STUDIES OF SURFACE PHASES ON CHARCOAL AND COPPER

Thesis for the Degree of Ph. D.
MICHIGAN STATE COLLEGE
Robert Earle Vander Vennen
1954

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By

Robert Earle Vander Vennen

A THESIS

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Department of Chemistry

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ABSTRACT

A study has been made of the nature of the surface of activated charcoal, of the manner in which electrolytes are adsorbed by charcoal, and of the reaction at room temperature between oxygen and metallic copper.

Very little precise information is available about the structure of the surface of activated charcoal. A review of the literature showed that the dominant role in determining the surface properties of charcoal is played by oxygen chemisorbed on the carbon surface. By suitable changes in the conditions of activation of charcoal the nature of the carbon oxides on the surface changes and the adsorption properties of the charcoal also change. The structure of charcoal activated at 400°C. and the adsorption of cations by this charcoal from aqueous solutions was the chief interest of the present investigation.

Ash-free charcoals were prepared from pure sugar and activated under controlled conditions. Analyses for the elements present were performed and the adsorption of iodine by the charcoals was measured under standard conditions. The charcoals were further characterised by their abilities to adsorb acids and bases. The magnetic susceptibilities of a number of charcoals activated under different conditions were determined at room temperature and also at 192°K. and 75°K. It was found possible by the magnetic measurements to determine the amount of

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oxygen adsorbed physically on the charcoal surface, since molecular oxygen is paramagnetic. Charcoal free from oxygen was prepared and it was found to be more diamagnetic than oxygen-containing charcoal and its susceptibility was independent of temperature.

Other methods of studying the nature of the surface carbon oxides of charcoal included direct chemical oxidation of the charcoal surface with sodium metaperiodate, which oxidation yielded carbon dioxide. The infrared absorption spectra of several charcoals prepared as mulls were obtained in an attempt to obtain information about the structure of surface oxides. Studies were made of the reaction at room temperature of charcoal with water enriched in the oxygen isotope O^{18}.

In a study of the nature of the adsorbed phase when electrolytes were adsorbed on charcoal, the magnetic susceptibilities of salts of iron, cobalt, and manganese adsorbed on charcoal were determined. The magnetic susceptibilities of these salts were found to be the same in the adsorbed state as they are in the crystalline form.

From magnetic measurements at low temperatures, these salts in the adsorbed state were found to obey the Curie-Weiss law for paramagnetic substances. It was concluded from these results that the salts were held on the charcoal surface by bonds between metal and oxygen atoms, and a mechanism for the adsorption process was postulated.

The surface oxidation of granulated metallic copper was studied at room temperature and at 100°C. by the method of magnetic susceptibilities. It was found that the reaction could be accounted for magnetically by the formation c

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by the formation of cuprous oxide, cupric oxide, and by the presence of physically adsorbed oxygen. From independent determinations of the total amount of oxygen adsorbed and from magnetic measurements at room temperature, 195°K., and 75°K. the amounts of each of the constituents present were calculated. The gram susceptibilities of cuprous oxide and cupric oxide were also determined at the three temperatures.

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SURFACE OF ACTIVATED CHARCOALS

Introduction

There is probably no aspect of the adsorption by charcoal that has received so much attention as that dealing with the adsorption of electrelytes. Many points of view have been expressed and many different theories have been advanced, but as yet there is no comprehensive explanation to account for the behavior of charcoal toward electrolytes. This is no doubt due to the extreme complexity of the charcoal surface and to the vastly diverse properties it imparts to the charcoal. No fundamental study of electrolyte adsorption by charcoal can be pursued without searching into the nature of the surface of the charcoal at hand. And the study of the surface of charcoal is necessarily no less complicated than the study of adsorption itself.

It is generally agreed that the dominant role in determining the surface properties of charcoal is played by oxygen chemisorbed on the carbon surface. It is amazing that although it was postulated already in 1913 that oxygen and carbon at the charcoal surface reacted to form surface complexes,[1] very little precise information is available today about the structures or physical properties of these oxides, even though these have been the subject of many investigations. There is general agreement that there are two distinctly different types of charcoals, one of which is formed by activation in air or oxygen at

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400°C., and the other at higher temperatures, around 800°C. The low-temperature charcoal adsorbs primarily bases from aqueous solution and the high-temperature charcoal adsorbs primarily acids.

The purpose of the present investigation, as contained in Parts I and II of this paper, was to examine by several methods the surface properties of charcoals activated at approximately 400°C. with particular emphasis upon the adsorption of inorganic cations by these charcoals and the nature of the adsorbed phase. The methods used to investigate the nature of the charcoal surface were: the extent of adsorption of acid and base, the magnetic susceptibilities of pure charcoals, direct chemical oxidation of the charcoal surface, infrared spectra of the charcoals, and isotope exchange studies. The nature of the adsorbed phase and of the forces which bind the cations to the charcoal surface were studied by determining the magnetic susceptibilities of adsorbed paramagnetic cations.

Historical Background

Charcoal has often been assumed to be completely amorphous carbon, but that this is not completely true has been shown by x-ray investigations by a number of workers.[2,3] The x-ray patterns are diffuse and show a graphite-like structure corresponding to a two-dimensional graphite lattice. This has been confirmed by electron diffraction studies.[4] Thus charcoal can be said to be amorphous because there exists no three-dimensional network, but it must be borne in mind that charcoal is not entirely devoid of all pattern or regular arrangement of atoms.

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The carbon atoms in charcoal are held together by very strong chemical bonds, as witnessed by its extremely high decomposition temperature. So far as these bonds are strong, the bonds or free valencies "left over" at the edge or surface of charcoal must also be strong, and it is these residual forces that are responsible for the chemisorption of oxygen.[5] These forces at the surface are so strong that it is very difficult to get a charcoal surface entirely free from oxygen.

Most charcoals used in adsorption experiments have been in some contact with air. It is known from several investigations that slow combustion of carbon takes place even at room temperature.[6] In addition to this, during the process of activation to impart adsorptive properties to charcoal, reaction with oxygen is inevitable. The importance of the existence of surface oxides in the adsorption of electrolytes on charcoal was first mentioned by Schilow and Tschmutow.[7,8] These workers later[9] postulated the existence of two basic surface oxides and one acidic oxide in order to account for the adsorption of electrolytes. The theory of Schilow and co-workers will be discussed later.

It should be remarked that with the present incomplete state of knowledge of the nature of the surface of charcoal, characterization of a given charcoal can only be made by giving a detailed account of the method used for its manufacture, the source of the raw material, and the results of adsorption experiments. Untold confusion has resulted from reports of the properties of very poorly defined, and often very impure charcoals.

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Early investigators of electrolyte adsorption on charcoal used chiefly charcoal of animal origin containing from five to fifty percent ash. Owing to the use of such contaminated products the investigators obtained very contradictory results. Using charcoals with high ash content made it impossible to ascertain with any degree of definiteness whether the adsorption of ions depended on the carbon or on the inorganic impurities in the material. Even though the charcoals were very often washed with acid much of the ash could not be removed, and it was often doubtful whether all the acid had been washed off. A major advance in the study of charcoal adsorption was made by Bartell and Miller[10] when they devised a method to prepare ash-free charcoal from impure starting material. Although this method of purification is not widely used today because charcoals can be made more easily from pure starting material, their work first showed the supreme importance of using ash-free charcoals in studies of electrolyte adsorption.

Miller and co-workers were the first to characterize the adsorption of electrolytes on pure charcoals activated at about 900°C. They found that, of inorganic electrolytes, these charcoals adsorbed acids and all anions except the hydroxyl ion, but did not adsorb alkali hydroxides nor alkali metal ions. Inorganic electrolytes were adsorbed hydrolytically, that is, only one of the ions was adsorbed. In 1929 Kruyt and de Kadt[11] discovered that charcoals activated at a considerably lower temperature than that used by Miller had practically the reverse properties. Alkali hydroxides and inorganic cations were adsorbed, acids and anions were not adsorbed, a

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Some theories of the adsorption of electrolytes by charcoal will now be discussed. The earliest theory of significance was offered by Miller as the result of his studies of adsorption on charcoals activated at high temperatures.[12,13] He considered that the adsorption of electrolytes was entirely electrolytic, that, for example, a solution of sodium chloride was slightly hydrolyzed and the chloride ion adsorbed as molecular hydrochloric acid. Evidence for this was the fact that upon adsorption of the chloride from sodium chloride the solution became less acidic; also that small amounts of adsorbed acid were not able to invert cane sugar at 80°C. The greatest difficulty with this theory lies in the interpretation of some of Miller's own experimental work; he observed that from organic sodium salts both cation and anion were adsorbed, whereas he had also shown that sodium hydroxide was never adsorbed by his charcoals. But undoubtedly he was correct in stating that cation and anion are not always adsorbed to the same extent.

Soon after the first report on the properties of charcoals activated at low temperatures, Burstein and Frumkin[14] described experiments with charcoals outgassed at 1000°C. on which no adsorption of electrolytes could be observed. Schilow and Tschmutow[8] found that the adsorption of acid depended on the oxygen pressure in the system, and that below two mm. pressure the adsorption of acid rapidly decreased. The latter authors ventured the explanation that oxides were formed on the surface of the charcoal in the presence of oxygen. The adsorption of hydrochloric acid was interpreted

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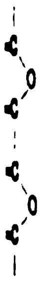

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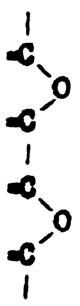

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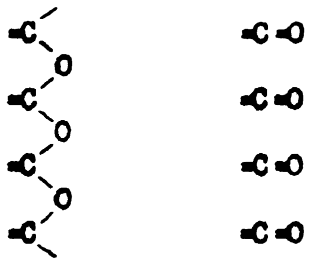

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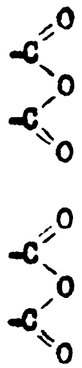

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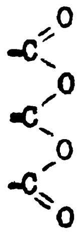

Oxides A and B would be expected to be alkaline and C acidic; D is a type of inner oxide which would be amphoteric. The existence of these surface oxides is still hypothetical. A more complete theory regarding the adsorption of electrolytes on all types of charcoals was later presented by Kruyt and de Kadt[15] along the same lines as that of Schilow and his co-workers.

Although the oxide theory has met with objections from various quarters, it has obtained general support during recent years. Perhaps the chief obstacle to its acceptance is the hypothesis regarding the existence of alkaline carbon oxides, since substances of a corresponding nature and stability are not known in organic chemistry. However, the oxide theory seems very satisfactory in its broad outlines for charcoals activated at low temperatures.

Frumkin and his co-workers[16] used the classical electrochemical theory as a starting point and assumed that charcoals suspended in solutions of electrolytes behaved as reversible gas electrodes. The charge on the charcoal was thought to depend upon the concentration of the ions in solution and the nature and pressure of the gas which was in equilibrium with the system. A charcoal in contact with hydrogen was believed to be negatively charged due to ionization of adsorbed hydrogen atoms. The negative charge on the carbon surface was assumed to attract cations from the electrolyte, thus causing adsorption. The presence of oxygen on the charcoal was believed to give a positive charcoal due to ionization of hydroxyl ions. This theory has been subject to many criticisms and was modified in nearly every paper published by Frumkin and his co-workers.[16,17]

Steenberg[18] made a very extensive investigation of the adsorption of electrolytes, chiefly on high-temperature charcoal. He made the interesting discovery that the adsorption of strong electrolytes on high-temperature charcoal could be inhibited by the presence of organic non-electrolytes, and that electrolytes adsorbed in the absence of non-electrolytes could be removed from the charcoal by adding strongly adsorbed non-electrolytes. For low-temperature charcoal the presence of organic non-electrolytes had no effect whatever on the adsorption of electrolytes, and it was not possible to desorb the electrolytes from low-temperature charcoal. This he considered as evidence in favor of

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the oxide theory of adsorption for low-temperature charcoals, and he suggested that adsorption on these charcoals could be interpreted as a cationic change.

For the high-temperature charcoals Steenberg concluded that the adsorption forces were the same for electrolytes as for non-electrolytes. From this starting point he developed a theory of electrolyte adsorption on high-temperature charcoals based on the assumption that all cations except hydrogen on these charcoals were capable only of secondary adsorption, that is, that they existed only in the electrical double layer; anions, on the other hand, were primarily adsorbed. He postulated that the strongest adsorptive forces on high-temperature charcoals were van der Waals' forces, and demonstrated that it was possible to apply the Donnan theory to a solution of electrolytes in contact with high-temperature charcoal. On the basis of the Donnan theory Steenberg presented a theory of hydrolytic adsorption of electrolytes on high-temperature charcoal. Since low-temperature charcoals were the main interest in the present investigation this theory will not be discussed. A significant aspect of Steenberg's work is the fact that his theory of the adsorption of electrolytes does not require any assumptions as to the nature of the surface of the charcoal nor as to the nature of the adsorption forces.

Wilson and Bolam[18] have made important studies on the relation of chemisorbed oxygen to the adsorption of acid and base. They found that unoxidized outgassed charcoal adsorbed appreciable amounts of acid but no base, but that after oxidation at 400°C. the adsorption of base was

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very marked and that of acid was reduced to very small proportions. Thermal treatment of the charcoal in a vacuum or under nitrogen decreased the adsorption of base and increased that of acid to an extent dependent upon the temperature and the time of heating. The amount of adsorbed oxygen removed from the charcoal by this treatment was determined, as was the decrease in adsorptive capacity of the charcoal. Upon removal of the first part of the adsorbed oxygen the loss of two atoms of oxygen corresponded to a decrease in adsorption of one molecule of base. This led the authors to conclude that two types of surface oxygen complex were involved in the sorption of base, the ratio of atoms of oxygen to molecules of base being two to one in the one case and four to one in the other. Since they found that the adsorption of iodine was very similar to the adsorption of acid, the acid was probably physically adsorbed, and oxygen chemisorbed on charcoal did not form basic complexes instrumental in adsorbing the acid.

The studies of King have been very revealing as to the points of difference and similarity between low-temperature and high-temperature charcoals.[20] From studies of charcoals activated at a series of different temperatures King concluded that charcoals activated in the region 800 to 850°C. had the following properties: maximum acid adsorption, maximum physical adsorption, minimum base adsorption, maximum pH of aqueous suspension, maximum electrophoretic mobility of particles suspended in water, maximum efficiency as oxidizing catalyst, and minimum efficiency in the decomposition of hydrogen peroxide. Charcoals

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activated at 400°C. have in most cases the reverse properties. King was able to prepare only charcoals which were negatively charged when suspended in water, although some authors have claimed that positive charcoals were formed by ionization of hydroxyl ions from the charcoal.[21,22,23] King was able to find definite correlations between the pH of aqueous suspension of charcoals and both temperature of activation and acid and base adsorption.[24] Between the activation temperatures of 200 and 800°C. the pH of an aqueous suspension rose linearly with the temperature of activation. Charcoals activated at 400°C. gave a pH of about five, and charcoals activated at 800°C. gave a pH slightly greater than eight. Charcoals which gave low pH values were best able to adsorb base, and charcoals which gave high pH values were best able to adsorb acid.

Several studies of adsorption and the adsorbed state have been made by means of magnetic susceptibility measurements, but few of these studies have dealt with the adsorption of electrolytes. Bhatnagar and co-workers[25] investigated the adsorption of salts of iron, nickel, cobalt, and manganese on charcoal and silica gel. They reported that these salts, all normally paramagnetic, became diamagnetic when adsorbed on charcoal, and in fact the charcoal itself appeared to become more diamagnetic. With silica gel the susceptibilities were not far from additive, that is, the salts had the same susceptibility in the adsorbed state as in solution.

A recent study by Kobozev and co-workers[26] on the paramagnetism of adsorbed layers is very interesting. They observed that when the percentage of the surface covered by adsorbed salts was decreased the

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paramagnetism increased by large amounts, corresponding in many cases to magnetic moments of tens of Bohr magnetons. When cobalt (II) chloride hexahydrate was adsorbed on silica gel, the magnetism of the adsorbed layer was equal to that of the pure salt when one percent of the surface was covered; when the surface coverage was decreased to 0.12% the paramagnetism of the adsorbed salt increased to 5.2 times that of the pure salt. For nickel (II) nitrate hexahydrate adsorbed on charcoal at surface coverages of at least 86% the susceptibilities of adsorbed and pure salt were equal, but when the surface coverage was 0.06% the paramagnetism of the adsorbed nickel was 18.9 times as great as that of the pure salt. The susceptibility of platinum adsorbed on alumina gel was found to be 36,000 times as great as that of bulk platinum. Iron adsorbed on charcoal was paramagnetic rather than ferromagnetic proving that dilute layers of iron on a carrier are atomic, not crystalline, in nature. The sharp increase of atomic susceptibilities with dilution was characteristic of adsorbed layers and was not found in merely mechanical mixtures of the same substances. Ferromagnetic contamination was ruled out by the fact that susceptibilities were independent of field strength.

Paramagnetism of dilute adsorbed layers was found also with normally diamagnetic silver, only the free atom of which is paramagnetic. The susceptibility of silver dispersed on an inert support was negative (diamagnetic) only on relatively dense layers, but became increasingly positive with increasing dilution. This is in contrast to the findings of Selwood a

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of Selwood and Dallas[27] who tried to detect paramagnetic silver and copper by dispersing these metals on alumina gel. A sample of supported silver containing 2% silver was examined and the authors reported that no large fraction of the silver became paramagnetic. Very careful efforts by these authors to detect paramagnetic copper were also not fruitful.

The Russian investigators[26] concluded from their studies that the very large paramagnetism of dilute layers in the adsorbed state was due to a decrease of the randomness of spin, that is, orientation of the magnetic atoms must be markedly enhanced. They called this anomalous magnetism of dilute adsorbed layers "superparamagnetism". This work must be regarded with some reservation until confirming researches are reported, since the errors of measurement are large when small amounts are adsorbed.

Selwood[28] has carried out extensive investigations of paramagnetic salts dispersed on inert supports such as magnesia, rutile, and alumina. These studies have led to conclusions of great interest both from the point of view of catalytic reactions and of the structure of the supported salt. It has been possible to calculate the magnetic moment of the supported paramagnetic ion and its valence state, and also to make estimates of the state of aggregation and the number of magnetic neighbors of each atom.

Boutaric and Berthier[29,30] investigated the magnetic properties of the hydroxide and chloride of iron (III) adsorbed on bentonite. The susceptibilities were found not to be additive, but those of the adsorbed

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iron compounds appeared to increase. When substances were adsorbed on sols of iron (III) hydroxide, however, the susceptibility of the iron appeared to decrease.

When Goldsmith[31] investigated magnetically the adsorption of bromine on graphite he found that the magnetic data were neither consistent with the adsorption of bromine as atoms (paramagnetic) nor as molecules (diamagnetic). He concluded that bromine was present on graphite partially as atoms and partially as undissociated molecules. Juza et al.[32] also found that the susceptibility of the carbon-bromine system is not simply the sum of the susceptibilities of the carbon and bromine.

Very thorough magnetic studies of the adsorption of oxygen by charcoal have been made by Juza and co-workers.[32,33] Their results showed that the adsorption of oxygen by charcoal was not simple but that under most conditions part of the oxygen was adsorbed physically or molecularly and part adsorbed chemically in the form of oxides. Oxygen adsorbed physically was paramagnetic to the same extent as was gaseous oxygen, but the surface oxides were diamagnetic. The paramagnetism of adsorbed oxygen decreased slowly upon standing and also upon thermal treatment of the charcoal due, presumably, to a chemical combination between oxygen and the charcoal. From magnetic data these investigators were able to calculate how much oxygen was adsorbed physically and how much chemically. Juza[34] has also investigated the adsorption of oxygen by charcoal at -183°C. Noting that the susceptibility of liquid oxygen is about 30% smaller than that of gaseous oxygen

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at this temperature, the above author observed that the susceptibility of the amount of oxygen adsorbed was the same as that of gaseous oxygen; however, the susceptibility slowly decreased as more oxygen was taken up until for thick layers the susceptibility was essentially that of liquid oxygen.

In another magnetochemical study Juza[25] investigated the adsorption of nitrogen dioxide and dinitrogen tetroxide on charcoal. Since the former compound is paramagnetic and the latter diamagnetic it was possible to estimate magnetically the degree of dissociation of the dimer on charcoal. The degree of dissociation was found to depend on the amount adsorbed. Similar studies have been reported by Reyerson and Wertz.[26]

Courty has carried out numerous investigations of the magnetic susceptibilities of oxygen, air, and water adsorbed by charcoal.[27] When water was adsorbed by charcoal the resultant susceptibility was found not to be simply the sum of the susceptibilities of water and charcoal, presumably because the water was not able completely to displace air trapped in the pores of the charcoal.[28] In another study the susceptibility of water adsorbed on charcoal was found to be the same as that of pure water.[29] When air or oxygen was adsorbed on charcoal the susceptibility of the mixture was found to decrease with time. Unfortunately Courty's charcoals contained so much ferromagnetic and paramagnetic impurity that the samples showed a resultant paramagnetism or ferromagnetism, and any charcoals heated to high temperatures were worthless because of the formation of strongly ferromagnetic iron oxides.

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Burstein and Miller[40] have published a paper, unavailable to the writer, in which they stated that small amounts of oxygen adsorbed by charcoal lost their paramagnetism but large amounts remained paramagnetic.

General Experimental Methods

Preparation and Activation of Charcoals

Most of the charcoals used in the present investigation were prepared from pure saccharose; however, one commercial charcoal was used in some of the experiments. This was Eimer and Amend C. P. sugar charcoal, prepared from cane sugar, and its characterization will be given later.

