

charcoals gave an S-shaped curve when plotted against their hydrogen contents, increasing with the hydrogen content to a maximum value. The maximum value was assumed to be given by charcoal heated below temperatures at which shrinkage occurs, the observed values being low by an approximately constant value because of a relatively small volume of impenetrable capillary space. As the hydrogen content decreased, or as the temperature to which the samples had been heated increased, shrinkage occurred and this impenetrable volume became relatively larger, thereby giving a lower apparent density.

6. That the sorptive capacity of the samples increased with increasing hydrogen content was shown to be in accordance with the view, which is consistent with all known available evidence, that so-called amorphous carbons are hydrocarbons of low hydrogen content built up of polymerized residues from the thermal decomposition of hydrocarbons of greater hydrogen content, and that any treatment which tends to increase the unsaturation of these residues will increase the sorptive capacity of the charcoal.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY AND THE WESTERN ELECTRIC COMPANY, INCORPORATED]

A STUDY OF THE RATE OF OXIDATION OF CERTAIN CHARCOALS

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In connection with the work on "The Relation between the Hydrogen Content of Certain Charcoals and Some Other Properties," described in the preceding paper, a study of the rate of oxidation of some of these charcoals was undertaken. This work was nearing completion before the relation between the maximum temperature of roast and the hydrogen content was discovered, and hence the temperatures chosen for this work were unfortunately not those which would now appear best suited for the purpose. Ten of the 23 samples used in the previous investigation were chosen for the present study. These were all non-activated charcoals prepared by heating granular anthracite coal in a gas-fired furnace in the manner described in the previous paper. These ten samples were selected primarily with a consideration of their extent of surface since, from theoretical considerations, if the surfaces were all of the same material, the rate of oxidation should be proportional to the surface exposed to the oxygen, analogous to rate of solution phenomena. However, no strict proportionality need exist between the extent of surface as determined and the surface exposed to the oxygen, available for oxidation, since the distribution of the surface within the capillaries of the various samples most probably is not the same.

After performing a series of over 150 preliminary experiments, the following procedure was adopted for determining the rate of oxidation.

A 0.5g. sample was heated at 1030° for 45 minutes in a stream of carefully dried hydrogen, cooled in hydrogen, and transferred to a closed weighed vessel. The object of this preliminary treatment was to drive off sorbed gases and water, so that the samples would be in as nearly comparable conditions as possible, since the preliminary experiments had shown that sufficient accuracy was not obtained by a direct determination on the untreated sample. After this preheat in hydrogen, the sample was carefully weighed and transferred to a combustion furnace. Commercial oxygen, dried over phosphorus pentoxide, was passed through the combustion tube at the rate of 60 ± 2 cc. per minute as determined by a calibrated flow-meter. The temperature of the furnace was maintained at $450^\circ \pm 3^\circ$ for the period of combustion of 60 minutes. The percentage loss in weight of the sample was calculated from the gain in weight of soda lime tubes through which the gas passed on leaving the furnace, and was used as a measure of the rate of oxidation.

On the basis of fourteen determinations on one of the samples, the average deviation of a single observation from the mean was found to be $\pm 10\%$. Each of several possible factors in the degree of precision of the results was carefully studied in the preliminary experiments but with the most careful control and manipulation $\pm 10\%$ was the highest degree of precision obtainable (that is, average deviation of a single observation). Since the percentage loss in weight of carbon for most of the samples was less than 5% which represents 0.025 g. on the basis of a 0.5g. sample, this $\pm 10\%$ indicates that the average deviation of a single observation from the mean was for most samples less than ± 0.0025 g. of carbon oxidized. In view of the observed precision, several determinations would be necessary for each sample in order to obtain figures of much significance. However, on only five of the ten samples were a sufficient number of experiments performed to give the indicated degree of accuracy to the

TABLE I

RATE OF OXIDATION OF CERTAIN CHARCOALS AT 450°

Temperature of combustion, 450° \pm 3°. Oxygen flow, 60° \pm 2 cc. per min. Preheat, 45 min. at 1030° in hydrogen.

