal should not reduce gold salts. On the other hand, unless special precautions are taken, the reduction in any particular case may well be due to impurities in the charcoal.

Lazowski¹ states that ignited wood charcoal reduces not too concentrated solutions of the salts of tin, copper, mercury, silver, platinum, palladium and gold, provided they contain no free acid. One of the interesting things about this is that with copper the metallic coating varies from blue to red which presumably means that he had colloidal copper.

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¹ Chem. Gazette, 1848, 43.