Unactivated sugar charcoal was prepared from Eimer and Amend C. P. saccharose in the following manner.[19] The sugar was charred in a mullite casserole until the black mass had solidified. It was then ground with a mortar and pestle and returned to the casserole. The full heat of a Fisher burner was applied for a few minutes, and the charcoal allowed to cool in air. A quantity of this material was put into a combustion tube and heated at 1000°C. under vacuum for about ten hours; this processing was found sufficient to remove essentially all the active surface oxides, and to remove all capacity of the charcoal for adsorbing acid and base. This charcoal was used as a starting material for preparing activated charcoals.

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The equipment used to prepare activated charcoals was very simple. For temperatures above 700°C. a high temperature electric furnace* was used. The combustion tube used with this furnace was a mullite tube, 1.18 inches inside diameter. For temperatures below 700°C. it was found more convenient to use a small, hinged-type electric tube furnace; with this furnace a silica combustion tube was used. A vacuum pump** was connected to the combustion tube through a barium oxide trap and a cold trap maintained at -78°C. with a Dry Ice-isopropanol mixture.

Activation in air or oxygen was carried out in the following manner. About 10 or 15 g. of charcoal was put into the combustion tube, and the tube slowly evacuated until a pressure of a fraction of a mm. was attained. Then the sample was heated to the proper temperature and the tube isolated from the vacuum pump. The activating gas, air or oxygen, was slowly admitted until atmospheric pressure was attained, and then a slow stream of activating gas was passed over the charcoal. The rate of flow of gas was set as desired by use of a flowmeter, and was usually about one liter per minute. Time of activation was one to two hours, although occasionally longer times were allowed. When activation was completed, nitrogen was admitted from a cylinder to the system, and the sample cooled to room temperature in an atmosphere of nitrogen. All gases admitted to the charcoal were first passed through Ascarite and barium oxide.

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* Burrell Corp., Pittsburgh, Pa., Model T-2-9.

** Kinney Mfg. Co., Boston, Mass., Type CVD-3431.

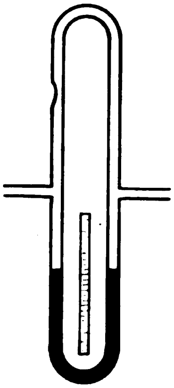

Figure 1. Flowmeter

The flowmeter used to measure the rate of flow of gases was of glass construction (see Figure 1). A section of capillary tubing was sealed into the upper part, and the bottom part of the apparatus contained vacuum-pump oil. The difference in the height of oil in the lower arms, as measured by a mounted scale, was proportional to the rate of flow of gas.

The flowmeter was calibrated with oil-pumped nitrogen taken from a cylinder. After passing through the flowmeter the nitrogen was collected over water in a bottle with a volume of 958 ml., as determined from the weight of water required to fill it. The time required to displace all the water from the inverted bottle at a steady flow rate of nitrogen was measured with a stopwatch, and the height of the oil in each of the arms was read. Room temperature was 25°C. and the

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barometric pressure 739.2 mm. The gas volume was corrected for the partial pressure of water vapor and was reduced to standard temperature and pressure. The results are shown in Table I.

TABLE I

CALIBRATION OF FLOWMETER

Difference in Height Centimeters	Time Minutes	Rate of Flow ml./sec./cm.
2.50	2:35.5	2.12
4.75	1:32.4	1.89
7.30	1:07.2	1.69
9.90	0:52.3	1.55

The temperature of the furnace was determined by means of a Chromel-Alumel thermocouple inserted directly into the combustion tube. The electromotive force generated was read from a recording potentiometer* and, since a reference junction was not used, the correction for room temperature was made.

The hot areas of both furnaces were mapped to find regions of constant temperature. For the Burrell high temperature furnace, the thermocouple junction was inserted into the empty combustion tube, and the temperature of the furnace raised to about 700°C. The heating element of the furnace was nine inches long, and the junction was first placed one-half inch from the farthest end of the heating element, and

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* Minneapolis-Honeywell Reg. Co., Philadelphia, Pa.

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then successively withdrawn at half-inch intervals. The results are shown in Table II. It can be seen that over a distance of about four inches in the center of the furnace the temperature varied not more than about ten degrees at 770°C.

TABLE II

TEMPERATURE GRADIENT IN THE BURRELL FURNACE

Distance from Edge of Heating Element Inches	Temperature °C.
0.5	697
1.0	724
1.5	741
2.0	752
2.5	760
3.0	768
3.5	770
4.0	773
4.5	773
5.0	771
5.5	770
6.0	765
6.5	758
7.0	570
7.5	390

Similar data are shown in Table III for the small hinged-type tube furnace. The heating element was again nine inches long, and the thermocouple junction was first placed at the farthest end of the heating element, and then successively withdrawn at one-half inch intervals. There was a region of about four inches at the center of the furnace over which the temperature varied not more than about five degrees at 700°C.

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TABLE III

TEMPERATURE GRADIENT IN THE HINGED-TYPE FURNACE

Distance from Edge of Heating Element Inches	Temperature °C.
0.0	349
0.5	580
1.0	618
1.5	649
2.0	665
2.5	678
3.0	688
3.5	690
4.0	690
4.5	692
5.0	692
5.5	692
6.0	692
6.5	688
7.0	678
7.5	636
8.0	600
8.5	536
9.0	430
9.5	310

The combustion tubes were charged with charcoal in the following manner. A piece of glass tubing was procured which was the largest size able to fit into the combustion tube. An aluminum disk was machined to fit loosely inside this glass tube, and this disk was attached at right angles to a long aluminum rod one-quarter inch in diameter. The desired amount of charcoal was placed into one end of the glass tube, the glass tube was inserted the proper distance into the combustion

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combustion tube, and the charcoal was pushed out of the glass tube with the aluminum plunger or "piston". This loaded the sample of charcoal into the combustion tube at the desired location.

A simpler but equally effective way to produce charcoal activated at 400°C. in air was by use of a muffle furnace.* An evaporating dish containing unactivated charcoal was placed in a muffle furnace preheated to 400°C. When heated for at least three hours, charcoal treated by this method was found to have a relatively high activity.

Several charcoal samples were activated with ammonia or sulfur.** Charcoals of this type have been reported to have large surface areas and great activities.[41] The method of preparation of the nitrogen-containing samples was based on the work of Wibaut.[42] The apparatus used was essentially that described above. The charcoal sample (about ten grams) was heated under a vacuum at 700°C. for three to four hours. Then ammonia was admitted to the charcoal, and after atmospheric pressure was attained, ammonia was passed over the charcoal at a flow rate of ten to twenty liters per hour for two or three hours. Then nitrogen was substituted for ammonia and was passed through the system until the furnace had cooled to room temperature. The purpose of the nitrogen treatment was to remove ammonia gas and physically adsorbed ammonia from the charcoal. In some cases the charcoal was also evacuated at room temperature, or at 400°C., for a time to insure removal of all

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* Blue M Electric Co., Chicago, Ill., Model M 10-A.

** The writer is indebted to Mr. W. A. McAllister for assistance in the preparation of these samples.

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ammonia.[42] The ammonia and nitrogen were freed from oxygen by bubbling the gases through an alkaline solution of pyrogallol. The spent ammonia and the hydrogen cyanide produced in the activation process were passed through a solution of potassium hydroxide to trap the hydrogen cyanide.

One sulfur-containing charcoal was prepared by heating ten grams of sugar charcoal with four grams of sulfur in an open dish. The product was put into the combustion tube and heated at 900°C. for six hours in a stream of nitrogen. Addition of a little hydrochloric acid to a portion of the final product gave a detectable odor of hydrogen sulfide.

Adsorption Techniques

The adsorptions of acids, bases, and salts from aqueous solutions on charcoal were carried out according to the following general pattern. A known volume of a standard solution was added to a known weight of dried charcoal, usually contained in a stoppered Erlenmeyer flask. The flask was shaken vigorously for a few minutes and thereafter shaken intermittently. All the adsorption determinations were carried out at room temperature. The time of contact of solution with charcoal was at least 18 hours, and in some cases 36 or 48 hours.

The mixtures obtained after equilibration of the solutions with charcoal were filtered through a sintered glass filter. In some cases the charcoal was then washed three times with distilled water to remove excess solution, and the filtrate and washings were diluted to a standard volume for chemical analysis. In other cases, after filtration aliquot portions of the undiluted filtrate were withdrawn for analysis.

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All reagents used in the present investigation were C. P. grade and were used without further purification.

Analytical Methods

Acid-base analyses. A suitable test of the capacity of a charcoal for adsorbing anions or cations from solution is its ability to adsorb acids or bases from aqueous solutions. Accordingly, after each preparation and activation of a charcoal, a sample of it was tested for its ability to adsorb sodium hydroxide and hydrochloric acid from solution. Five or ten ml. of 0.2 N solutions were used with one-half or one gram samples of charcoal. After equilibration for 18 to 24 hours, the mixture was filtered, and the charcoal washed three times with water to free it from excess solution. The filtrate and washings were combined and titrated with standard acid or base solution.

The sodium hydroxide and hydrochloric acid solutions were always prepared nearly 0.2 N. Solutions of sodium hydroxide were prepared from pellets of the solid and the solution stabilised with respect to carbonate by the addition of a small amount of barium chloride. These solutions were standardised against weighed amounts of potassium acid phthalate. The hydrochloric acid solutions were prepared by dilution of C. P. concentrated hydrochloric acid, and were standardized against the sodium hydroxide solutions.

At times it was desirable to determine the change in acidity of solutions after they had been equilibrated with charcoal. Some of the salt soluti

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salt solutions for which changes in acidity were determined were the chlorides and sulfates of nickel (II), cobalt (II), iron (III), and manganese (II). Standard solutions of these salts, usually about 0.5 N, were prepared, and 10.00 ml. samples added to known weights of charcoal with a pipette. After equilibration and filtration, the filtrate and washings were quantitatively diluted to 250 ml., and 50 ml. aliquots withdrawn. To each of these aliquots was added two drops of methyl red indicator, and the solutions titrated with 0.2 N sodium hydroxide solution to the endpoint. For comparison, 10.00 ml. of standard stock solutions was diluted to 250 ml., and 50 ml. aliquots titrated in the same manner. From the difference between the amounts of standard base needed for titration, the change in acidity of the solution during adsorption could be calculated. In the case of the iron (III) salts 10 ml. of a 2.5% sodium fluoride solution was added to each 50 ml. aliquot to prevent precipitation of ferric hydroxide.

Sometimes it was informative to determine the pH which pure water attained after being in contact with a charcoal for several hours. In such cases the pH was determined with a pH meter.*

<u>Cation analyses</u>. The cations nickel (II), cobalt (II), manganese (II), iron (II), and iron (III) were present as essentially pure simple salts in aqueous solution, and a description of each type of analysis follows.

Nickel (II). Dimethylglyoxime was used as the precipitating agent and the standard analytical procedure was followed.[44] The nickel

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* Beckman Instrument Co., South Pasadena, Cal., Model G.

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dimethylglyoximate was collected on a fritted porcelain filter; the solution concentration was usually adjusted so that about 250 mg. of precipitate was obtained.

Cobalt (II). The cobalt salts were determined by potentiometric titration with ferricyanide in an ammonium citrate-ammonium hydroxide solution.[43] The potassium ferricyanide, when standardized against 0.1 N sodium thiosulfate, was found to have a normality of 0.03475. Thirty ml. aliquots of this solution were added to the citrate buffer, and each was titrated with the cobalt filtrate which had been diluted to a suitable volume. The equivalence point was determined potentiometrically using a Fisher Titrimeter. This method gave very accurate and reproducible results.

Iron (II). Iron (II) was titrated directly with standard ceric ammonium sulfate solution, using o-phenanthroline-ferrous complex (ferroin) as indicator. The cerate solution was standardized against iron wire which was dissolved in dilute hydrochloric acid and passed through a silver reductor to obtain iron (II) chloride.

Iron (III). Iron (III) was reduced to iron (II) in a silver reductor and titrated as above with standard cerate solution.

Manganese (II). Manganese analyses were attempted by the standard bismuthate method,[44] but it was found impossible to obtain reproducible results. A potentiometric method was tried which proved very successful.[45] To 10.00 ml. of the manganese solution to be analyzed was added 200 ml. of saturated sodium pyrophosphate buffer solution. Bromthymol blue indicator was added, and enough hydrochloric acid added to give

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a solution with a pH of six, as matched against a standard buffer solution containing the same concentration of indicator. This solution was then titrated with 0.015 N potassium permanganate solution. The equivalence point was detected potentiometrically using the Fisher Titrimeter. The equivalence point was extremely sharp, and this method proved very satisfactory.

Anion analyses.

Chloride. In many cases chloride analyses were made by quantitatively precipitating the chloride with silver nitrate solution and weighing the silver chloride. When a number of these analyses had to be made, Volhard's method was used.[44] To aliquots of the chloride solution was added 20.00 ml. of standard 0.1 N silver nitrate solution. The silver chloride precipitate was filtered and the excess silver ion titrated with standard 0.1 N sodium thiocyanate. Sodium thiocyanate solution was standardized against standard silver nitrate.

Sulfate. Sulfate analyses were made by adding barium chloride to precipitate barium sulfate. The precipitate was ignited and weighed according to standard procedures.[44]

Ash analyses. Determination of the ash content of charcoals was done by ashing the charcoals in a muffle furnace. Silica crucibles were heated to constant weight at 900°C., and samples of charcoal weighed into them. Ashing was carried out by heating the samples to 900°C. for four hours, and the cooled crucible and ash were weighed. For most charcoals prepared in this investigation the ash content was negligibl

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negligible, usually less than 0.01%. However, the commercial charcoal (Eimer and Amend sugar charcoal) was found to have about 4.35% ash, and a qualitative analysis was made of the ash. The ash gave tests for sodium, magnesium, calcium, and sulfate ions. A complete description of the analysis is given in the Appendix.

Magnetochemical Techniques

Apparatus and calibration. The magnetic susceptibilities were determined by the Gouy method, which involves measuring the apparent gain or loss in weight of a sample when it is placed in an inhomogeneous magnetic field. The sample was contained in a Pyrex tube which was suspended by means of a gold chain to the left pan of a semi-micro balance. The sample experiences a downward or upward force in the magnetic field depending upon whether it is paramagnetic or diamagnetic, respectively. This force, which appears as a change in weight of the sample, is measured by the balance, and is expressed by the relation:[47]

$$g \Delta w = 1/2(K_1 - K_2)(H_1^2 - H_2^2) A \qquad (1)$$

where

*K_1 = volume susceptibility of the sample

K_2 = volume susceptibility of air

A = cross-sectional area of the tube

H_1 = maximum field strength

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* K will be used in place of the customary Greek letter kappa to denote volume susceptibility, and X in place of chi to denote mass susceptibility.

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H_2 = minimum field strength

g = gravitational constant

Δw = apparent change in weight of the sample

For each magnetic measurement the tube was filled with sample to a reference mark near the top. In practice this mark was made high enough so that the magnitude of H_2^2 at this point was negligible compared with the square of the maximum field strength H_1^2. Calibrations were made with substances of known magnetic susceptibility, and the formula for calculating volume susceptibilities became:

$$K - K_{air} = \frac{\Delta w}{\Delta w_s} (K_s - K_{air}) \qquad (2)$$

where the subscript s refers to the calibrating standard.

To convert from volume susceptibilities to gram susceptibilities it was necessary only to divide the volume susceptibility by the density of the sample. The density could be obtained from the weight of sample required to fill the known volume of the tube.

The essential parts of the apparatus have been previously described.[48] A diagram of the apparatus is given in Figure 2. The electrical control circuit for operating the electromagnet differs from that used previously[48] and is shown in Figure 3.

The procedure used to operate the magnet was as follows. The double pole switch was closed to posts C and the reversing switch D left open. The last switches to be closed were the knife switches E and F. The current through the magnet was controlled by adjusting the field

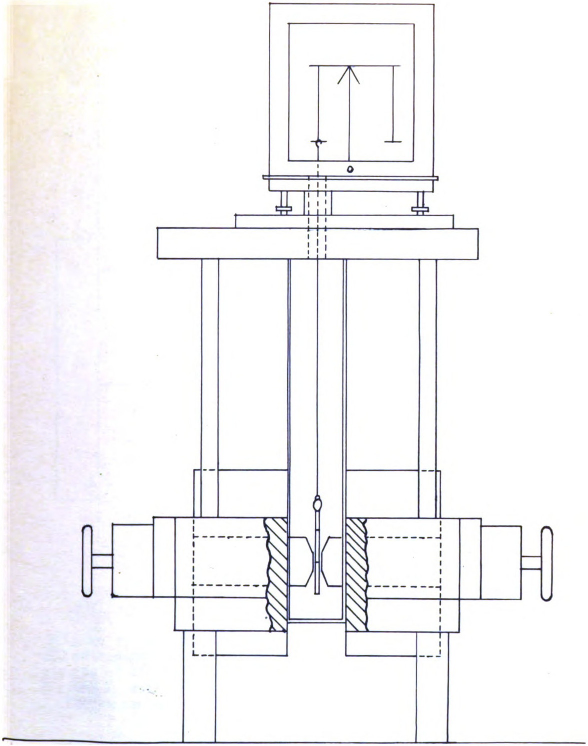

Figure 2. Gouy Magnetic Balance

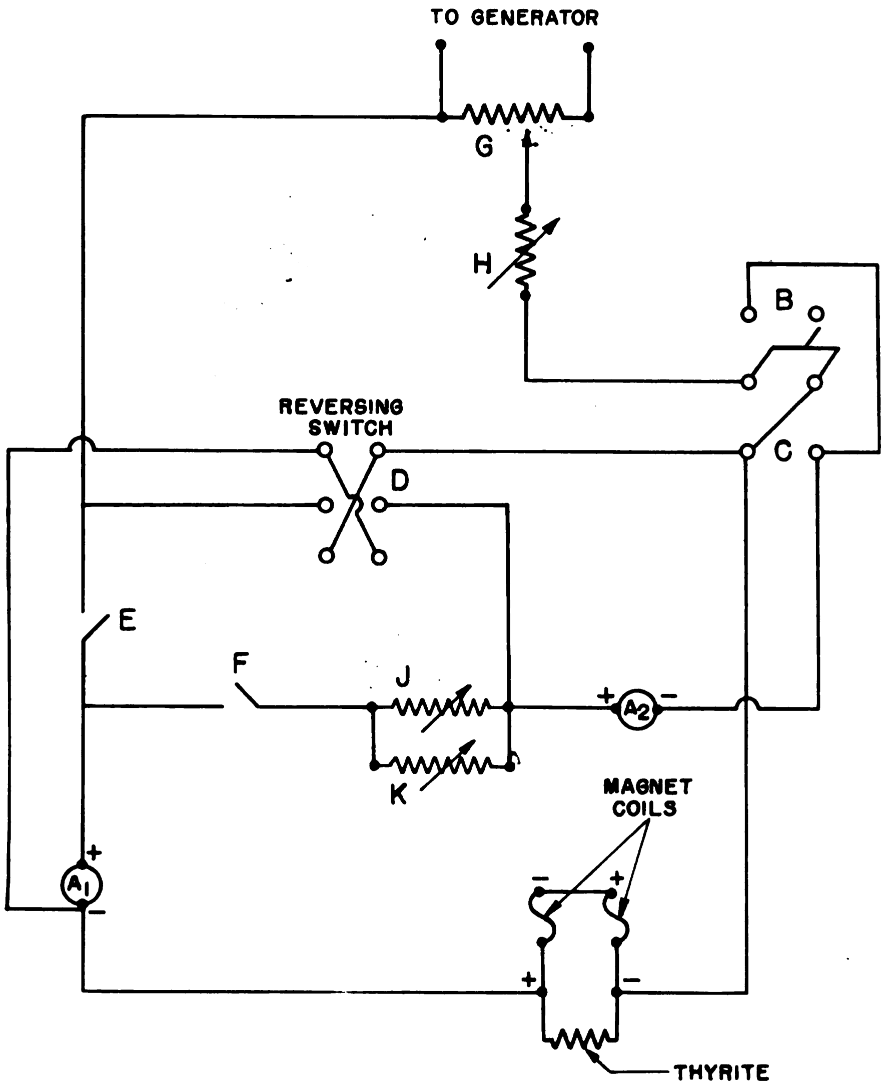

Figure 3. Electrical Control Circuit for Operating the **Electromagnet:** A_1 and A_2, ammeters; B and C, opposite posts of the double throw switch; D, reversing switch; E and F, knife switches; G, field resistor; H, heavy-duty variable resistor; J and K, slide-wire rheostats.

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resistor G, the large resistor H nearest the double pole switch, and, for fine adjustment, the two slide-wire rheostats J and K. Through these rheostats cold water was continuously circulated. The current through the magnet was read on the ammeter A_1 in series with the magnet, and the reading of the other ammeter A_2 (which was always the smaller) was ignored.

When a magnetic measurement had been completed the current was reduced to two or three amperes by means of the resistors before any switches were opened. After each magnetization, the magnet core was demagnetized in the following manner. The double pole switch was closed to the posts B, both knife switches were left open, and the reversing switch closed to either side. By means of the variable resistors the current was adjusted to twelve amperes. Then the current was reduced to two amperes, the reversing switch thrown to the opposite side, and the current raised to eleven amperes. The current was again reduced to two amperes, the reversing switch thrown to its original position, and the current raised to ten amperes. This was continued in one-ampere steps to zero current.