Sample	Percentage of C lost in 60 min.	Surface in m. ² per g.	Percentage of chemically combined hydrogen
23	1.62 \pm 0.04	0.6	0.21
14	2.20 \pm 0.07	1.0	.27
3	2.9 ^a	2.5	.30
4	2.79 \pm 0.08	5.5	.38
1	4.16 \pm 0.39	5.8	.40
5	5.5 ^a	8.8	.44
2	4.65 ^b	13.8	.40
6	5.09 \pm 0.09	15.4	.38
21	5.7 ^a	17.8	.49
18	8.0 ^a	32.2	.53

^a Single observation, that is, $\pm 10\%$.

^b Single observation at 458°

mean values recorded in Table I. The values reported for the five remaining samples were determined by a single observation at 450° but experiments at other temperatures indicated that the values were approximately correct.

When the data in Table I are represented diagrammatically as in Fig. 1, the relation of the rate of oxidation of the charcoals both to the extent of surface, as determined by the sorption of water vapor in the preceding paper, and to the amount of chemically combined hydrogen is quite evi-

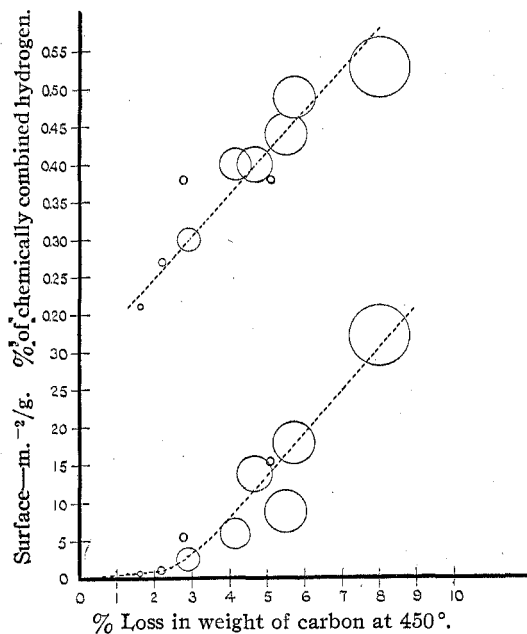


Fig. 1.—The relation of rate of oxidation of charcoals to the extent of the surface and to the percentage of chemically combined hydrogen. The circles represent the deviations of the percentage loss in weight of carbon.

dent. The larger the surface and the greater the amount of chemically combined hydrogen, the greater was the rate of oxidation. As pointed out in the discussion of the relation of the chemically combined hydrogen to some other properties of charcoal, the amount of such hydrogen is an indication of the previous history of the charcoal and it is not to be expected that the carbon associated with these small amounts of hydrogen differs much in its chemical reactivity. Hence, the data indicate that there must be a proportionality between the surface exposed to the oxygen by each sample and that experimentally determined. Considering the undetermined amount of shrinkage which may have taken place to different extents in the different samples during the preheat at 1030°, since not all the samples had been previously heated at so high a temperature, the observed relationship between the extent of surface and rate of oxidation may be regarded as very satisfactory.

Since low-temperature oxidation is one of the standard methods of causing activation of charcoals and since an increase in surface accompanies activation,¹ the data on the relation of extent of surface to rate of oxidation given in Table I would indicate that at a given temperature the rate of

¹ Compare Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, **11**, 420 (1919).

oxidation of a charcoal increases with the length of time that the oxidation is continued. Preliminary experiments by Wheeler² showed that the low temperature oxidation of charcoals could be regarded as unimolecular and that van't Hoff's expression $\frac{1}{t} \cdot \frac{C_0}{C_t} = K$ could be employed for determining the relative rates. The considerations given above, however, would seem to limit the use of the "K" values for a measure of the rates of oxidation of different charcoals to equal periods of oxidation similar to the practice used in the present investigation, since it would be expected that "K" would not be constant over long periods but would increase in value with increase in time of oxidation.

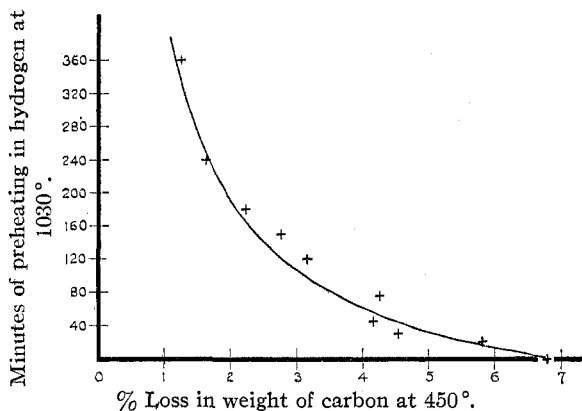


Fig. 2.—Influence of time of preheating a charcoal at 1030° on its rate of oxidation. Sample No. 1.