The magnet was calibrated every time a different pole spacing or different sample tube was used. Calibrating agents were: conductivity water, freshly boiled to remove dissolved gases; standard aqueous solutions of nickel chloride, approximately thirty percent by weight; and powdered Mohr's salt (ferrous ammonium sulfate). Each calibration was made with at least two different calibrating agents. From the measured tube dimensions and the known magnetic susceptibility of the calibrating agent the magnetic field strength at the center of the pole faces could be calculated for each amperage. A typical set of data is given in Table IV and plotted in Figure 4. The calibrating agent was a 28.77% nickel chloride solution, and the pole gap was 0.357 inches. The magnitude of the field strength is not useful for calculations, but it is desirable to know what range of field strengths is covered in a particular measurement.

TABLE IV

DATA FOR CALIBRATION OF ELECTROMAGNET

Current Amperes	Change in Weight Grams	Field Strength Oersteds
1	-0.0114	3,153
2	.0463	6,348
3	.108	9,700
4	.180	12,520
5	.274	15,450
6	.373	18,030
7	.445	19,670
8	.501	20,880
9	.538	21,630
10	.564	22,160
11	.587	22,610
13	.620	23,240
15	.644	23,660

The sample tubes for determining magnetic susceptibilities were all constructed of Pyrex tubing, and were double, or compensated tubes. The essential feature of this type of tube is that a solid glass septum at right angles to the walls of the tube separates the upper from the lower part. The tube hangs with its septum in the homogeneous

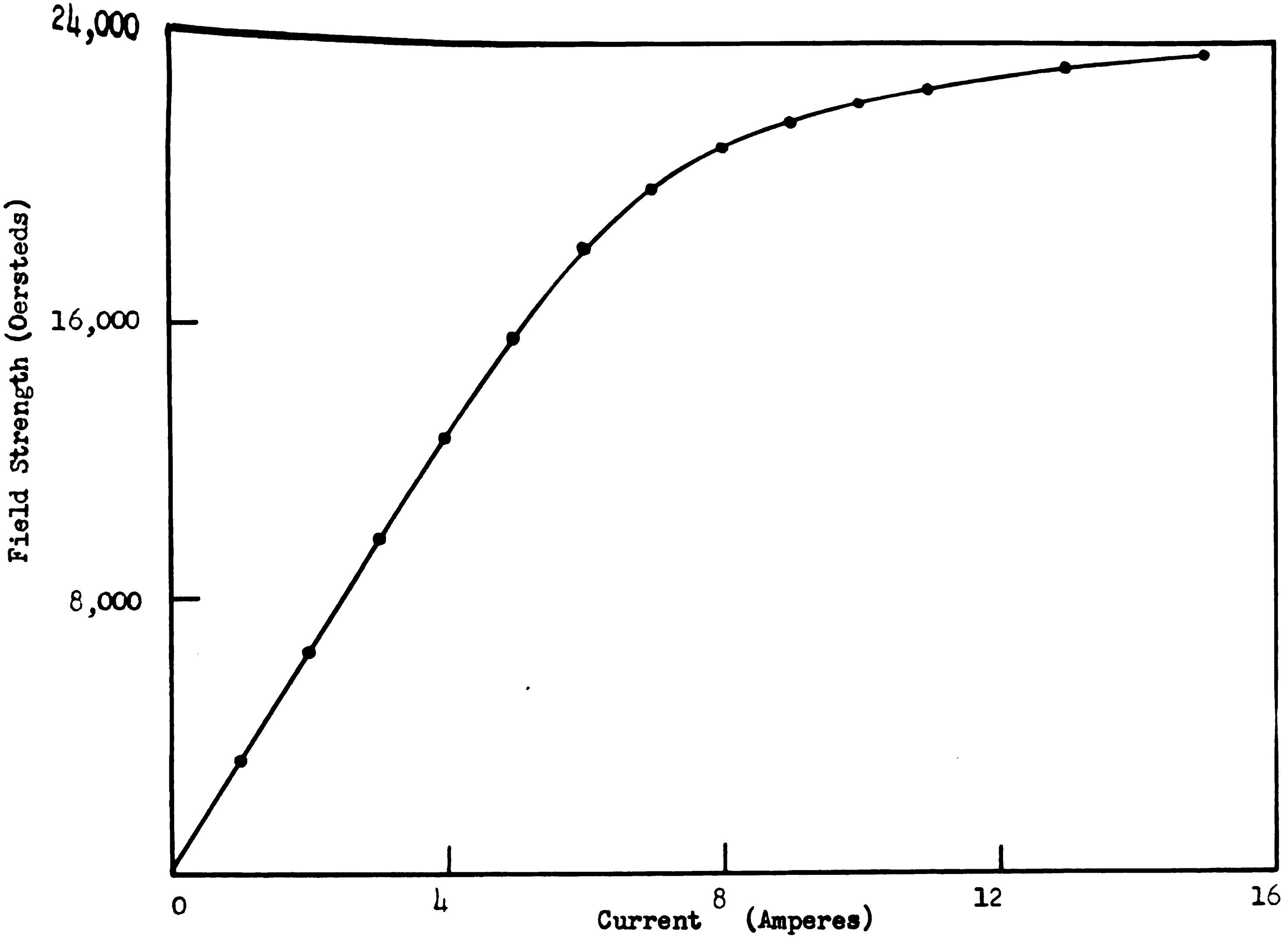

Figure 4. Calibration of Electromagnet

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region of maximum magnetic field strength, and both ends of the tube are in regions of negligible field strength so that the tube itself exerts little or no resultant pull when the magnetic field is applied. Usually the change in weight of the empty tube due to the presence of the magnetic field must be measured and, if not negligible, it must be applied as a correction to the Δw values measured for the samples.

Three different susceptibility tubes were used in this present investigation and all were alike in their general construction, differing only in size. At the top of each tube was sealed a female standard-taper ground joint; the corresponding male joint, which closed off the tube, was provided with a loop to which could be attached the suspending chain.

Susceptibility Tube A, which has been described in detail elsewhere,[48] was constructed from 12 mm. tubing, and the distance from septum to reference mark was 9.43 cm. The volume of this tube was 7.75 cc. It was verified experimentally that this tube experienced no resultant vertical force in the presence of the magnetic field.

Susceptibility Tube B was constructed from seven mm. Pyrex tubing with a volume of 1.97 cc; it had a distance of 10.45 cm. between septum and reference mark. This distance was arrived at after making magnetic measurements on water filled to various levels in the tube. Since the pole gap for this study was 0.357 inches, the smallest ever used, undoubtedly a distance of nine or ten cm. above the septum is sufficient to reach regions of negligible field strength in all the measurements reported in this study. The correction for change in weight of th

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weight of this empty susceptibility tube with field strength at room temperature is given in Table V.

Susceptibility Tube C was also constructed from seven mm. Pyrex tubing; the distance from septum to reference mark was 9.76 cm. and the volume was 1.80 cc. Since this tube was used for measurements at low temperatures as well as at room temperature, the change in weight of the empty tube with field strength was determined at liquid nitrogen temperature (-195°C.) as well as at room temperature. From these data a tube correction for -80°C. was interpolated. The results are shown in Table VI. A diagram of this tube is given in Figure 5b.

TABLE V

CHANGE IN WEIGHT OF SUSCEPTIBILITY TUBE B
WHEN A MAGNETIC FIELD IS APPLIED

Current Amperes	Weight Grams	Change in Weight* Grams
0	19.0345	-----
2	.0345	0.0000
4	.0343	-0.0002
6	.0341	-0.0004
10	.0338	-0.0007
15	.0337	-0.0008

* The appropriate change in weight must be subtracted algebraically from the observed changes in weight of the sample.

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TABLE VI

CHANGE IN WEIGHT OF SUSCEPTIBILITY TUBE C
WHEN A MAGNETIC FIELD IS APPLIED

Current Amperes	Change in Weight Grams		
	Temperature (°C.)		
	20	-80*	-195
5	-0.00002	-0.00002	-0.00001
8	-0.00007	-0.00005	-0.00002
11	-0.00014	-0.00010	-0.00005
15	-0.00019	-0.00015	-0.00010

* Estimated.

For each magnetic susceptibility determination the weight of the sample was measured in the absence of the magnetic field and for at least four different values of field strength. After these weighings the magnet core was demagnetized and the set of weighings repeated. From this double set of values an average weight was obtained which was used to calculate the magnitude of the magnetic susceptibility at each field strength. It was desirable to cover a range of field strengths in this way to detect traces of ferromagnetic impurities. Such impurities, even in amounts too small to be detected chemically, change the magnetic susceptibility of the sample and cause it to vary with field strength.

For magnetic measurements on liquids, the liquid was merely introduced into the sample tube and the tube filled to the height of the reference mark. Filling the sample tube with solids was somewhat more difficult. The sample was added a little at a time, and with each

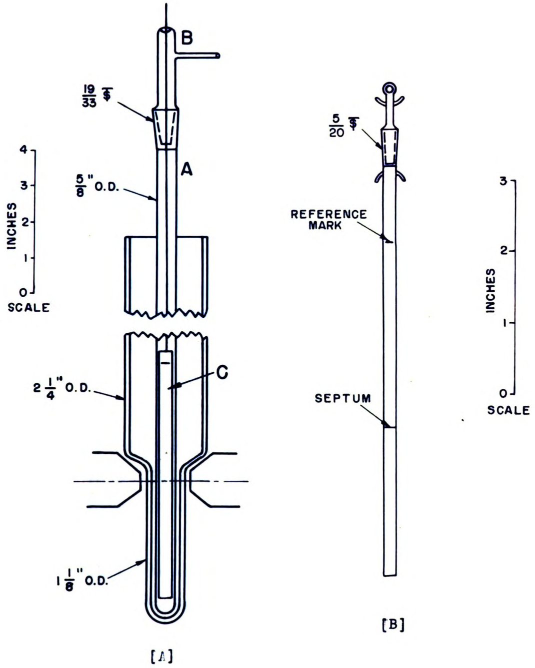

Figure 5. Apparatus for Magnetic Susceptibility Determinations. [A] Assembly for low-temperature magnetic measurements; A, tube isolating the susceptibility tube from the refrigerant bath; B, tube permitting the entrance of the susceptibility tube and of dried nitrogen; C, susceptibility tube. [B] Susceptibility tube C.

addition the sample tube was tapped firmly several times to get uniform packing. It is of prime importance that the sample be packed homogeneously in the tube, and Selwood states[47] that even with the most careful packing it is difficult with powders to get an accuracy of magnetic measurement better than one percent.

Low-temperature measurements. Special equipment and techniques were required to make magnetic susceptibility measurements at low temperatures. A specially constructed silvered Dewar vacuum flask was used to contain the refrigerant. A diagram of the apparatus is given in Figure 5a. The lower part of the Dewar flask was constructed to have one-half the diameter of the upper part so that the pole gap could be kept as small as possible, in this case 1.375 inches. Inside the Dewar flask was located a section of Pyrex tubing A of such diameter that it fit rather closely inside the lower part of the Dewar flask. The bottom part of this tube was sealed off, and to the top part was connected, through a standard taper glass joint, a tube B of the same diameter. This tube had a side arm and a small circular opening at the top. Within this tube hung the susceptibility tube C suspended by a gold chain from the left pan of the semi-micro balance.

The procedure for making a susceptibility determination at low temperatures was as follows. When the susceptibility tube was suspended in position, a piece of rubber tubing with an outside diameter of about five mm. was run to the bottom of the glass tube. Through this tubing was passed nitrogen taken from a cylinder and dried with anhydrous calcium sulfate. The dry nitrogen was passed through for a few minutes to

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minutes to remove most of the moisture and oxygen around the susceptibility tube. Then the refrigerant, either liquid nitrogen or Dry Ice-isopropanol mixture, was added. About an hour was allowed for the system to come to thermal equilibrium while a continuous stream of dry nitrogen was passed around the susceptibility tube. Before the susceptibility determination was made the rubber tubing was withdrawn and connected to the side arm of the glass tube; a slight positive pressure of nitrogen was maintained until the measurements were completed to prevent moisture or oxygen from entering.

The temperature of the system was determined by means of a calibrated copper-constantan thermocouple using the freezing point of water as the reference temperature. The thermocouple junction was located in the liquid refrigerant. Electromotive force measurements were made with a precision potentiometer.*

Whenever the susceptibility of a powdered sample was determined at a low temperature the air surrounding the powder in the susceptibility tube was removed and replaced by helium. This was necessary to prevent the excessive adsorption of air by charcoal which takes place at low temperatures, and also because the susceptibility of air is temperature-dependent. The susceptibility tube was attached to the vacuum line (see Figure 22) and evacuated to a low pressure. Then helium from a cylinder** was passed through anhydrous calcium sulfate and admitted to the vacuum system until atmospheric pressure was

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* Leeds and Northrup Co., Philadelphia, Pa., Type K-2.

** Matheson Co., Inc., Joliet, Ill.

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attained. The helium was then removed by the vacuum pump and the pump isolated from the vacuum system. This admission and removal of helium was repeated two or three times to insure that all the air had been removed from the vacuum system and from the charcoal. Finally helium was admitted to the charcoal sample at slightly greater than atmospheric pressure, the susceptibility tube was removed from the vacuum system and the glass standard-taper plug quickly replaced on the top of the susceptibility tube.

The following series of measurements was undertaken to determine the temperature gradients that existed both vertically and horizontally within the Dewar flask. The refrigerant was in all cases a Dry Ice-isopropanol mixture containing an excess of powdered Dry Ice.

First the thermocouple junction was located directly within the refrigerant bath, and the temperature determined as a function of the vertical position of the junction in the bath. The original location of the junction was at the bottom of the wide section of the Dewar flask. When the junction had been in that location a few minutes so that thermal equilibrium had been established, the electromotive force was measured. Then the junction was moved upward half an inch and the measurement repeated. This was repeated until a total distance of five inches had been covered by the thermocouple junction. The results are summarized in Table VII.

Next the thermocouple junction was located in the air space between the glass tube and the susceptibility tube. The junction was

TABLE VII

TEMPERATURE GRADIENT IN THE REFRIGERANT BATH

Distance Above Starting Position Inches	Electromotive Force Microvolts	Temperature °C.
0.0	-2755	-79.8
0.5	2761	79.9
1.0	2761	79.9
1.5	2764	80.0
2.0	2763	80.0
2.5	2761	79.9
3.0	2763	80.0
3.5	2764	80.0
4.0	2764	80.0
4.5	2744	79.4
5.0	2733	79.0
0.0	2760	79.9

first located at the bottom of the glass tube, and was then moved upward one inch for each subsequent measurement. In this manner a vertical distance of eleven inches was traversed. The center of the pole faces of the magnet was about 3.5 inches above the starting position. The results are shown in Table VIII.

Next the thermocouple junction was put directly into the susceptibility tube, in contact with a charcoal sample. At the starting position the junction was at the bottom of the upper part of the tube, just above the septum. For each subsequent measurement the entire susceptibility tube was raised a measured amount and time allowed for thermal equilibrium to be established. The results are given in Table IX.

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TABLE VIII

TEMPERATURE GRADIENT BETWEEN THE SUSCEPTIBILITY TUBE AND THE GLASS TUBE

Distance Above Starting Position Inches	Electromotive Force Microvolts	Temperature °C.
0	-2478	-70.8
1	2565	73.5
2	2643	76.0
3	2703	78.2
4	2756	79.8
5	2772	80.2
6	2772	80.2
7	2772	80.2
8	2769	80.2
9	2765	80.1
10	2737	79.2
11	2674	77.1

TABLE IX

TEMPERATURE GRADIENT WITHIN THE SUSCEPTIBILITY TUBE

Distance Above Starting Position Inches	Electromotive Force Microvolts	Temperature °C.
0.0	-2773	-80.3
0.5	2795	80.9
1.0	2799	81.2
1.5	2800	81.2
3.5	2799	81.2
0.0	2770	80.2

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In a final measurement the thermocouple junction was raised three inches above the septum of the susceptibility tube, with the tube itself in its normal position. The measured electromotive force was -2795 microvolts and the corresponding temperature -81.0°C.

It is apparent from these data that with Dry Ice-isopropanol mixture as the refrigerant, the temperature does not vary throughout the length of the sample by more than one degree. Also, the temperature of the sample itself is not more than one degree different from the temperature in the refrigerating bath nor from that in the air space separating the susceptibility tube from the bath. Therefore in all subsequent temperature measurements the thermocouple junction was located at the bottom of the refrigerant bath.

Adsorption Studies

Elemental Analyses of Charcoals

In order to be able to correlate adsorption properties with the composition of various charcoals, carbon-hydrogen analyses and ash determinations were made on several charcoal samples. For the charcoals activated with nitrogen or sulfur, analysis for these elements was also performed. From the results of the analysis the percentage of oxygen was calculated by difference. The samples were sent to a microanalytical laboratory for analysis.* The results of these analyses are shown in

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* Clark Microanalytical Laboratory, P. O. Box 17, Urbana, Ill.

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Table I. To identify these charcoals unambiguously the number of each charcoal has been prefaced by the letter "C" to indicate that a sample of the charcoal had been analysed by the Clark Laboratory.

The method of preparation of each of these charcoals will now be described in some detail. As can be seen from Table I, C-1 through C-6 were activated in nitrogen, C-7 was activated in sulfur, and C-8 through C-12 contained just carbon, hydrogen, and oxygen.

C-1. A ten gram sample of charcoal was used as starting material. It was outgassed at 700°C. for four hours, and ammonia was passed through for three hours at the rate of 10-15 liters per hour. Then nitrogen was passed over the sample until the furnace and sample had cooled to room temperature. This was the general pattern of activation for subsequent samples as well. Odors of hydrogen cyanide and ammonia were detectable on this charcoal. The yield was 7.98 g. of charcoal.

C-2. This charcoal was prepared in the same way as C-1 except that the rate of flow of ammonia was increased to 20 liters per hour. The odor of hydrogen cyanide, but not of ammonia was detectable on the product.

C-3. The starting material for this activation process was charcoal which had been activated in air at 400°C. It was then activated with ammonia in essentially the same manner as C-2.

C-4. The starting material was charcoal outgassed to remove surface activity. The rate of flow of ammonia was increased to 24 liters per hour, and time of contact with ammonia was increased to eight hours.

C-5. The procedure was the same as that used for C-4.

Sample Number	C
C-1	9
C-2	9
C-3	9
C-4	9
C-5	9
C-6	9
C-7	9
C-8	9
C-9	8
C-10	9
C-11	9
C-12	7

Notes: a.
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TABLE I

ELEMENTAL ANALYSES OF CHARCOALS

Sample Number	Carbon %	Hydrogen %	Nitrogen %	Oxygen (Diff.) %	Notes
C-1	94.66	1.53	0.71	3.10	a
C-2	94.23	1.07	0.65	4.05	--
C-3	97.68	0.71	0.75	0.86	--
C-4	98.12	0.31	0.55	1.00	--
C-5	97.88	0.01	0.68	1.43	--
C-6	95.51	0.58	2.17	0.86	b
C-7	95.06	0.46	----	1.55	c
C-8	98.87	0.42	----	0.71	d
C-9	87.55	2.61	----	8.09	e
C-10	96.44	0.80	----	1.19	f
C-11	93.92	1.09	----	4.71	g
C-12	71.37	1.85	----	25.42	h

Notes:
a. Dried at 100°C. *in vacuo*.
b. Ash = 0.88%, non-alkaline.
c. Sulfur = 2.93%.
d. No ash.
e. Special drying to constant weight at 110°C. *in vacuo*, loss of weight = 1.75%; no ash.
f. Ash = 1.57%.
g. Ash = 0.28%.
h. Special drying to constant weight at 100°C. *in vacuo*, loss of weight = 0.92%; ash = 0.44%.

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C-6. Commercial charcoal (Eimer and Amend) was outgassed and activated in the same manner as C-1.

C-7. Ten g. of unactivated charcoal and four g. of sulfur were mixed and heated together in an open dish. The product was transferred to a combustion tube and heated at 900°C. for six hours in a stream of nitrogen. When a little dilute hydrochloric acid was added to a portion of the charcoal an odor of hydrogen sulfide was produced.

C-8. This charcoal had been heated under vacuum at 1000°C. for ten hours, a treatment which was found to remove all capacity of the charcoals for adsorbing acids and bases. No special precaution was taken to keep this charcoal out of atmospheric oxygen, however, and two or three weeks elapsed between the degassing treatment and the actual analysis.

C-9. This sample was charcoal which had been prepared from saccharose in the usual manner and had received no further treatment. It was the starting material from which other charcoals were made.

C-10. This charcoal was activated in air at 800°C. after it had been thoroughly outgassed. Activation proceeded for 2.5 hours with a rate of flow of air of ten liters per hour over the 21.4 g. sample. After activation the charcoal was cooled to room temperature in a stream of dry nitrogen. The yield of activated charcoal was 16.0 g.

C-11. This charcoal was activated in air at 400°C. A 35 g. sample of charcoal was heated at a temperature of 700°C. and at a pressure of 0.1 mm. for 24 hours. The temperature was then lowered to 400°C. and air introduc

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air introduced to bring the sample tube to atmospheric pressure. The rate of flow of dry air was set at about 60 cc. per minute, and activation proceeded for 12 hours. The charcoal was then cooled to room temperature in a stream of nitrogen. The yield of charcoal was 31.0 g.

C-12. This charcoal was activated at 400°C. in air for four hours in a muffle furnace.

Adsorption of Iodine

The extent of adsorption of iodine from potassium iodide solution was determined for the 12 charcoal samples for which elemental analyses were made. This gave information as to the relative activities of these charcoals toward the adsorption of a species which is not a simple ion. Iodine adsorption is also a measure of relative surface area.[49]

One liter of a 0.1 N solution of iodine in potassium iodide was prepared by the method of Hillebrand and Lundell.[50] The solution was standardized against 0.1147 N sodium thiosulfate. Three 20.00 ml. aliquots of the iodine solution were equivalent to 19.24 ± 0.02 ml. of thiosulfate; thus the iodine solution was 0.1104 N, or 0.0552 M. This solution was restandardized each day.

The adsorption procedure was as follows. To 0.500 g. of the charcoal in a 250 ml. iodine number flask was added 150.0 ml. distilled water. Then 20.00 ml. of the iodine solution was added, the mixture shaken briefly and then allowed to stand in the stoppered flask for exactly 30 minutes. After this time the mixture was filtered through a

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Gooch crucible, under as gentle suction as practicable, and a 100.0 ml. portion of the filtrate withdrawn for analysis. The iodine was titrated with standard 0.1 N sodium thiosulfate in accord with accepted procedures.[81]

A blank determination was run as follows. To 150.0 ml. of water was added 20.00 ml. of standard iodine solution, and the mixture was allowed to stand for a few minutes. Then the solution was filtered through a Gooch crucible in the usual manner and 100.0 ml. of this solution analyzed. For three such blank determinations the amounts of sodium thiosulfate required were 11.20, 11.24, and 11.20 ml. Since the fraction of iodine analyzed was 10/17 of that taken, multiplying the average volume of thiosulfate, 11.22 ml., by 1.700 gives 19.10 ml. The average volume of thiosulfate used for the standardizations was 19.24 ml. Since the blank was reproducible and within 0.7% of the value obtained for the standardization of the iodine solution, it appears that this method will give results which are inherently reproducible and accurate.

The amount of iodine adsorbed as a function of time is shown in Table XI. It appears that adsorption equilibrium is not reached within 30 minutes, but in view of the volatility and instability of iodine it was considered inadvisable to use contact times of more than 30 minutes.

The results of the adsorption of iodine by the charcoals are given in Table XII. The values given have a mean deviation of about five percent, and are the averages of at least two determinations.

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TABLE XI

IODINE ADSORPTION AS A FUNCTION OF TIME

Weight of Charcoal Grams	Contact Time Minutes	Volume Thiosulfate* Ml.	Adsorption**
0.5004	5	9.96	0.265
.5006	15	9.73	.312
.5010	30	9.49	.357

*Normality = 0.1147.
**Millimoles iodine adsorbed per gram of charcoal.

TABLE XII

ADSORPTION OF IODINE BY CHARCOAL

Charcoal	Iodine Adsorbed Millimoles	Percentage of Original Iodine Adsorbed
C-1	0.912	42.9
C-2	.945	42.6
C-3	.533	24.0
C-4	.302	13.6
C-5	.314	14.1
C-6	.392	17.6
C-7	.628	28.3
C-8	.333	15.0
C-9	.667	30.1
C-10	.506	22.8
C-11	.590	26.6
C-12	.332	14.9

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Adsorption of Acids, Bases, and Neutral Salts

A great deal of study has been devoted to the adsorption of acids, bases, and highly-ionized salts on charcoal. It is generally recognized that charcoal outgassed at around 1000°C. will adsorb neither acids nor bases, nor will it adsorb ions from solution. Apparently this treatment removes from the charcoals the surface oxides which are responsible for the adsorption characteristics of the charcoals. Charcoals activated in air or oxygen at 400°C. are able to adsorb base and cations, but neither acid nor anions. On the other hand, charcoals activated in air or oxygen at 800°C. are able to adsorb acids and anions, but neither bases nor cations. Charcoals activated at intermediate temperatures adsorb both acids and bases, anions and cations, but the base adsorption is less than for charcoals activated at 400°C. and the acid adsorption is less than for charcoals activated at 800°C. From this information it is clear that the adsorptive capacity of a given charcoal for acids and bases is a useful way to characterize the charcoal. In this section are reported the results of a number of studies of acid, base, and salt adsorptions on a variety of charcoals. The charcoal samples were either commercial charcoals or those activated at 400°C.

Studies were made of the adsorbing properties of Eimer and Amend C.P. sugar charcoal (lot number 502415) which are reported in Table XIII. These studies were undertaken to determine the affinity of this charcoal for acids, bases, and neutral salts. The 0.01 N and 0.05 N solutions were prepared by quantitative dilution of the standard 0.2 N acid and

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TABLE XIII

ADSORPTION PROPERTIES OF COMMERCIAL CHARCOAL

(Equilibration for 20 hours of 5.000 g. of charcoal and 100.0 ml. of solution)

Adsorbate Solution	Titrant Used*	Amount Adsorbed
0.01 N NaOH	0.83 ml. 0.2N NaOH	All NaOH adsorbed, filtrate became acidic
0.05 N NaOH	none	Filtrate was neutral, all NaOH adsorbed
0.01N HCl	1.63 ml. 0.2 N NaOH	0.496 mequiv.
0.05 N HCl	10.19 ml. 0.2 N NaOH	1.80 mequiv.
0.1 N KCl	0.80 ml. 0.2 N NaOH	No chloride adsorbed, solution became acidic
Distilled water	none	pH = 3.30

*NaOH = 0.1999 N
HCl = 0.2077 N

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base solutions. It is apparent that this charcoal adsorbed the sodium hydroxide completely but adsorbed the hydrochloric acid only to a rather limited extent.

There are two possible explanations for the behavior of this charcoal toward these solutions. On the one hand the charcoal can be considered to have been activated at a relatively low temperature so that it has a great affinity for base but only a moderate capacity to adsorb acids. This would account for the inability of the charcoal to adsorb chloride ions from potassium chloride solution. It will be seen that the magnetic susceptibility of this charcoal gives some support to this argument.

On the other hand, it is possible that the surface of the charcoal contained a relatively large amount of acid which was used at some step in the preparation of the charcoal. Commercial charcoals are commonly leached with acid to remove some of the mineral impurity. Which of these alternatives is correct has not been definitely established.

An attempt was made to titrate this commercial charcoal directly with sodium hydroxide to a neutral equivalence point. One hundred ml. of standard 0.1 N potassium chloride solution was equilibrated with 5.00 g. of charcoal for two days. The pH of this mixture was 3.95 as measured by a pH meter with glass and calomel electrodes. A magnetic stirrer was used, and dropwise addition of about two ml. of standard 0.1999 N sodium hydroxide caused the pH to rise gradually to 6.3. The pH remained nearly constant from this point, and the next 20 ml. of alkali raised the pH slowly to 6.8. Addition of base at this point was a rather difficult procedure because each drop raised the pH about 1.5 units, and then the pH slowly returned to the region of 6.5 units. Each drop of sodium hydroxide solution was added very carefully so as to avoid a high local concentration of alkali which would damage the electrodes. These results seem to indicate that the first two ml. of base reacted with acid present, either in solution or on the surface of the charcoal; the next step may have been adsorption of base on the charcoal.

An adsorption study similar to that made for commercial charcoal was undertaken on outgassed charcoal. The charred product obtained from saccharose was put into a combustion tube and slowly evacuated while the temperature was raised to 940°C. This temperature was maintained for 12 hours while the charcoal was held at a pressure of 0.1 mm. The charcoal was cooled under vacuum. Adsorption studies were made using 5.000 g. of charcoal and an equilibration time of 24 hours in each case. The results are shown in Table XIV.

TABLE XIV

ADSORPTION PROPERTIES OF OUTGASSED CHARCOAL 940°C

(Equilibration for 24 hours of 5.000 g. charcoal and 50.00 ml. of solution)

Adsorbate Solution*	Titrant Used*	Amount Adsorbed
NaOH	47.83 ml. HCl	none
HCl	50.20 ml. NaOH	0.35 mequiv.
0.1 N KCl	none	Solution was very slightly alkaline
Distilled water	none	pH = 7.7

*NaOH = 0.1999 N
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The obvious conclusion from these data is that this treatment of the charcoal removed essentially all its adsorbing properties, except perhaps for a small acid adsorption. This was the charcoal that was used as the starting material in the preparation of activated charcoals.

Most charcoals activated at 400°C. were tested for sodium hydroxide adsorption, and in some cases hydrochloric acid adsorption, to measure the success of the activation process. Data for several charcoals activated by somewhat different methods are given in Table XV. The adsorption procedures in all cases were very similar. To a weighed amount of charcoal was added 10.00 ml. of a standard 0.2 N acid or base. The time of contact was at least 12 hours, and in most cases 24 hours or longer; during this time the mixture was kept in a stoppered flask. The mixture was then filtered through a sintered glass filter, care was taken to remove all filtrate solution from the flask, and the charcoal was washed quickly three times with distilled water. The filtrate was then titrated with standard 0.2 N acid or base to the methyl red endpoint. It should be noted that approximately 2.0 milliequivalents of acid or base were present initially, and that adsorption is given in terms of milliequivalents adsorbed per gram of charcoal.

The differences in the activation methods and starting materials for these charcoals will now be discussed. All the charcoals were activated at atmospheric pressure. As indicated in Table XV, charcoals F through M were activated in the muffle furnace, and E was the starting material for all of those charcoals except J.

TABLE XV

ADSORPTION OF ACID AND BASE ON CHARCOAL ACTIVATED AT 400°C.

Charcoal	Weight of Charcoal Grams	Adsorbate	Adsorption Mequiv./g.	Activation*
A	2.178	HCl	0.081	1 hr. in air
A	2.148	NaOH	0.629	
B	2.163	HCl	0.057	1 hr. in air
B	2.054	NaOH	0.141	
C	2.769	NaOH	0.561	4.5 hr. in O_2
D	2.930	NaOH	0.663	8 hr. in O_2
D	1.413	NaOH	1.160	
E	2.175	NaOH	0.005	Outgassed
F	2.935	NaOH	0.021	10 min.
G	3.442	NaOH	0.049	20 min.
H	2.738	NaOH	0.108	30 min.
I	2.358	NaOH	0.573	90 min.
J	2.020	NaOH	1.035	120 min.
K	1.648	NaOH	0.766	190 min.
L	2.042	NaOH	0.876	5 hr.
M	2.347	NaOH	0.858	8 hr.

* Charcoals F through M were activated in air in a muffle furnace.

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A. About 15 g. of charcoal was activated in air at 400°C. with a flow rate of air of 20 cc. per minute. At this flow rate the exothermic reaction of air with charcoal caused a noticeable increase in temperature; as a result, about 15 minutes after the activation began the rate of flow of air was decreased to about five cc. per minute. The total activation time was one hour. The charcoal was cooled to room temperature in an atmosphere of dry nitrogen.

B. Activating conditions were essentially the same as for charcoal A, but the charcoal was cooled to room temperature in air. It is possible that the very low activity of this charcoal compared with charcoal A is due to the deactivation of charcoals which is known to occur at a fairly rapid rate when they are exposed to air in the temperature range 100 to 200°C.

C. Seven grams of outgassed charcoal was activated at 400°C. in dry oxygen taken from a cylinder. The flow rate of oxygen was 250 cc. per hour, and activation proceeded for 4.5 hours. The charcoal was exposed to air while the furnace cooled to room temperature.

D. The activation of this charcoal was identical to that of C except that the duration of activation was extended to eight hours. Two samples, one twice as large as the other, were tested for base adsorption to find how the extent of adsorption depended upon the sample weight. Clearly the amount of base adsorbed per gram of charcoal was much larger for the smaller sample. Most of the charcoal samples weighed close to two grams so that valid comparisons of adsorption could be made among the samples.

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E through M. Sample E was outgassed charcoal from which the subsequent charcoals were prepared. An exception to this is sample J, for which the starting material was charred sugar which had not been outgassed.

It is evident from the data presented that the most successful ways to produce charcoal which adsorbed large amounts of alkali from solution were to activate in pure oxygen for relatively long periods or to heat the charcoal in an open dish in a muffle furnace. There was relatively little adsorption of hydrochloric acid from 0.2 N solutions by these charcoals.

Adsorption of Acid and Base by Charcoals Activated with Ammonia or Sulfur

The adsorption of sodium hydroxide and hydrochloric acid from solution by nitrogen and sulfur-charcoals is presented in Table XVI. The acid and base solutions were all standardized and were approximately 0.2 N. After equilibration the mixture was filtered through a sintered glass filter, the charcoal quickly washed three times, and filtrate and washings titrated with 0.2 N acid or base to the methyl red endpoint.

For the nitrogen-containing charcoals the adsorption of base was very small, and that of acid was always the larger for a given sample. It is impossible to say with certainty how much of the acid adsorption was due to reaction with ammonia which might have been present on the surface of the charcoals even after treatment to remove it. On the other hand, ammonia could produce other kinds of basic groups on the

TABLE XVI

ADSORPTION OF ACID AND BASE BY CHARCOALS ACTIVATED WITH AMMONIA OR SULFUR

Charcoal	Weight of Charcoal Grams	Adsorbate	Acid Adsorption Mequiv./g.	Base Adsorption Mequiv./g.
C-1	1.995	20 ml. HCl	0.420	
C-1	2.000	20 ml. NaOH		0.095
C-2	0.996	10 ml. HCl	0.418	
C-2	1.001	10 ml. NaOH		0.070
C-3	0.498	5 ml. HCl	0.174	
C-3	0.500	5 ml. NaOH		0.032
Starting Mat'l	0.500	5 ml. HCl	0.080	
for C-3	0.500	5 ml. NaOH		0.090
C-4	0.495	5 ml. HCl	0.090	
C-4	0.495	5 ml. NaOH		0.062
C-6	0.500	5 ml. HCl	1.068	
C-6	0.502	5 ml. NaOH		0.000
Starting Mat'l	0.500	5 ml. HCl	0.798	
for C-6	0.502	5 ml. NaOH		0.000
C-7	0.503	5 ml. HCl	0.000	
C-7	0.499	5 ml. NaOH		0.290
Starting Mat'l	0.496	5 ml. HCl	0.000	
for C-7	0.497	5 ml. NaOH		1.438

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charcoal which would be able to adsorb acid. It is interesting in this connection to compare these adsorption data with the nitrogen contents of these charcoals. For charcoals C-1 through C-4 there is no apparent relationship between adsorption and nitrogen content. For C-6, however, the adsorption of acid was much the greatest, the adsorption of base was negligible, and this charcoal contained about three times as much nitrogen as any of the others. Clearly the nitrogen is present in predominantly a basic form, and the amount of hydrogen cyanide present must be too small to react with any of the sodium hydroxide.

The sulfur-activated charcoal C-7, which was found to contain 2.93% sulfur, was able to adsorb only a fraction of the base that its parent charcoal could adsorb. This points to the presence of sulfur in a non-acidic form on the charcoal.

Chemical Studies of the Adsorption of Paramagnetic Salts on Charcoal

Complete Chemical Analyses of Filtrates. Studies were undertaken in which paramagnetic salts were adsorbed from aqueous solution by various charcoals. Complete chemical analyses were made of the changes that occurred in solution, that is, of changes in concentration of cation, anion, and changes of pH. Salts for which such total analyses were made were cobalt (II) chloride and nickel (II) chloride.

To 7.308 g. of commercial charcoal which had been washed with sulfuric acid was added 10.00 ml. of standard 0.4912 M cobalt chloride solution. After equilibration for 24 hours the mixture was filtered and the filtrate and washings diluted to 200.0 ml. Aliquot portions of

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this filtrate were used to analyze for the concentrations of cobalt and chloride ions, and to measure the pH. The results were compared with data for the similar analysis of the standard solution. The filtrate was also analyzed quantitatively for sulfate ion, since some was removed from the charcoal surface during equilibration. The results of these analyses, in terms of the changes which took place during contact of the solution with charcoal, are shown in Table XVII.

TABLE XVII

EQUILIBRATION OF COBALT CHLORIDE SOLUTION
WITH COMMERCIAL CHARCOAL

Milliequivalents Adsorbed		Milliequivalents Desorbed	
Co^{++}	1.12	H^+	2.24
Cl^-	0.07	$SO_4^=$	2.26

It is apparent that in an ion exchange process of this kind electrical neutrality of both solution and charcoal must be maintained. For example, if cations are removed from solution by the charcoal, a corresponding number of milliequivalents of anion must be adsorbed, or cations desorbed from the charcoal. Table XVII clearly shows that approximately one milliequivalent of cationic species was adsorbed by the charcoal for which there was no recorded electrical balance. A possible explanation is that cations such as sodium, calcium, or magnesium, all of which were known to be present as impurities in the charcoal, may have been removed from the charcoal and dissolved in the filtrate solution.

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It should be noted that when a decrease of pH was observed for a system of this type, it could have been caused by either the adsorption of hydroxyl ions or the desorption of hydrogen ions. In most of the systems under investigation, however, the solutions were slightly acidic initially, so that the adsorption of hydroxyl ions to any extent was not likely. For the particular system presented above the charcoal was known to contain acid, so there could be no doubt that the pH decrease upon equilibration was caused by removal of hydrogen ions from the charcoal.

Cobalt (II) chloride was adsorbed also on a sample of charcoal prepared as follows. Sugar was charred until brittle, and a 25 g. sample heated at 500°C. in a vacuum for seven hours. Chlorine was passed through for one hour at the rate of ten liters per hour, and the charcoal was evacuated for two hours at 500°C. Then hydrogen was passed over the charcoal for one hour at room temperature and one hour at 500°C. The charcoal was transferred to a platinum dish, treated with concentrated aqueous hydrogen fluoride, and digested for one-half hour. It was then diluted with water, filtered and dried, then heated strongly. Next the charcoal was mixed with concentrated hydrochloric acid and boiled one hour. After being diluted with water, the charcoal was filtered and washed with water until free from chloride. It was then dried and evacuated for one hour. It is reported that this treatment removes all inorganic impurities from the charcoal.[82]

To 3.320 g. of this charcoal was added 10.00 ml. of standard 0.4912 M cobalt (II) chloride solution. The filtrate and washings, diluted to 200.0 ml., were analysed for cobalt and chloride ions, and the pH was measured. These data were compared with the results of similar analyses of 10.00 ml. of the standard solution diluted to 200.0 ml. The results are presented in Table XVIII. From the point of view of electrical neutrality one can consider that the cobalt ions displaced hydrogen ions from the charcoal; however, this leaves 0.073 milliequivalents of cobalt ion unbalanced electrically, and to this must be added the 0.033 milliequivalents of chloride ion desorbed from the charcoal. Thus there is the electrical charge of about 0.106 milliequivalents of cation adsorbed (or anion desorbed) which is not accounted for by the analysis. Since the charcoal was prepared from sugar which was almost entirely free from inorganic impurities, and since drastic treatment was given the charcoal to free it from small amounts of inorganic salt, it seems very unlikely that any inorganic impurities were leached from the charcoal during equilibration with the cobalt (II) chloride solution. There is at present no way to account for the discrepancy.

TABLE XVIII

EQUILIBRATION OF COBALT CHLORIDE SOLUTION
WITH SPECIALLY PURIFIED
CHARCOAL

Milliequivalents Adsorbed		Milliequivalents Desorbed	
Co^{++}	0.177	H^+	1.04
		Cl^-	0.033

Ten ml. of 0.5 M solutions of cobalt (II) chloride and nickel (II) chloride solutions were each equilibrated with 2.1 g. of charcoal activated in air at 400°C. (charcoal A, Table XV). The conditions of adsorption and the analytical procedures used were the same as in the two preceding accounts of the adsorption of cobalt (II) chloride on charcoal. The results for these adsorptions are presented in Table XIX. In the case of cobalt chloride adsorbed on this charcoal electrical balance was approximately maintained, but for nickel chloride again about 0.1 milliequivalents of cation were adsorbed for which the process maintaining electrical neutrality of charcoal and of solution is unknown.

TABLE XIX

EQUILIBRATION OF COBALT CHLORIDE AND NICKEL CHLORIDE SOLUTIONS WITH LOW-TEMPERATURE ACTIVATED CHARCOAL

Adsorbate	Milliequivalents Adsorbed		Milliequivalents Desorbed	
$CoCl_2$	Co^{++} Cl^-	0.162 0.095	H^+	0.049
$NiCl_2$	Ni^{++} Cl^-	0.132 0.00	H^+	0.00

Exchange of Paramagnetic Ions for Sodium Ions on Charcoal. Three g. of charcoal activated in air at 400°C. was left in contact with 10.00 ml. of 0.2246 N sodium hydroxide. After equilibration the filtrate and washings were titrated with 0.1980 N hydrochloric acid to the methyl red endpoint. The results of this analysis are shown in Table XX. This charcoal was divided into two portions, one of which was used to adsorb iron (III) sulfate, and the other cobalt (II) chloride. To one portion was added 10.00 ml. of 0.2825 M iron (III) sulfate solution. The filtrate and washings were titrated, after reduction, with 0.09577 M ceric ammonium sulfate. To the other portion was added 10.00 ml. of 0.4912 M cobalt (II) chloride solution. Titration of filtrate and washings was carried out in the usual manner. The results of these exchange studies are given in Table XX.

TABLE XX

EXCHANGE OF PARAMAGNETIC IONS FOR SODIUM IONS ON CHARCOAL

Weight of Charcoal Grams	Adsorbate Solution	Adsorption Mequiv./g.
3.1	10.00 ml. 0.2245 M NaOH	0.691
1.464	10.00 ml. 0.2825 M $Fe_2(SO_4)_3$	0.400
1.613	10.00 ml. 0.4912 M $CoCl_2$	0.654

It is not possible to make valid quantitative comparisons of adsorption unless the same volumes of solution of the same concentration are equilibrated for the same length of time with exactly the same weights of charcoal; it can be stated with assurance, however, that the presence of sodium hydroxide on this charcoal increased the capacity of the charcoal to adsorb paramagnetic ions by about five-or ten-fold. Presumably the paramagnetic ions displaced sodium ions from the charcoal.