During the study of the various factors which might affect the precision of the measurements of rate of oxidation, the observation was made that for a given charcoal the loss in weight at 450° decreased proportionately to the length of time the sample was left in the hydrogen at 1030° during the preheat. These data are given in Table II and graphically in Fig. 2.

TABLE II
INFLUENCE OF TIME OF HEATING AT 1030° IN HYDROGEN ON THE RATE OF OXIDATION AT 450°

		SAMPLE 1									
Minutes of pre-heating at 1030°	0	20	30	45	75	120	150	180	240	360	
% loss in wt. in 60 min. at 450°....	6.78	5.82	4.54	4.16	4.26	3.16	2.76	2.23	1.63	1.25	

Thus, by heating to 1030° in hydrogen for six hours the rate of oxidation at 450°, as represented by the percentage loss in weight of carbon, was

² Wheeler, *Engineering*, 115, 667 (1923).

reduced to less than a fifth of the value obtained with no preheating. The explanation of this effect may be either that the extent of surface was reduced or that the resistance of the carbon atoms themselves to oxidation was increased, or a combination of the two effects. Both explanations involve the assumption of the formation of methane according to the equation, $C + 2H_2 \rightleftharpoons CH_4$. The equilibrium constant of this reaction, $K = p_{CH_4}/p_{H_2}^2$, at 1030° is 0.0118 as calculated from the free energy of the reaction as given by Lewis and Randall in a discussion of the "Free Energy of Carbon Compounds."³ This means that an equilibrium mixture of hydrogen and methane in the presence of carbon at 1030° at atmospheric pressure would contain about 1% of methane and 99% of hydrogen. It was experimentally determined by analysis of the effluent gases that during the preheat in hydrogen there was a loss in weight of the carbon which amounted to 0.3% in one hour and 1.4% in five hours. These values correspond to about 0.2% of methane in the hydrogen as the gas left the furnace, which seems reasonable since sufficient time was not given for the gases to reach equilibrium.

As pointed out in the preceding paper, shrinkage of charcoal accompanied by a decrease in pore volume and extent of surface occurs when charcoal is heated above 900° and, therefore, since the preheat was carried out at a considerably higher temperature such a decrease in extent of surface might possibly be sufficient to account for the decrease in rate of oxidation with increase in length of time of preheating at 1030° . The effective surface might also be decreased by the decomposition of the methane, formed during the preheat, closing the entrance to the pores of the charcoal and thus rendering a certain portion of the surface inaccessible.

It would also be expected that the resistance to oxidation would be increased by the formation of methane, since the atoms of carbon which were chemically the most active would themselves be removed by such a reaction. In view of these considerations, the decrease in rate of oxidation with increase in length of time of heating in hydrogen at 1030° is readily intelligible.

TABLE III
INFLUENCE OF TEMPERATURE OF PREHEATING IN HYDROGEN AND OF TEMPERATURE OF OXIDATION ON THE RATE OF OXIDATION OF CHARCOAL

Sample 2				
Oxygen flow, 60 cc. per min. Preheat in hydrogen, 45 min.				
Temperature of oxidation, °C.	412	432	458	472
Percentage loss in weight				
1. Preheat at 1030°	1.04	1.90	4.65	8.87
2. Preheat at 1070°	0.83	1.49	3.55	7.23
Ratio 1:2	1.25	1.27	1.31	1.23

³ Lewis and Randall, THIS JOURNAL, 37, 468 (1915).

It was found that, for a given period of heating in hydrogen, the decrease in rate of oxidation was greater, the higher the temperature of the preheat, as would also be expected. These data are given in Table III together with the results of determinations of the influence of the temperature of oxidation on the rate of oxidation. As may be seen from the table or from Fig. 3, the oxidation increases at an accelerating rate as the temperature is raised. Also, the ratio of the rates of oxidation at different temperatures of samples treated at 1030° to those treated at 1070° is constant.