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Removal of Paramagnetic Ions from Charcoal. A 2.554 g. sample of charcoal which was activated in air at 400°C. for two hours was equilibrated with 10.00 ml. of 0.2825 M iron (II) sulfate. Analysis of the filtrate showed that 0.068 milliequivalents of iron was adsorbed. This charcoal was left in contact with ten ml. of concentrated hydrochloric acid for 24 hours. Then the mixture was filtered, the charcoal washed three times, and the filtrate and washings titrated with 0.1099 N cerate. It was found that of the 0.068 milliequivalents originally adsorbed 0.028 milliequivalents was removed by leaching with hydrochloric acid.

A similar qualitative study was made of nickel (II) chloride adsorbed on charcoal. Initial leaching with hydrochloric acid removed only a fraction of the nickel, and several subsequent washings with acid were carried out, all of which showed the presence of appreciable amounts of nickel.

These studies show that the adsorbed salt is bound to the charcoal in such a manner that it is only slowly removed from the charcoal even by acid solutions in which the salts are extremely soluble.

Magnetic Susceptibilities of Pure Charcoals

Magnetic Susceptibilities of Pure Charcoals at Room Temperature

A number of determinations were made of the magnetic susceptibilities of charcoals containing no adsorbate other than oxygen from the atmosphere or the activating medium. The purpose of this study was to determine what effect the activation process had on the magnitude of the susceptibility.

The results of these measurements are shown in Table XXI. The sample with the greatest diamagnetism, -0.938×10^{-6}, was that from which active surface oxides were removed by outgassing at 1000°C. Charcoals activated at 800°C. had gram susceptibilities approximately -0.7×10^{-6}, and those activated at 400°C. were mostly in the range -0.3 to -0.5×10^{-6}. The charcoal which had not been treated after the original charring had a susceptibility of about -0.4×10^{-6}, or essentially the same as charcoal activated at 400°C.; earlier studies showed its capacity for the adsorption of acid and base to be essentially that of the 400°C. charcoal also (see Table XIII).

The commercial charcoals had susceptibilities in the range -0.4 to -0.5×10^{-6}, indicating that they had been activated in the 400°C. range, again in agreement with the results of acid and base adsorption.

It is apparent from Table XXI that the freshly dried charcoals were slightly less diamagnetic (less negative) than they were just before being dried. This is apparently due to the loss of adsorbed water, which has the susceptibility -0.720×10^{-6}. The samples were all stored in tightly-stoppered sample bottles to minimize the adsorption of water.

All of these samples showed the presence of traces of ferromagnetic impurity. The susceptibility values varied by about 15 to 20% for an increase in field strength from 4,000 to 10,000 oersteds. In all cases the values at the highest field strength used (15 amperes current through the magnet coils) were reported, as these values are nearest the true values for the samples. Unfortunately charcoal is seldom

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Number	X
1	-0.4
2	-0.4
3	-0.3
4	-0.2
5	-0.3
6	-0.4
7	-0.4
8	-0.4
9	-0.79
10	-0.9
11	-0.4
12	-0.39
13	-0.47
14	-0.4
15	-0.9
16	-0.73
17	-0.5
18	-0.3
19	-0.4

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TABLE XXI

MAGNETIC SUSCEPTIBILITIES OF PURE CHARCOALS AT ROOM TEMPERATURE

Number	X x 10^6	Description
1	-0.433, -0.408	Unactivated, made by charring saccharose
2	-0.422	Unactivated, sample C-9, contained 8.09% oxygen
3	-0.305	Activated 400°C. with air 1 hour in combustion tube; sample C-11, contained 4.71% oxygen
4	-0.232	Activated same conditions as #3
5	-0.377	Activated 400°C. 4 hours in muffle, from #2
6	-0.489	#5 after 5 days; sample C-12, contained 25.42% oxygen
7	-0.480	#5 after 6 months
8	-0.432	#7 dried 2 hours at 110°C.
9	-0.791	Activated 4.5 hours in muffle from C-8
10	-0.902	#9 after 14 days
11	-0.445, -0.353	Activated at 400°C., washed with 0.2 N NaOH
12	-0.397, -0.471, -0.190*	Activated at 400°C., washed with 2 N H_2SO_4
13	-0.476*	Activated at 400°C., washed with 2 N HCl
14	-0.464*	#13 washed with 0.2 N NaOH
15	-0.938	Outgassed to remove adsorbing properties; sample C-8, contained 0.71% oxygen
16	-0.738, -0.707	Activated at 800°C.; sample C-10, contained 1.19% oxygen
17	-0.508	Commercial charcoal (Eimer and Amend lot #502415)
18	-0.386	#17 dried 2 hours at 130°C.
19	-0.462	Commercial charcoal (Eimer and Amend lot #484448)

Where two or more values are given these refer to additional samples activated in an identical manner.

* Activated 2 hours in muffle furnace, dried under nitrogen at 110°C. for 2 hours.

prepared that is free from ferromagnetic impurities.[53] Washing the charcoal with acid was often helpful but rarely removed all the impurity; from the point of view of the adsorption studies washing with acid was undesirable because the acid could never be completely removed either.

Magnetic Susceptibilities of Pure Charcoals at Low Temperatures

The magnetic susceptibilities of seven pure charcoals were determined at the three temperatures: room temperature, the temperature of Dry Ice-isopropanol mixture, and the boiling point of liquid nitrogen. The results are shown in Table XXII. The first four samples listed are those for which carbon-hydrogen analyses were made (see Table X) and the other three are random samples whose susceptibility values at room temperature are also given in Table XXI.

Sample C-10 was activated at 800°C., all the others except C-9 were activated at 400°C., and C-9 was material which was obtained from charring sugar and which had received no further treatment.

For a simple diamagnetic substance there should be no change in susceptibility with temperature, although in practice the susceptibilities of many diamagnetic materials do actually show a slight temperature dependence. For paramagnetic substances, however, the susceptibility bears an approximately inverse relation to temperature.

The temperature dependence of susceptibilities for these charcoals is much larger than that expected for pure diamagnetic substances. It is also quite different from that of graphite, the susceptibility of which[54] at -170°C. is -6.0×10^{-6}, and at 20°C. is -3.5×10^{-6}.

TABLE XXXI

MAGNETIC SUSCEPTIBILITIES OF PURE CHARCOALS AS FUNCTIONS OF TEMPERATURE

Charcoal	Temperature °K.	X x 10^6	Intercept (A) x 10^6	Slope (B) x 10^6
C-9	300	-0.408	-0.550	39.3
	192.0	-0.355		
	77.6	-0.042		
C-10	299	-0.707	-0.860	50.0
	194.8	-0.592		
	76.7	-0.223		
C-11	296.7	-0.232	-0.520	85.3
	194.8	-0.081		
	77.6	-0.582		
C-12	297.7	-0.480	-0.515	11.4
	195.5	-0.455		
	77.0	-0.373		
Table XXI, #12	295.7	-0.471	-0.518	14.0
	195.2	-0.446		
	75.2	-0.332		
Table XXI, #13	298	-0.476	-0.518	11.7
	193.6	-0.456		
	75.5	-0.356		
Table XXI, #14	299	-0.464	-0.533	27.5
	194.9	-0.406		
	73.0	-0.176		

The obvious interpretation of the data is that there is here a mixture of diamagnetic and paramagnetic materials; specifically, a mixture of diamagnetic charcoal and paramagnetic molecular (or atomic) oxygen. If this be the case, then the susceptibility should be the following kind of fjunction of temperature:

$$X = A + \frac{B}{T} \qquad (3)$$

where A and B are constants independent of temperature. The interpretation of this equation is that the susceptibility is composed of two parts, the diamagnetic part which is independent of temperature, and the paramagnetic part which is inversely proportional to temperature, and these two parts are assumed to be additive.

For each of the charcoals plots of gram susceptibility versus reciprocal temperature were made (see Figures 6 to 12), and in every case the three points lay very nearly on a straight line, as predicted by the above equation.

We have then this picture of these charcoals. The charcoal itself consists of amorphous carbon upon the surface of which exists chemisorbed oxygen, hydrogen, moisture, and perhaps small amounts of nitrogen. Besides this the charcoal contains oxygen in the molecular or atomic state: it is not possible from these data to distinguish between these alternatives because both forms of oxygen are paramagnetic. This oxygen can be designated as physically adsorbed, if the criterion for physical adsorption be that no chemical bond be formed at the surface.

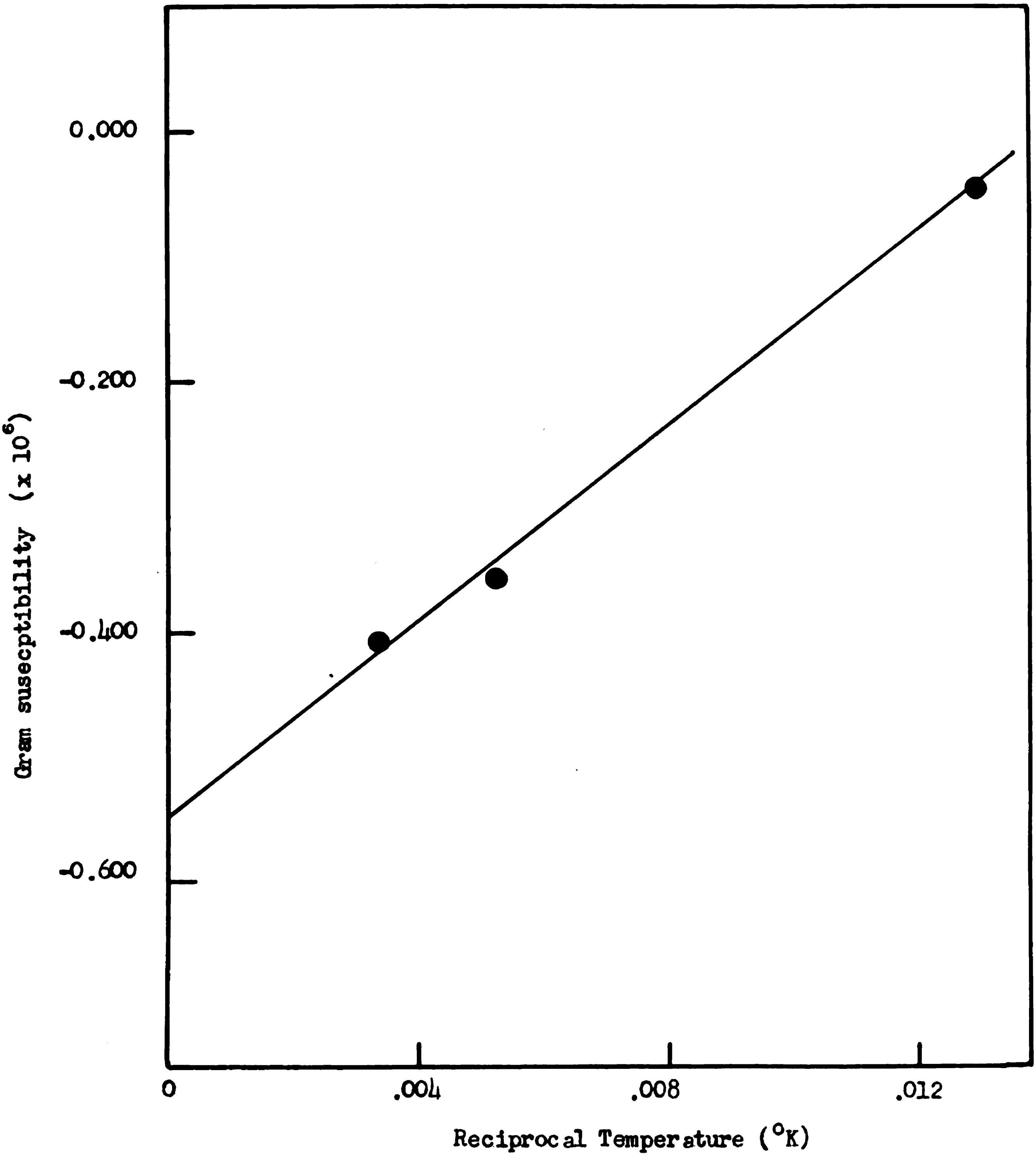

Figure 6. Gram susceptibility as a function of reciprocal temperature for charcoal C-9.

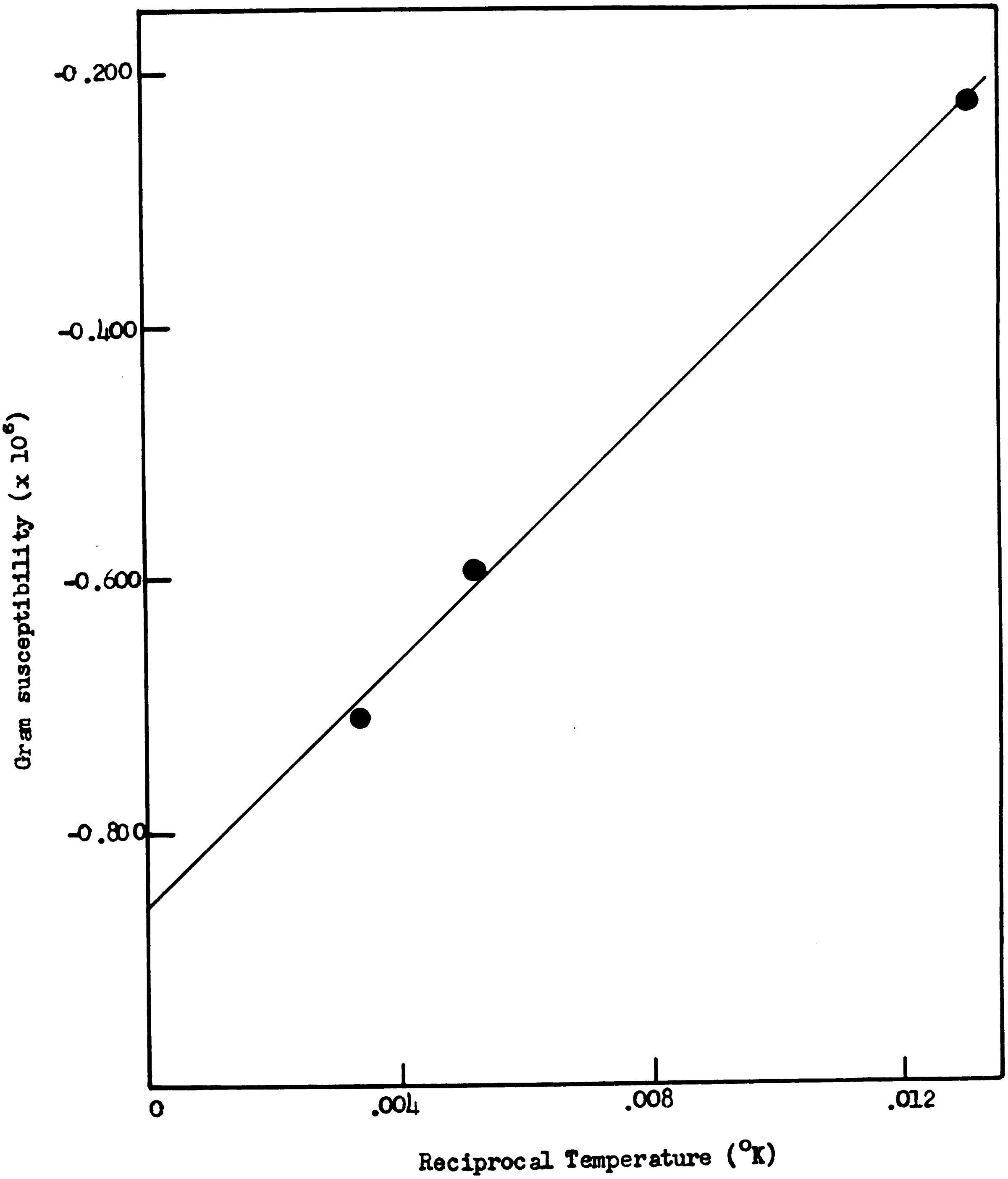

Figure 7. Gram susceptibility as a function of reciprocal temperature for charcoal C-10.

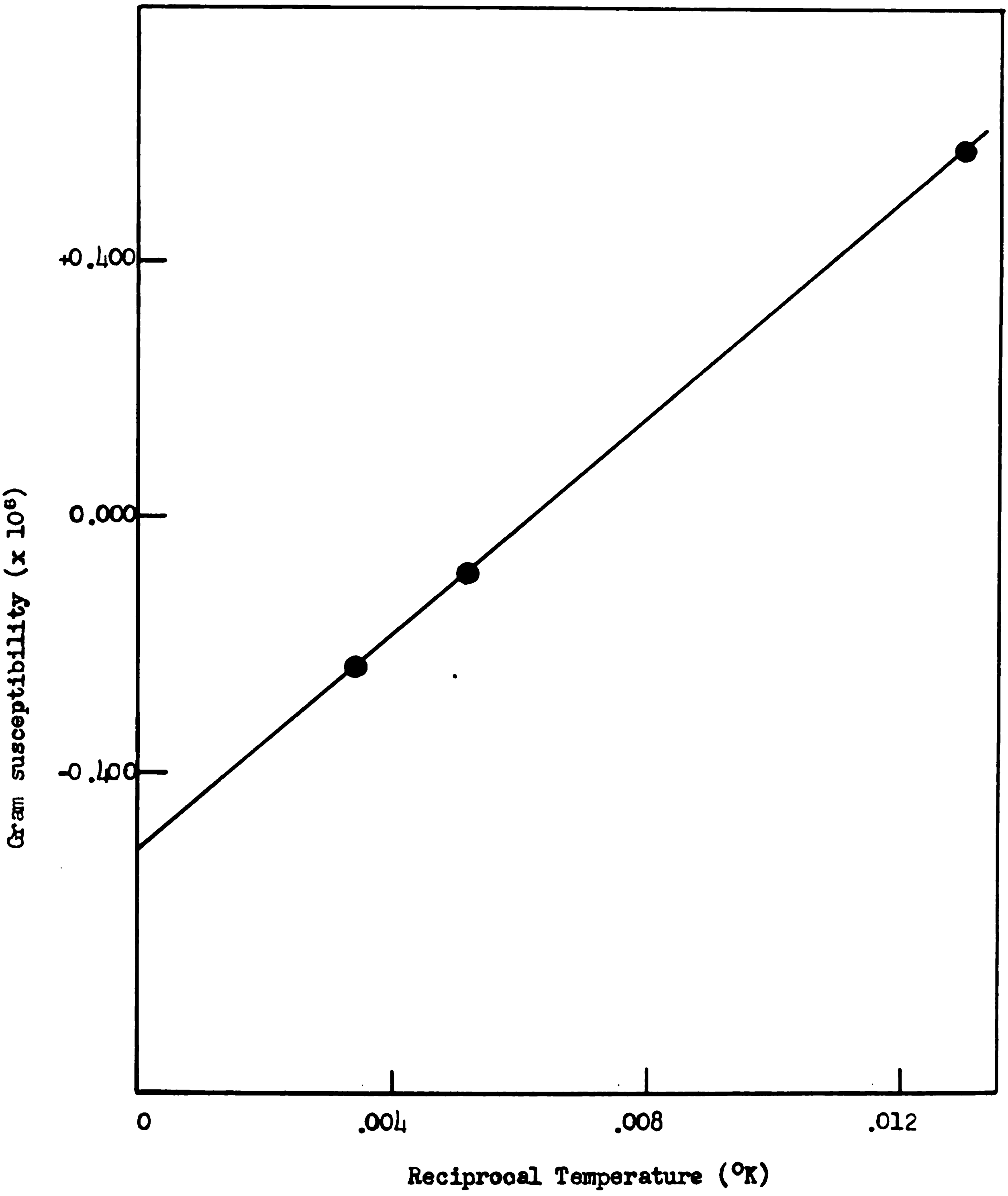

Figure 8. Gram susceptibility as a function of reciprocal temperature for charcoal C-11.

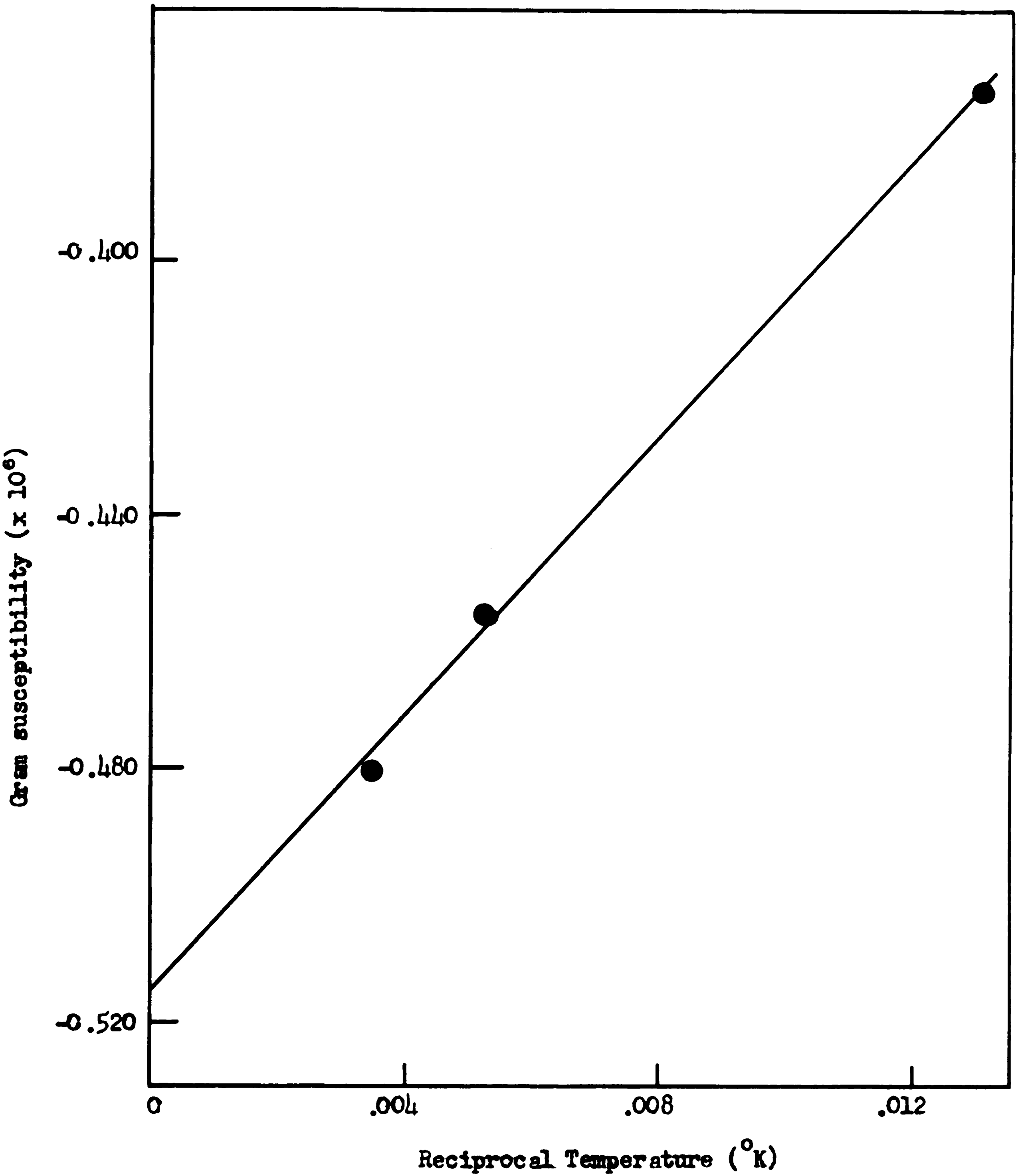

Figure 9. Gram susceptibility as a function of reciprocal temperature for charcoal C-12.

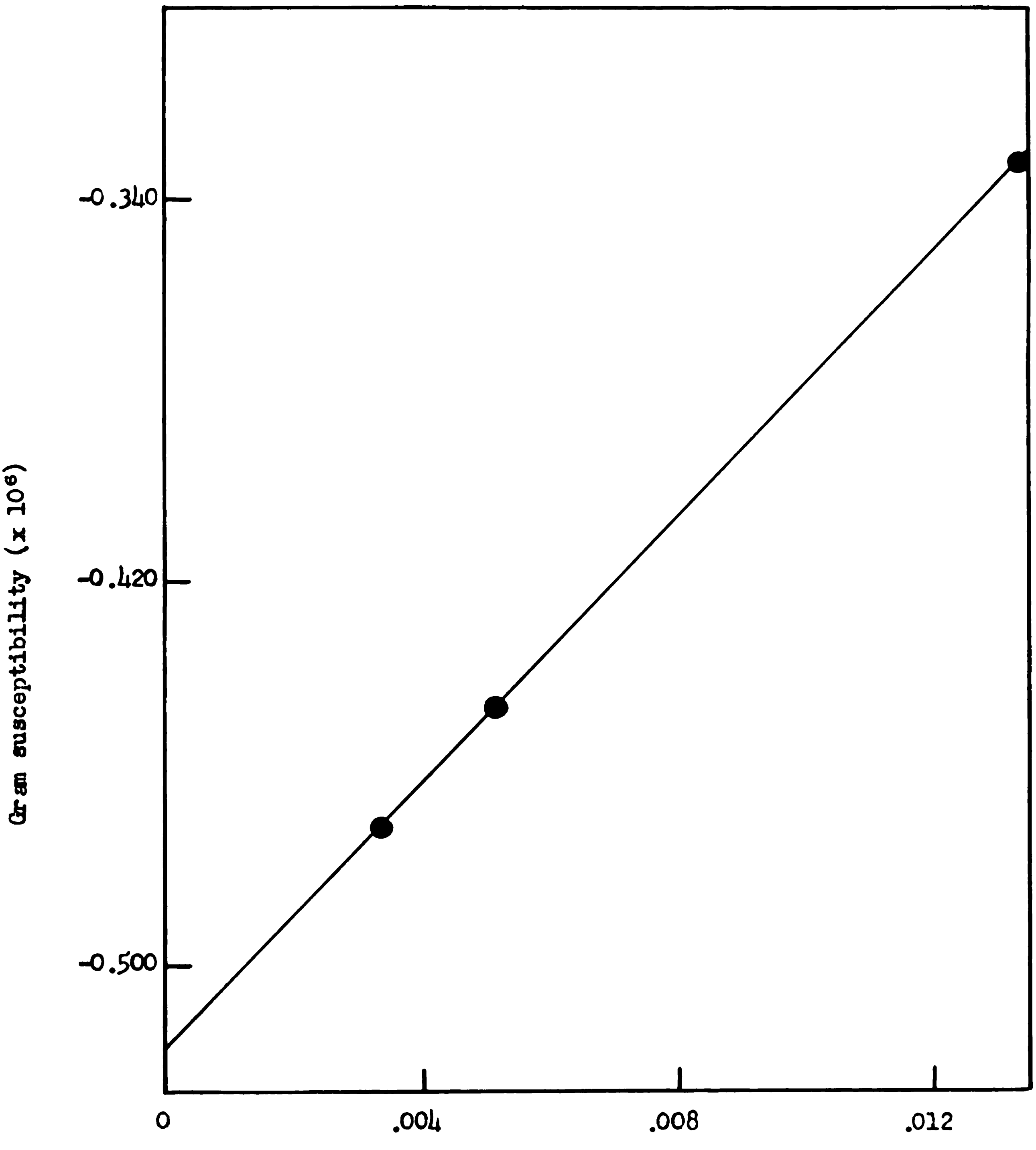

Figure 10. Gram susceptibility as a function of reciprocal temperature for charcoal 12, Table XXI.

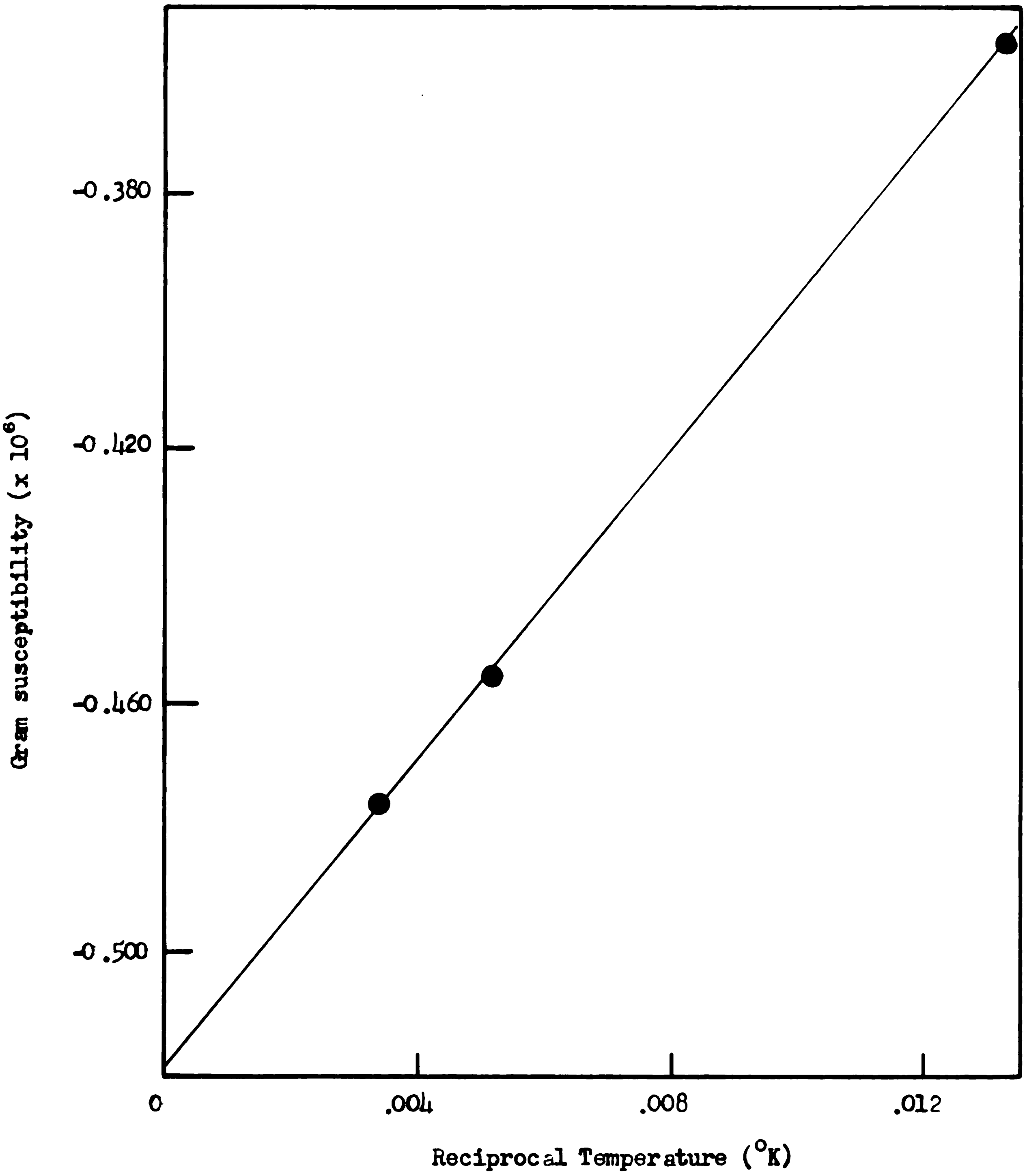

Figure 11. Gram susceptibility as a function of reciprocal temperature for charcoal 13, Table XXI.

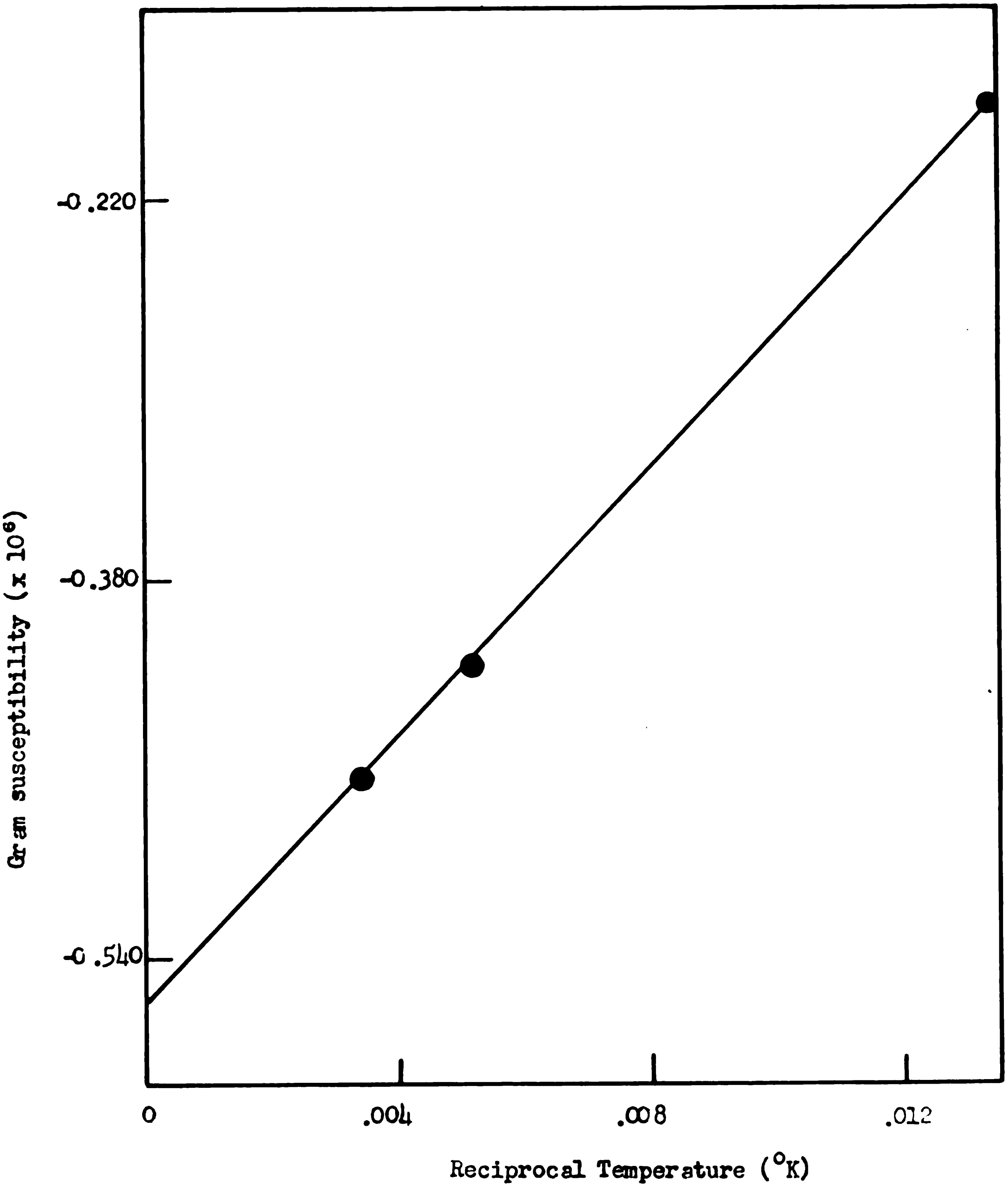

Figure 12. Gram susceptibility as a function of reciprocal temperature for charcoal 14, Table XXI.

Table XXII shows that for all the charcoals activated at 400°C. the value of the intercept, or of the diamagnetic temperature-independent component of susceptibility, lies between -0.518 and -0.553×10^{-6}. The intercept for the charcoal activated at 800°C. is -0.860×10^{-6}. This is noteworthy in view of the fact that the charcoals activated at 400°C. have variations of susceptibility with temperature which are quite different from each other. The fact that the diamagnetic part of the susceptibility of the charcoal activated at 800°C. is much different from those charcoals activated at 400°C. indicates a specific diamagnetic contribution from each type of surface oxide.

It is most likely that the temperature dependent part of the magnetic susceptibility is due to the presence of oxygen molecules adsorbed on the surface, since it has been shown that the susceptibility of oxygen physically adsorbed by charcoal is the same as pure oxygen.[52,51] If we assume that the paramagnetic parts of the susceptibilities of these charcoals are due entirely to oxygen molecules, it is possible to calculate approximately the amount of oxygen physically adsorbed. The gram susceptibility of oxygen is:[47]

$$\chi_{gm} = \frac{0.0310}{T} \qquad (4)$$

For a mixture of oxygen with a diamagnetic material the value of the Curie constant, 0.0310, will appear to decrease in the proportion that the weight percentage of oxygen in the sample decreases. Thus if the oxygen is present in the sample to the extent of 10% by weight, the

Curie constant will in effect have decreased to 0.00310. Conversely, if the Curie constant for oxygen in a mixture appears to be 0.00310, this number can be divided by the true Curie constant to obtain the weight fraction of oxygen in the mixture. In the present case the slope of the plot of susceptibility versus reciprocal temperature, which has been called the constant "B", is the apparent Curie constant; dividing this by 0.0310 gives the weight fraction of oxygen. Thus we have

$$\frac{B \times 100}{0.0310} = \% \text{ oxygen by weight.}$$

~~"B" must be multiplied by the molecular weight of oxygen because 0.0310 is the molar value of the Curie constant.~~

When this is applied to the seven charcoals under examination percentages of molecular oxygen are obtained which are shown in Table XXXII.

It is interesting to compare these results with those of Juza and co-workers.[59,60] These investigators were able by susceptibility measurements on charcoal at room temperature to determine how much oxygen was adsorbed physically and how much was in the form of surface carbon oxides. Charcoal was outgassed for 1.75 hours at various temperatures, and a known weight of the charcoal was left in contact with oxygen at known pressure and temperature for 15 minutes. From the pressure decrease in the system of known volume the total amount of oxygen adsorbed was calculated. Then the magnetic susceptibility was determined; from the difference in susceptibilities between outgassed and oxygenated charcoal the amount of molecular physically adsorbed oxygen was calculated, and

TABLE XXIII

PERCENTAGE OF MOLECULAR OXYGEN ADSORBED ON CHARCOAL

Charcoal	B x 10^6	Molecular Oxygen %	Description of Charcoal
C-9	39.3	0.126	Unactivated, contained 8.09% oxygen
C-10	50.0	.167	Activated at 800°C., contained 1.19% oxygen
C-11	85.3	.274	Activated at 400°C., contained 4.71% oxygen
C-12	11.4	.0368	Activated at 400°C., contained 25.4% oxygen
Table XXI #12	14.0	.0451	Activated at 400°C.
Table XXI #13	11.7	.0377	Activated at 400°C.
Table XXI #14	27.5	.0885	Activated at 400°C.

the amount of oxygen bound as surface oxide was computed by difference. The assumptions were made that physically adsorbed oxygen has the same susceptibility as molecular oxygen, and that surface oxides are diamagnetic. Some of their results are shown in Table XXIV.

Further studies by the German workers showed that longer exposure times and higher temperatures favored oxide formation rather than physical adsorption. The results of the present study are in qualitative agreement with this. The relatively high temperatures and long exposure times of the present investigation would favor formation of surface oxides from physically adsorbed oxygen. It seems that the reaction with oxygen to form surface oxides is a relatively slow one under most conditions.

TABLE XXIV

OXYGEN PHYSICALLY AND CHEMICALLY ADSORBED ON CHARCOAL (JUZA)

Temperature of Activation °C.	Adsorption as O_2 mg./g.	Adsorption as Oxide mg./g.	Oxygen Pressure mm.
20	5.15	0	290
100	4.95	0	300
400	4.78	0.63	274
700	4.17	1.67	243
950	3.22	3.43	179
1075	3.51	4.68	168
1150	3.58	3.93	162

With the method outlined by Juza and co-workers to determine the relative amounts of the two kinds of adsorbed oxygen it is necessary to know the susceptibility of the charcoal starting material and the susceptibility of the oxygenated charcoal at one temperature. The main assumption of this method is that the surface carbon oxide does not contribute appreciably to the susceptibility of the oxygenated charcoal, or at least that its susceptibility is not far different from that of charcoal. To get the same result by the method used in the present study it is necessary to know the susceptibility of the oxygenated charcoal at two temperatures but the susceptibility of the charcoal substrate need not be known at all. The assumption is made that the temperature dependence of susceptibility of oxygenated charcoal is due to the molecular oxygen alone.* In either case the total amount of oxygen adsorbed

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*As will be seen in the next section, charcoal which is essentially oxygen-free has the same susceptibility at -195°C. as it has at 24°C.

must be known, and it is assumed that physically adsorbed oxygen has the same susceptibility as the oxygen molecule in the free state. It would be interesting to compare these two methods by making complete enough measurements on a single sample to make the calculations by both methods.

Preparation of Oxygen-Free Charcoal

Since the magnitude of the magnetic susceptibility of charcoal appears to depend critically upon the amount of oxygen adsorbed and upon whether that oxygen is adsorbed chemically or physically, it was deemed desirable to attempt the preparation of a charcoal that was essentially oxygen-free and to determine its susceptibility both at room temperature and at low temperatures. Such charcoal could be expected to have susceptibility values appreciably different from those of oxygen-containing charcoals, and if no molecular oxygen were present, there would probably be no temperature dependence of susceptibility. Also, it has been suggested[53] that charcoal may exhibit surface paramagnetism, and if so this might be detected. Following is an account of the preparation of an oxygen-free charcoal and of its magnetic properties.

A quantity of charcoal was prepared from saccharose by charring in the usual manner. Ten grams of this material was placed in a mullite combustion tube having one tapered end. The other end of the combustion tube was closed off with a new solid rubber stopper which had been boiled in sodium hydroxide solution to remove sulfur. From the tapered end of the tube a short section of rubber pressure tubing connected the combustion tube to the vacuum system and accessory apparatus shown in Figure 13. The apparatus was constructed entirely of glass. The bottom end of the Y tube was connected through a large-bore vacuum stopcock to a 5/20 standard taper male joint. The susceptibility tube was connected to the system through this joint, and the joint was carefully lubricated with a high-vacuum grease to assure a vacuum-tight connection.

The charcoal in the combustion tube was heated with the Burrell high temperature furnace. At the same time that the furnace was turned on, slow evacuation of the charcoal was begun. The temperature was raised to 1200°C. and the charcoal outgassed at a low pressure. This heating at 1200°C. under vacuum was continued for 48 hours, and the pressure during this time fell from 90 to 45 microns of mercury.

At three different times during the outgassing process helium was passed into the combustion tube until atmospheric pressure was reached. The purpose of this was to wash out of the system traces of oxygen which might be present, and to leave helium as the residual gas. Helium from a cylinder was passed through alkaline pyrogallol, Ascarite, and anhydrous calcium sulfate (Drierite), in that order. Before the heating was begun helium was passed through the pyrogallol-Ascarite-Drierite system for a time to be sure that it contained no oxygen or water vapor. Then the stopcock leading to this arm was closed and the evacuation begun.