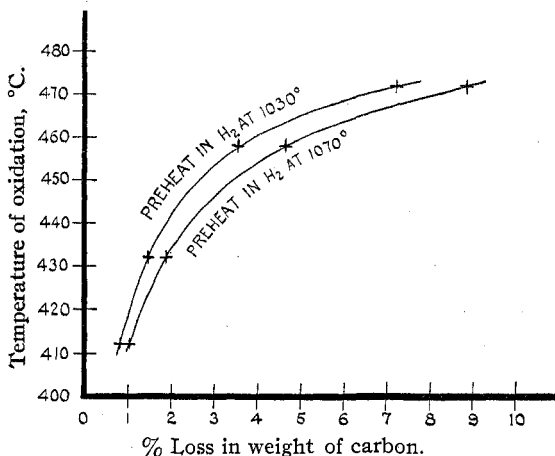


Fig. 3.—Influence of the temperature of preheating and of the temperature of oxidation on the rate of oxidation of a charcoal. Sample No. 2.

Summary

It has been shown by determinations on ten different charcoals prepared from anthracite coal that the rate of oxidation of the samples at 450° is roughly proportional to the amount of chemically combined hydrogen and to the extent of surface, as calculated from data on the sorption of water vapor. The latter relationship was shown to be in accordance with the viewpoint regarding the oxidation of the charcoal as analogous to rate of solution phenomena.

These data were interpreted to indicate that the rate of oxidation of the charcoals would increase with the length of time of oxidation.

The rate of oxidation at 450° was less, the longer the period of preheating in hydrogen at 1030° and at 1070° , the higher temperature being more effective. These facts were explained by an increase in resistance of the carbon atoms to oxidation, and by a decrease in the available surface due (1) to shrinkage of the charcoal and (2) to the decomposition of methane formed by the direct action of the hydrogen on the carbon with clogging of the capillaries of the charcoal.

The oxidation of a charcoal was shown to increase with the temperature of oxidation at an accelerating rate.

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THE ABSORPTION SPECTRUM OF GELATIN AS A FUNCTION OF THE HYDROGEN-ION CONCENTRATION

BY HENRY PARKER HIGLEY AND J. HOWARD MATHEWS

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Loeb¹ has shown in numerous experiments that the iso-electric point of the gel form of gelatin lies at P_H 4.7.

Thomas and Kelly,² as well as Porter,³ have shown that the iso-electric point of collagen, or hide protein, has approximately the same value as that for gelatin, at room temperature. But the work of Davis and Oakes indicates an iso-electric point for the sol form of gelatin at about P_H 8. In experiments upon the bating of calf skin at 40°, with varying hydrogen-ion concentrations, Wilson and Daub⁴ observed that a point of minimum swelling occurred in the region of P_H 8, but not at 4.7. The work of Smith⁵ and of Lloyd⁶ suggests that the change from the gel to the sol form takes place both with rise of temperature and with rise of Sørensen (P_H) value.

The recent work of Kelly⁷ on the rate of tanning as a function of hydrogen-ion concentration has an important bearing upon this problem. It was found that the rate of combination of hide protein and tannin decreases to a minimum at P_H 5, increases to a maximum at about 8, and then decreases rapidly towards zero, with increasing Sørensen values. Since tannin is negatively charged, this work would seem to indicate that collagen carries a positive charge between the iso-electric points of its two forms. Between the iso-electric points of the two forms of any protein, any of the gel form present would have a negative charge and any of the sol form a positive charge, the net charge of the system being determined by the preponderance of one of the forms.

The similarity of behavior of collagen and gelatin indicates the possibility of a wider use of data on gelatin in tannery problems. The experiments also suggest that only the sol form of collagen is convertible into gelatin and that the sol forms of the two proteins may actually be identical. The fact that the transition from gel to sol form occurs near the neutral point makes the work of great importance in biological problems.

The object of the investigation to be described here was to observe

¹ Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., 1922.

² Thomas and Kelly, *THIS JOURNAL*, **44**, 195 (1922).

³ Porter, *J. Soc. Leather Trades Chem.*, **5**, 259 (1921).

⁴ Wilson and Daub, *J. Ind. Eng. Chem.*, **13**, 1157 (1921).

⁵ Smith, *THIS JOURNAL*, **41**, 135 (1919); *J. Eng. Ind. Chem.*, **12**, 878 (1920).

⁶ Lloyd, *J. Biochem.*, **14**, 147 (1920).

⁷ Margaret W. Kelly, "The Hydrogen Ion and Ion Factors in the Fixation of Tanning by Hide Substances." Read before the Leather Division at the meeting of the American Chemical Society, Pittsburgh, September, 1922.