When the outgassing had proceeded for 48 hours, the furnace was turned off and the vacuum maintained until the charcoal had cooled to room temperature. Then helium was introduced until atmospheric pressure

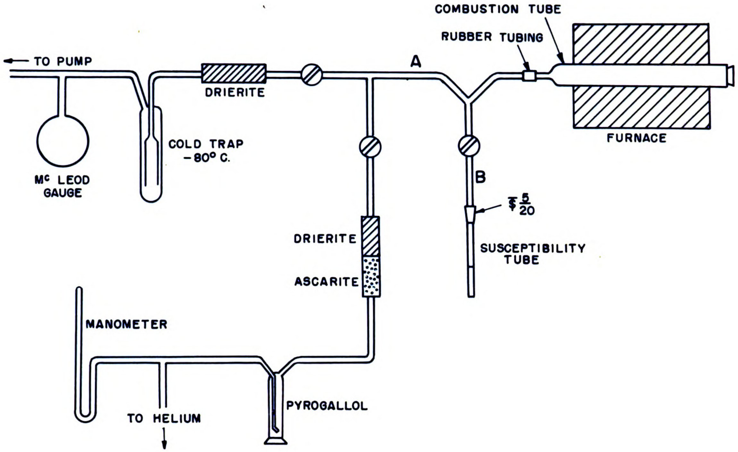

Figure 13. Apparatus for the preparation of oxygen-free charcoal.

had been reached. The system was sealed off atpoint A with a hand torch. The combustion tube was removed from the furnace, and by judicious tipping of the combustion tube the charcoal was brought over to the susceptibility tube. When sufficient charcoal had accumulated in the susceptibility tube, the latter was sealed off from the rest of the apparatus at point B. Then, in a helium atmosphere, the male standard taper joint was quickly removed and replaced by the plug or stopper of the susceptibility tube. The values obtained for the magnetic susceptibility of this charcoal at several magnetic field strengths and three temperatures are recorded in Table XXV.

There appears to be a slight trace of iron present, as seen by the small drift of susceptibility values from low to higher field strengths. This might account for the very slightly lower susceptibility values found at low temperatures.

TABLE XXV

SUSCEPTIBILITY OF OXYGEN-FREE CHARCOAL

		Temperature °K.	
Field Strength Oersteds	297	192.6	77.6
		Susceptibility $X \times 10^6$	
4,780	-1.34	-1.25	-1.28
7,360	-1.36	-1.33	-1.33
9,060	-1.37	-1.36	-1.34
10,470	-1.38	-1.37	-1.32
Average	-1.36	-1.34	-1.32

These susceptibility values are appreciably more negative than values obtained for any charcoals, activated or unactivated, which contained oxygen. Corriez[85] reported that sugar charcoals heat treated at 1200°C. had susceptibilities of -0.91 and -0.98×10^{-6}. When still higher temperatures were used, the susceptibilities became increasingly more diamagnetic, approaching but not attaining to the value of graphite (-4.1×10^{-6}). X-ray patterns of these charcoals showed beginnings of a graphite-like structure at high temperatures.

Meyer[86] reported that the gram susceptibility of gas carbon was -1.4×10^{-6} at room temperature. This material was probably an inactive form of amorphous carbon containing very little oxygen, and is probably comparable to charcoal obtained by removing oxygen.

Studies of the Nature of Surface Oxides

Chemical Methods

Assuming that the surface of activated charcoals contains appreciable amounts of carbon oxides, it might be possible by suitable oxidation to remove some of these oxides from the surface, obtaining in aqueous solution low molecular weight compounds of carbon, hydrogen, and oxygen. It was reported by King[87] that simply washing certain activated charcoals with water removes from the charcoal surface a substance identified as oxalic acid. It has been observed in the course of the present investigation that certain ash-free charcoals when washed with 2 N sulfuric or hydrochloric acid produced a substance which could be slowly oxidized by ceric ammonium sulfate solution.

A suitable oxidant for organic oxidations of this type is sodium metaperiodate. The great advantage to the study of periodate oxidation of organic matter consists in its ability to promote a specific type of molecular cleavage. The cleavage of organic molecules by periodic acid oxidation involves the breaking of carbon to carbon linkages of carbon atoms which carry hydroxyl or carbonyl substituent groups. Thus in the case of the oxidation of a simple compound such as ethylene glycol the periodate supplies one atom of oxygen in being reduced to the iodate and the carbon to carbon bond is broken with the degradation of ethylene glycol to two molecules of formaldehyde. On the other hand, periodate under the same conditions is without action on such an equally simple organic molecule as ethyl alcohol. In general, periodate oxidizes 1,2 glycols, α-hydroxy aldehydes, α-hydroxy ketones, 1,2 diketones, and α-hydroxy acids. Olefins, secondary alcohols, 1,3 glycols, ketones, and aldehydes are not affected. Because the reactions are not instantaneous and because degradation products such as formaldehyde and formic acid are reducing in character they are studied at room temperature or lower in some cases.[88]

The study of the oxidation of charcoal with periodate was carried out as follows. A quantity of charcoal was activated in air at 400°C., and 24.8 g. of this was mixed with 100 ml. of 0.1 M sodium metaperiodate. The mixture was stirred vigorously for eight hours after which it was filtered through a sintered glass filter. The filtrate was found to have a pH of four. One hour after filtration the periodate was destroyed by the addition of 10 g. of sodium sulfite and the solution was diluted to 200 ml.

A test for formaldehyde in the filtrate was carried out according to the following method suggested by Professor J. C. Speck.[59] Ten ml. aliquots of the filtrate were transferred with a pipette to separate volumetric flasks equipped with glass stoppers. To each was added 0.5 ml. of 10% chromotropic acid and five ml. of 14 M sulfuric acid. The flasks were put into a boiling water bath, the stoppers inserted, and the heating continued for 30 minutes. Then the flasks were cooled to 25°C. and the solutions diluted to 50 ml. with distilled water. Excess sulfur dioxide was removed by bubbling air saturated with water vapor through the solution for 15 minutes at the rate of one liter per minute. The color of the solution at this point was a pale yellow rather than the cherry-red color indicative of the presence of formaldehyde. A blank was run using the same procedure, and it had the same color as the filtrate solution. This test is sensitive to about one microgram of formaldehyde per ml., and apparently formaldehyde was not present above this concentration.

The presence of formic acid in the filtrate was tested for by a method similar to that used for formaldehyde.[60] Three drops of the filtrate solution was mixed with three drops of 2 N hydrochloric acid and magnesium powder was added until there was no further evolution of gas. At this point the liquid was poured off, and to it were added three ml. of 72% sulfuric acid and a little chromotropic acid. This was heated for 10 minutes at 60°C. Again there was no positive test but only a pale yellow solution. The limit of identification of this test is one microgram of formic acid per ml.

To five ml. of the filtrate from the periodate oxidation reaction was added enough hydrochloric acid to give a pH of about two. Then barium chloride solution was added and a voluminous precipitate of barium sulfate was obtained. The precipitate was filtered, the filtrate made alkaline (pH about 12) with sodium hydroxide and more barium chloride was added. A white precipitate was formed which dissolved to give a clear solution when the solution was made acidic, and re-precipitated when the solution was again made alkaline. The precipitate was filtered, washed once with distilled water, and dissolved in dilute perchloric acid. One drop of 0.005 M potassium permanganate solution was added to this solution and the purple color persisted. When this solution was heated nearly to boiling the color disappeared, but upon the addition of another drop of the permanganate the purple color persisted. Thus there was apparently no oxalate present and the precipitate was most likely carbonate.

A spectrophotometric study was also made of the reaction products of the oxidation of charcoal by periodate. About 1.2 g. of sodium metaperiodate was dissolved in 50 ml. of distilled water, and 10 ml. of this was set aside as a blank. The other 40 ml. of the approximately 0.1 M periodate solution was mixed with 8.42 g. of charcoal which had been activated at 400°C. in air. To a 7.37 g. sample of the same charcoal was added 50 ml. of distilled water. These mixtures were each stirred continuously for eight hours, then filtered, and the filtrates saved. The spectra were examined with a spectrophotometer* using matched Corex (glass) cells with a one cm. path length. The percentage transmission of the periodate-charcoal filtrate was measured against the pure periodate as a reference solution, and the water filtrate was measured against pure distilled water. The wave length range 800 to 320 millimicrons was covered, but there was no absorption from either solution in this range. This indicates that no organic molecules of any complexity were removed from the charcoal by the periodate treatment. However small molecules like oxalic acid and pyruvic acid absorb at shorter wave lengths than those used and therefore could not be detected in this measurement.

In conclusion, under the conditions used in this study there was found no evidence for the presence of formaldehyde, formic acid, oxalic acid, or of molecules which have absorption bands in the region 800 to 320 millimicrons. However, evidence was found for the presence of carbonate. It is possible that the periodate oxidized some of the surface material of the charcoal all the way to carbon dioxide.

Studies of Infrared Absorption Spectra

An attempt was made to obtain infrared absorption spectra of several charcoal samples in the hope that such spectra, if obtained, would produce some information about the nature of surface oxides. The samples

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*Beckman Instrument Co., South Pasadena, Cal., Model DU.

were prepared for infrared examination by grinding them in an agate mortar with a suitable dispersing agent and then pressing the mull obtained between sodium chloride windows. The dispersing agents were Fluorolube S[*] and Nujol;[**] all of the charcoals were examined in Fluorolube and some were examined in Nujol also. The spectra were obtained between two and seven microns for Fluorolube and between two and fourteen microns for Nujol. The absorption spectra of both Fluorolube and Nujol have been published by Miller and Wilkins.[61]

The instrument used was a Perkin-Elmer recording infrared spectrometer.[***] The compensating beam of the spectrometer contained empty sodium chloride windows similar to the windows used to contain the samples. One of the Fluorolube mulls was examined with a microscope having a calibrated eyepiece, and it was found that most of the charcoal particles were one to two microns in diameter.

The charcoals examined were chiefly those for which complete elemental analyses had been made (see Table X). In Table XXVI are given the descriptions of these charcoals and their methods of preparation for infrared analysis. One sample of charcoal C-12 was prepared by mulling the charcoal in carbon tetrachloride.[****] The mull was spread out on a sodium chloride window and when the carbon tetrachloride evaporated

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[*] Hooker Electrochemical Co., Niagara Falls, N.Y., Lot number 4-16-51.

[**] E. R. Squibb and Sons, New York, N. Y.

[***] Perkin-Elmer Corp., Norwalk, Conn., Model 21.

[****] Merck and Co., Reagent grade.

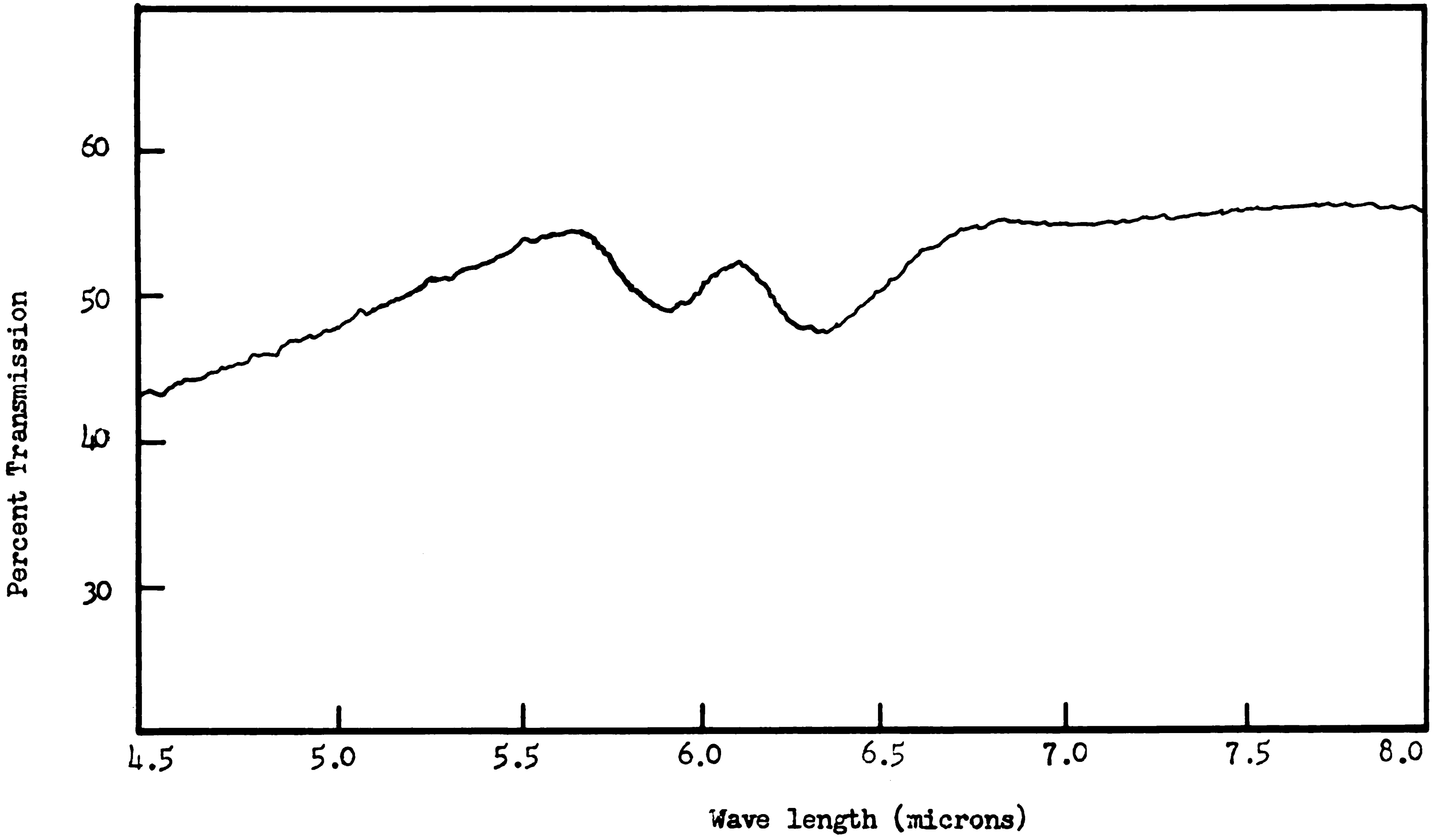

Figure 14. Infrared absorption bands of charcoal C-12.

a fine dry powder remained which was examined between sodium chloride windows.

The only charcoal samples whose spectra showed absorption bands that could not be assigned to Fluorolube or Nujol were the samples of C-12. This charcoal both in the Fluorolube mull and as the dry powder showed two absorption bands adjacent to each other at 5.6 to 6.0 microns and 6.0 to 6.5 microns. These are shown in Figure 14. The lower wavelength band is in the region of carbonyl absorption and the other band may be due to ethylenic carbon-to-carbon bonds or to adsorbed water.[62] These absorption bands are too broad to make fruitful any attempt to ascertain more precisely what kind of bonds might cause the absorption. Possibly the widths of the bands are indications that the absorbing groups are in quite different environments.

Isotope Exchange Reactions

It was thought that some information about the nature of the surface carbon oxides might be gained by equilibrating certain types of charcoals with water containing O^{18} and examining the charcoals for the presence of the heavy isotope of oxygen. There might be an exchange reaction between oxygen in the water and oxygen adsorbed on the surface of the charcoal, or possibly water might react with the carbon of the charcoal to produce surface oxide.

The method of study was to equilibrate a known weight of charcoal with a known weight of the water, then to dry the charcoal and evacuate

TABLE XXVI

EXAMINATION OF THE INFRARED ABSORPTION OF CHARCOALS

Charcoal Number	Description of Charcoal	Dispersing Medium
C-1	Activated in ammonia, contained 0.71% nitrogen, 3.10% oxygen.	Fluorolube
C-2	Activated in ammonia, contained 0.65% nitrogen, 4.05% oxygen.	Fluorolube Nujol
C-6	Activated in ammonia, contained 2.17% nitrogen, 0.68% oxygen.	Fluorolube Nujol
C-7	Activated in sulfur, contained 2.93% sulfur, 1.55% oxygen	Fluorolube
C-9	Unactivated charcoal, contained 8.09% oxygen.	Fluorolube
C-12	Activated in air at 400°C., contained 25.4% oxygen.	Fluorolube, dry powder
----	Oxygen-free charcoal.	Fluorolube
----	Charcoal with adsorbed $Fe_2(SO_4)_3$	Fluorolube

it at a high temperature to collect carbon monoxide and carbon dioxide. The carbon oxides were collected in Pyrex sample bottles and sent out for mass spectroscopic analysis.*

About 0.7 to 1.2 g. of charcoal was mixed with one or two grams of water containing 1.5% H_2O^{18}.** For a reaction vessel the bottom end of a Pyrex test tube, with a volume of about three ml. was used. The charcoal was weighed into this vessel, the water added and the vessel weighed again. A small cork was used for a stopper and the charcoal and water were agitated to mix them thoroughly. After an equilibration time of eight to sixteen hours the water was poured off and the charcoal was dried at 120°C. for one hour. It has been found that drying a charcoal at 115°C. for as long as three hours produces no change in the amount of surface complexes.[63] The dry charcoal was put into a platinum boat and evacuated at 200°C. to a pressure of about 5×10^{-4} mm. The stopcock nearest the vacuum pump was then shut off (see Figure 22) and the temperature of the charcoal was raised to 1000°C. and maintained at that temperature for five to eight hours. The platinum boat and combustion tube had been baked out previously at 1000°C. for five hours.

When both carbon dioxide and carbon monoxide were collected from the same sample of charcoal, the method of collecting gas samples was as follows. Two gas sample bottles were attached to the manifold of

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*Consolidated Engineering Corp., Pasadena, Cal.

**Stewart Oxygen Co., San Francisco, Cal., by permission of the Isotopes Division, U. S. Atomic Energy Commission.

the vacuum system. Each sample bottle consisted of a bulb of about 150 ml. capacity, a two mm. stopcock, and a 10/30 female standard taper joint. First, one of the sample bottles was immersed in liquid nitrogen to trap out carbon dioxide. Then the stopcock on this bottle was closed and the other sample bottle immersed in liquid nitrogen to increase the amount of the non-condensible carbon monoxide in the bottle, and the stopcock of this bottle closed. The stopcock of the first sample bottle was then opened to the vacuum to remove the carbon monoxide; the vapor pressure of carbon dioxide at this temperature is extremely low. The stopcock of this sample bottle was closed, the liquid nitrogen traps were removed, and the sample bottles removed from the vacuum system. For two charcoals the amount of carbon dioxide was so small that only carbon monoxide was collected. The pressure of gas collected was in the range of 100 to 150 mm. at room temperature.

Three different charcoals were investigated. The first was a charcoal activated at 400°C. previously identified as C-12. From it were collected Gas Sample 1 containing carbon dioxide and Gas Sample 2 containing carbon monoxide. The second charcoal sample contained iron (III) sulfate to the extent of 0.091 g. of salt per gram of charcoal. This charcoal yielded Gas Sample 3, which was carbon monoxide. The third charcoal sample was activated at 800°C., and has been designated previously as C-10. From this charcoal was taken Gas Sample 4 consisting of carbon monoxide. The results of the isotope analyses are presented in Table XXVII.

TABLE XXVII

OXYGEN ISOTOPE COMPOSITIONS OF CARBON OXIDES REMOVED FROM CHARCOALS

Gas Sample Number	Gas	$\frac{O^{18}}{O^{16}}$ Standard	$\frac{O^{18}}{O^{16}}$ Sample	$\frac{O^{18}}{O^{16}}$ Enrichment	Enrichment %
1	CO_2	0.002088	0.003783	0.001695	13.0
2	CO	.002015	.002924	.000909	7.0
3	CO	.002055	.003271	.001216	9.4
4	CO	.002020	.002748	.000728	5.6

Column three of Table XXVII gives the normal isotope ratios for the gases analyzed, column four gives the isotope ratios for the gas samples which were collected from the charcoals, and column five is the difference between columns three and four. If a gas sample were not enriched at all in the heavy isotope of oxygen its isotope ratio would be that given in column three. If it were enriched 100%, that is, if the water were instrumental in producing all the gases, its O^{18}/O^{16} ratio would be approximately 0.0150, which was the fraction of O^{18} in the water; this assumes that the water in contact with the charcoal contains appreciably more oxygen than does the charcoal. To find the extent to which oxygen from the water entered into the gases analyzed it is necessary to subtract the isotope ratio for the normal gas from the isotope ratio which would have been obtained had the gases contained only oxygen from the water, and to divide this into the value actually obtained for the isotope enrichment. This value, shown in column six, is simply the percentage of oxygen in the carbon monoxide or carbon dioxide gas which had its origin in the water.

It is evident that an appreciable amount of oxygen from the water entered into the carbon dioxide and carbon monoxide which were collected from the charcoals. On the basis of the drying operations it is considered unlikely that any appreciable amount of water remained adsorbed on the charcoals which might have reacted with the charcoal at higher temperatures. The only alternative is that the water reacted with the charcoal at temperatures not exceeding 200°C., the temperature at which the final removal of water took place. This reaction could be one of two types: first, the oxygen in water could exchange for oxygen on the charcoal surface leaving the system essentially intact after the exchange; or second, the water could react with the charcoal in some manner to form a surface oxide. Which of these two processes actually took place cannot be definitely determined from the data.

The second alternative seems favored on the basis of recent work by Smith et al.[64] These investigators studied the reactions of water with charcoals in the temperature range 25 to 200°C. After a suitable time of contact of water with the sample, the charcoal was baked out just below the softening point of Pyrex and the gases evolved were collected and analyzed. The authors concluded that the reaction of water and carbon gave H_2 and a carbon-oxygen complex. There seemed in fact to be two types of complex, one that decomposed at room temperature to give carbon dioxide, and another more stable complex that decomposed at high temperature with the evolution of carbon monoxide. Since the recovery of hydrogen was far below the stoichiometric amount the authors suggested

that the stable complex may contain hydroxyl groups. Charcoal which contained oxygen was much more reactive with water than charcoal treated with hydrogen at 1000°C. to remove oxygen.

The present work shows that the carbon dioxide sample collected contained the largest concentration of oxygen from the water, but that the carbon monoxide sample collected from the same charcoal contained only about one-half as much oxygen from the water. This indicates that two types of surface complex may be formed by water, one which is produced more readily and appears as carbon dioxide when the charcoal is baked out, and another which is not produced so readily by water and appears as carbon monoxide. Since the charcoal which furnished Gas Samples 1 and 2 contained about 25% oxygen the entire charcoal surface was most likely completely covered with oxygen, and it is difficult to see in this case how water could react with the carbon of the charcoal. Undoubtedly for this charcoal at least the decomposition of water occurred through the medium of the surface oxides. Sample 4, which was charcoal activated at 800°C., evolved carbon monoxide containing the least percentage of oxygen from the water, indicating that reaction between water and this charcoal to form a surface complex does not occur so readily as in the case of low-temperature activated charcoals. The presence of appreciable amounts of iron (III) sulfate on charcoal (Sample 3) appeared to have had some catalytic effect on the reaction of water with charcoal.

Discussion

The nature of the surface of activated charcoal has been studied by several methods, both chemical and physical. An attempt is made in this section to correlate the results of the various methods, to relate the results to the findings of other observers, and in some cases to postulate causes for the results in terms of the properties of the surface constituents. A summary of the properties of several charcoals is given in Table XXVIII.

Studies of the adsorption of acids, bases, and salts by specially prepared charcoals have resulted in no new information on this subject, but have been the means for characterizing the adsorption properties of the charcoals and for confirming the observations reported in the literature.[65] Charcoals from which most of the surface oxygen was removed were found to have a small capacity to adsorb acids, but bases and neutral salts were not adsorbed at all. Charcoals activated at approximately 400°C. were found to have a strong affinity for bases and to adsorb cations from inorganic salt solutions, but these charcoals adsorbed only small amounts of acids and of anions.

Unlike most substances charcoal appears to have no unique magnetic susceptibility, and in recent years it has become apparent that the magnetic susceptibility of a charcoal depends upon its past history, and in particular upon its oxygen content. A complicating factor in the study of the susceptibility of charcoal is the near impossibility of freeing the charcoal samples from all ferromagnetic and paramagnetic impurities.

TABLE XXVIII

SUMMARY OF THE PROPERTIES OF SEVERAL CHARCOALS

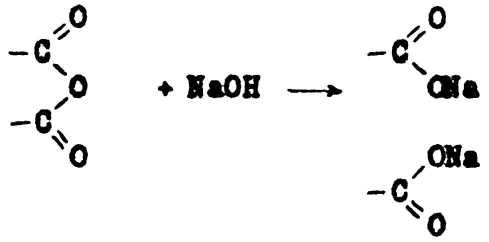
Charcoal	Activation	Oxygen Content %	Iodine Adsorption % Adsorbed	Adsorption of Acid Mequiv./g.	Adsorption of Base Mequiv./g.	Gram Susceptibility X x 10^6
C-1	Ammonia	3.10	42.9	0.420	0.095	----
C-2	Ammonia	4.05	42.6	0.418	0.070	----
C-3	Ammonia	0.86	24.0	0.174	0.032	----
C-4	Ammonia	1.00	13.6	0.090	0.062	----
C-5	Ammonia	1.43	14.1	-----	-----	----
C-6	Ammonia	0.86	17.6	1.068	0.000	----
C-7	Sulfur	1.55	28.3	0.000	0.290	----
C-8	Outgassed at 900°	0.71	15.0	-----	-----	-0.938
C-9	Unactivated	8.09	30.1	-----	-----	-0.422
C-10	800° in Air	1.19	22.8	-----	-----	-0.707
C-11	400° in Air	4.71	26.6	-----	-----	-0.305
C-12	400° in Air	25.42	14.9	-----	-----	-0.489

It is apparent from the present study that the magnetic susceptibility of charcoal depends upon the amount of oxygen adsorbed by the charcoal surface, or really upon both the amounts adsorbed physically and also chemically in the form of surface oxides. Oxygen adsorbed physically is responsible for the variation of the susceptibility of charcoal with temperature. The amount of oxygen adsorbed chemically in general determines the susceptibility of the charcoal at room temperature. Charcoal free from oxygen is strongly diamagnetic, charcoal activated at 400°C. is the most weakly diamagnetic, and charcoal activated at 800°C. possesses a diamagnetism intermediate between these two. For comparison[84] the gram susceptibility at room temperature of graphite is -3.5×10^{-6} and of diamond -0.4×10^{-6}. The fact that oxygen-free charcoal has a susceptibility of -1.36×10^{-6} but that charcoal with only 0.71% oxygen has a susceptibility of -0.94×10^{-6} suggests that the charcoal itself may become less diamagnetic when the first amounts of oxygen are adsorbed on its surface.

The elemental analyses and ash determinations of the charcoals used in the present study permitted calculation of the amounts of oxygen present in the charcoals. The methods of activation and extents of activation of the charcoals were revealed in their oxygen contents. Outgassed charcoal had a very low oxygen content, charcoal activated at 800°C. had a somewhat higher oxygen content, but the charcoal activated at 400°C. could always be distinguished by its very high oxygen content.

The adsorption of salts on charcoal, the analyses of both cations and anions, and the measurements of changes of pH produced results that are difficult to interpret. It was observed that neither charcoal nor adsorbate solution appeared to be electrically neutral after adsorption took place. Perhaps some electrically charged constituent of the charcoal surface passed into solution but was not detected by the analysis. This is probably related to King's observation[20] that charcoals were always negative when placed in contact with distilled water, even though their aqueous suspensions might be either acidic or basic. A negative charcoal would be able to become neutralized by adsorbing cations.

The fact that adsorption of cations by charcoals activated at 400°C. increased after treatment of the charcoals with sodium hydroxide is very interesting. It is possible that the reason for this can be found in the presence of acidic surface oxides. Schilow's acidic oxide is very much like the anhydride of a carboxylic acid, and perhaps the action of the sodium hydroxide solution on that oxide is in the nature of an alkaline hydrolysis:



In the presence of distilled water hydrolysis of the surface oxide proceeds to a limited extent and provides acidic hydrogen atoms which can be replaced by cations. But in an alkaline medium the reaction proceeds much more readily, analogous to the enhanced hydrolysis of acid

anhydrides in an alkaline medium,[66] and the sodium ions can subsequently be replaced preferentially by the divalent or trivalent metal ion.

Treatment of the charcoal surface with sodium metaperiodate in an attempt to obtain the products of a selective oxidation led to results that were inconclusive. The only product obtained was carbonate ion. The fact that the solutions were acidic at all times and that a fairly large amount of carbonate ion was found points to the fact that this was the product of the oxidation rather than simply the result of dissolution of carbon dioxide from the atmosphere. Apparently the conditions of oxidation were too drastic to permit the recovery of any intermediate oxidation products such as formic acid or formaldehyde.

The results of the infrared analyses of charcoals were also too meager to offer any conclusive ideas about the nature of the charcoal surface oxides. The fact that only the charcoal with 25% oxygen present showed any absorption bands indicates that this method may not be very sensitive to small amounts of surface oxides. However the absorption of infrared radiation in the carbonyl stretching region seems quite definite. Unfortunately the band is too broad to give information on what sort of carbonyl group or groups might be present. Obtaining the infrared spectra of charcoals may become a satisfactory way to examine charcoals if the methods of preparing the samples for infrared examination are improved.

It is difficult to relate the adsorption of iodine by charcoals to the results of other studies, but there does seem to be the greatest iodine absorption when the oxygen content of the charcoals is greatest. For the charcoals activated in ammonia there is no clear relation between the absorption of iodine and that of acid, although such a relationship has been reported for air-activated charcoals.[19]

MAGNETOCHEMICAL STUDIES OF THE NATURE OF ADSORBED PARAMAGNETIC SALTS

In any study of the nature of adsorption it is important to know the kind of forces that bind the adsorbed species to the adsorbent. A magnetochemical study of adsorption is often useful for this because the magnetic properties of the adsorbed substance depend upon the forces which bind it to the adsorbent. The results obtained by this method are particularly striking when the adsorbed substance is paramagnetic and may become diamagnetic upon adsorption.

Earlier studies have been made[48,67] of the adsorption of salts of nickel, manganese, cobalt, and iron on commercial sugar charcoal and on silica gel. From magnetic susceptibility determinations of the charcoal-adsorbate systems it was found that the susceptibilities of these adsorbed salts were essentially the same as the susceptibilities of the pure salts. Anomalous results were obtained, however, in the case of iron (III) salts.

In the present study salts of manganese, cobalt, and iron were adsorbed on specially prepared charcoals, and the magnetic susceptibilities of the resulting charcoal-adsorbate systems determined at low temperatures as well as at room temperature. The procedure was essentially as follows. To a known weight of charcoal was added 10.00 ml. of an approximately 0.5 M solution of the paramagnetic salt. The mixture was equilibrated for 18 to 24 hours, then filtered through a sintered glass filter. The charcoal was washed quickly with distilled water and the washings added to the filtrate; this was then analyzed for the amount of paramagnetic cation not adsorbed. The amount of salt adsorbed was calculated from the difference between the amount of salt in the filtrate and the amount present in 10.00 ml. of the standard solution. The charcoal with adsorbate was dried at 110°C. for two hours before its susceptibility was determined. For susceptibility measurements at low temperatures the charcoal samples were always in an atmosphere of helium.

When iron salts were used the solutions and charcoals were kept in an inert atmosphere as much as possible to prevent oxidation or reduction. During equilibration of charcoal and salt solution the mixture was kept in a stoppered flask from which the air had been replaced by nitrogen. The charcoal was dried by heating it in a test tube in which nitrogen was continuously circulated.

The iron sulfate solutions were stabilized by making them about two normal in sulfuric acid, and the iron chloride solutions contained enough hydrochloric acid to make them two normal. Before the susceptibilities of the pure charcoals used for reference were determined they were treated with acid of the same concentration as was present in the corresponding salt solution. These charcoals were also dried in an atmosphere of nitrogen so that their susceptibilities would in every way correspond to the true susceptibilities of the charcoals with no adsorbate.

The gram susceptibility of the adsorbed salt could be calculated from the additivity relation

$$\chi_{mixture} = P_c\chi_c + (1-P_c)\chi_{salt} \qquad (5)$$

where P_c = weight fraction of charcoal.

The temperature dependence of magnetic susceptibility of most paramagnetic substances is expressed by the Curie-Weiss law

$$\chi = \frac{C}{T + \Delta} \qquad (6)$$

where C = Curie constant

Δ = molecular field constant.

This law is a generalization of Curie's law

$$\chi = \frac{C}{T} \qquad (7)$$

A convenient way to express the susceptibility of a paramagnetic substance is by use of "effective Bohr magneton numbers", defined by the relation

$$\mu_{eff} = 2.839 \sqrt{\chi_M (T + \Delta)} \qquad (8)$$

where χ_M = susceptibility per mole. If the magnitude of Δ is not known but it is desired to get an estimate of the size of the magneton number, the following approximate relation is useful:

$$\mu_{eff} = 2.839 \sqrt{\chi_M T} \qquad (9)$$

The advantages to the use of the Bohr magneton number are that unlike the susceptibility itself the magneton number is independent of temperature, and also that the magneton number is related to the number of unpaired electrons in the substance by the simple expression

$$\mu_{eff} = \sqrt{n(n + 2)} \qquad (10)$$

where n = number of unpaired electrons.

This relation is based on the assumption that the paramagnetic susceptibility is due to spin only, that is, that there is no significant orbital contribution.

Duplicate experiments were carried out on the adsorption of iron (II) sulfate on commercial charcoal, and magnetic susceptibility determinations were made at room temperature. Since 10.00 ml. aliquots of the standard solution were equivalent to 53.74 ± 0.03 ml. of 0.09577 N ceric ammonium sulfate solution, this solution was 0.5147 M.

Charcoal samples of 7.344 g. and 7.030 g., denoted as samples I and II, respectively, were equilibrated with 10.00 ml. of the standard iron (II) sulfate solution, and the filtrates were equivalent to 45.24 and 50.13 ml. of cerate, respectively. Thus sample I contained 6.20 mg. of iron per gram of charcoal and sample II contained 2.75 mg. of iron per gram of charcoal. The gram susceptibilities of the pure charcoal and of charcoal containing adsorbed iron (II) sulfate are given in Table XXIX.

For divalent iron the number of unpaired electrons per atom is four and μ_{eff} is 4.90. Calculation of effective Bohr magneton numbers for samples I and II give, respectively, 5.17 and 5.85. Selwood[47] gives the range of experimental Bohr magneton numbers for iron (II) salts as 5.0 to 5.5.

TABLE XXIX

GRAM SUSCEPTIBILITIES OF CHARCOAL AND OF IRON (II) SULFATE ADSORBED ON CHARCOAL

Current Amperes	Pure Charcoal $\chi \times 10^6$	Sample I $\chi \times 10^6$	Sample II $\chi \times 10^6$
10	-0.352	+0.748	+0.346
12	.362	.739	.341
14	.372	.742	.334
16	.377	.747	.326
18	.387	.752	.326
20	.386	.742	.322

A similar study was made of iron (III) sulfate adsorbed on charcoal. To 1.464 g. of charcoal was added 10.00 ml. of 0.3 M iron (III) sulfate solution. The mixture was treated in the same manner as above. The filtrate was passed through a silver reductor and titrated with 0.09577 N cerate solution, requiring 56.95 ml. of cerate. Ten ml. of the standard iron (III) solution was equivalent to 58.99 ml. cerate; thus the standard solution was 0.2825 M. It was calculated that 7.45 mg. of iron were adsorbed per gram of charcoal. The gram susceptibilities of the pure charcoal, charcoal with adsorbent, and of the adsorbed salt are given in Table XXX.

The average value calculated for the gram susceptibility of the adsorbed iron (III) sulfate was 46.7×10^{-6}. From this the effective Bohr magneton number was found to be 4.74. The "spin only" value is 5.92 and the range of values found for iron (III) in pure salts by other experimenters is 5.4 to 6.0.

TABLE XXI

GRAM SUSCEPTIBILITY OF CHARCOAL AND OF IRON (III) SULFATE ADSORBED ON CHARCOAL

Current Amperes	Charcoal $X \times 10^6$	Charcoal with Adsorbent* $X \times 10^6$	Adsorbed Salt $X \times 10^6$
4	-0.399	+0.744	+45.0
6	.491	.674	46.0
10	.548	.661	47.7
15	.569	.653	48.0

*7.45 mg. iron adsorbed per gram of charcoal.

It was desirable also to make magnetic measurements at low temperatures to determine whether or not these adsorbed salts obey the Curie law for paramagnetic substances. Such measurements were made with manganese (II) sulfate, cobalt (II) chloride, and the sulfates and chlorides of iron (II) and iron (III).

Cobalt (II) chloride and manganese (II) sulfate were each adsorbed on samples of commercial charcoal by the method described above. The cobalt solution was 0.4912 M and 10.00 ml. contained 0.2895 g. of cobalt; and filtrate was found to contain 0.2506 g. of cobalt, so that 0.0389 g. were adsorbed by the 6.665 g. charcoal sample. The gram susceptibilities of the charcoal and of the charcoal-adsorbent mixture are given in Table XXXI. The susceptibility of the charcoal at room temperature was -0.46×10^{-6} and it was assumed to be independent of temperature.

TABLE XXXI

GRAM SUSCEPTIBILITY OF COBALT CHLORIDE ADSORBED ON CHARCOAL

Temperature °K	Charcoal $X \times 10^6$	Charcoal with Adsorbent* $X \times 10^6$	Adsorbed Cobalt $X \times 10^6$
293	-0.46	+0.47	159
196		+0.96	243
77		+2.85	568

*5.84 mg. of cobalt adsorbed per gram of charcoal.

These data can be analysed conveniently by the Curie-Weiss equation (6) which can be put into the form

$$\frac{C}{X} = T + \Delta \qquad (11)$$

If this equation be valid for the substances studied, the plot of reciprocal susceptibility as a function of temperature should be a straight line with the slope equal to C and intercept at the temperature axis equal to $(-\Delta)$. The susceptibilities of cobalt (II) chloride were calculated from equation (5) and the reciprocal susceptibility was plotted as a function of temperature as shown in Figure 15. It is evident that the three points do in fact lie on a straight line. The slope of the line was found to be 0.0497, in terms of the gram atomic susceptibility of cobalt, and the value of the intercept $(-\Delta)$ was six degrees.

Since from equation (6)

$$C = X(T + \Delta), \qquad (12)$$

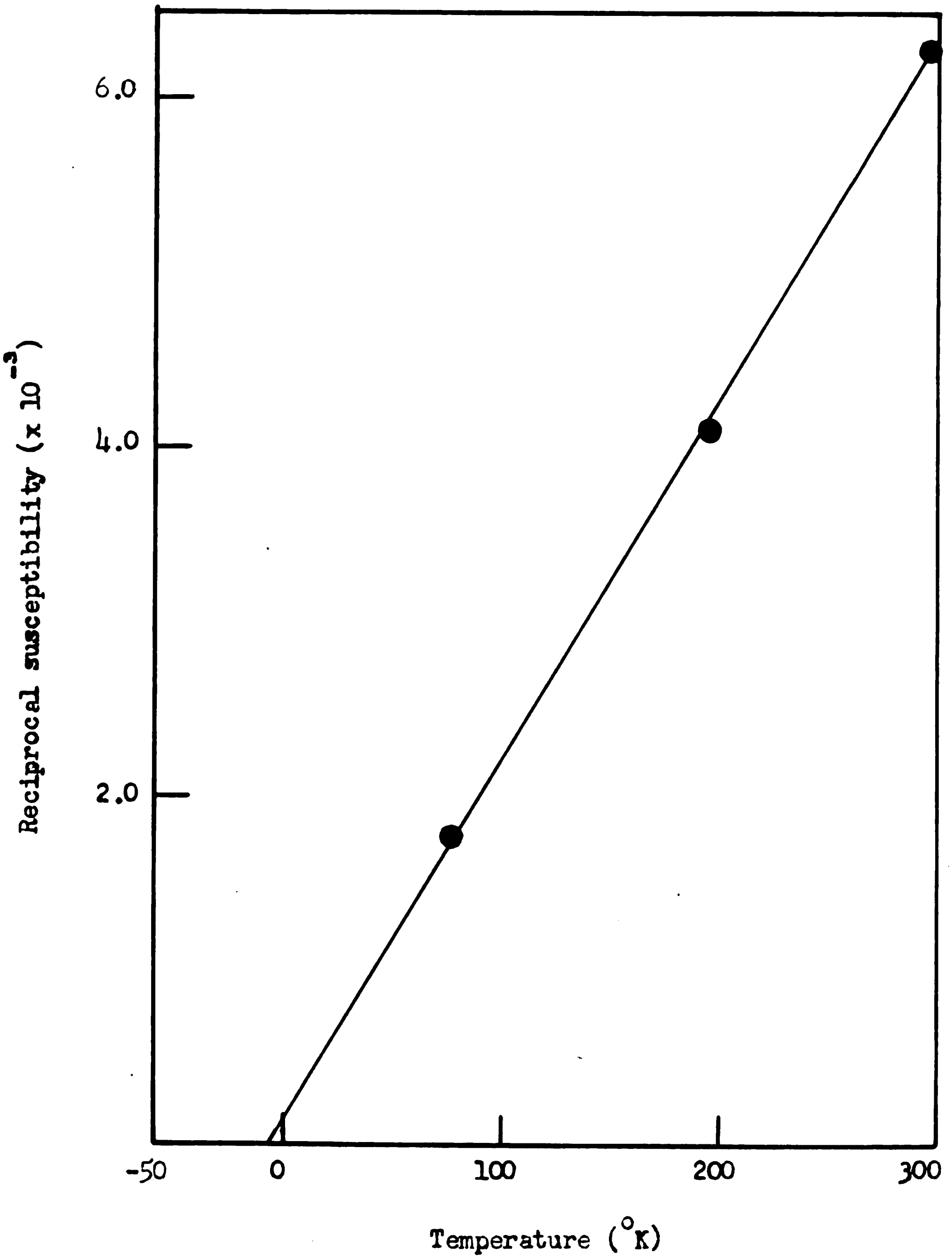


Figure 15. Reciprocal susceptibility as a function of temperature for cobalt (II) chloride adsorbed on charcoal.

the effective Bohr magneton number for the adsorbed cobalt could be calculated (equation (8)) from the slope of the line, and was found to be 4.87. The value for cobalt (II) chloride given by Stoner[68] is 5.01. Thus there was no appreciable difference in magnetic properties between adsorbed cobalt (II) chloride and the pure salt.

This study was repeated in essentially the same manner using manganese (II) sulfate as adsorbate. The standard manganese solution was 0.4045 M and the usual procedure was to dilute 10.00 ml. of the solution to 100.00 ml. and then titrate 40.00 ml. aliquots with standard 0.015 N potassium permanganate solution as described earlier. The 40.00 ml. aliquots of standard manganese (II) solution were equivalent in this manner to 40.94 ± 0.05 ml. of permanganate, and the filtrate solution was equivalent to 34.55 ± 0.10 ml. of permanganate. Thus on the 7.574 g. charcoal sample 12.6 mg. of salt were adsorbed per gram of charcoal.

The gram susceptibilities of the charcoal and of the charcoal-adsorbent mixture are given in Table XXXII. The susceptibility of the charcoal at room temperature was -0.46×10^{-6} and it was assumed to be independent of temperature. The susceptibility of manganese in each case could be calculated using the additivity law expressed by equation (5) and taking the susceptibility of charcoal to be -0.46×10^{-6}. The reciprocal susceptibility was plotted as a function of temperature and again the three points lay on a straight line, as shown in Figure 16. The value of the intercept was minus three degrees, indicating that this salt very nearly obeys Curie's law. The slope of the line was 0.0825,

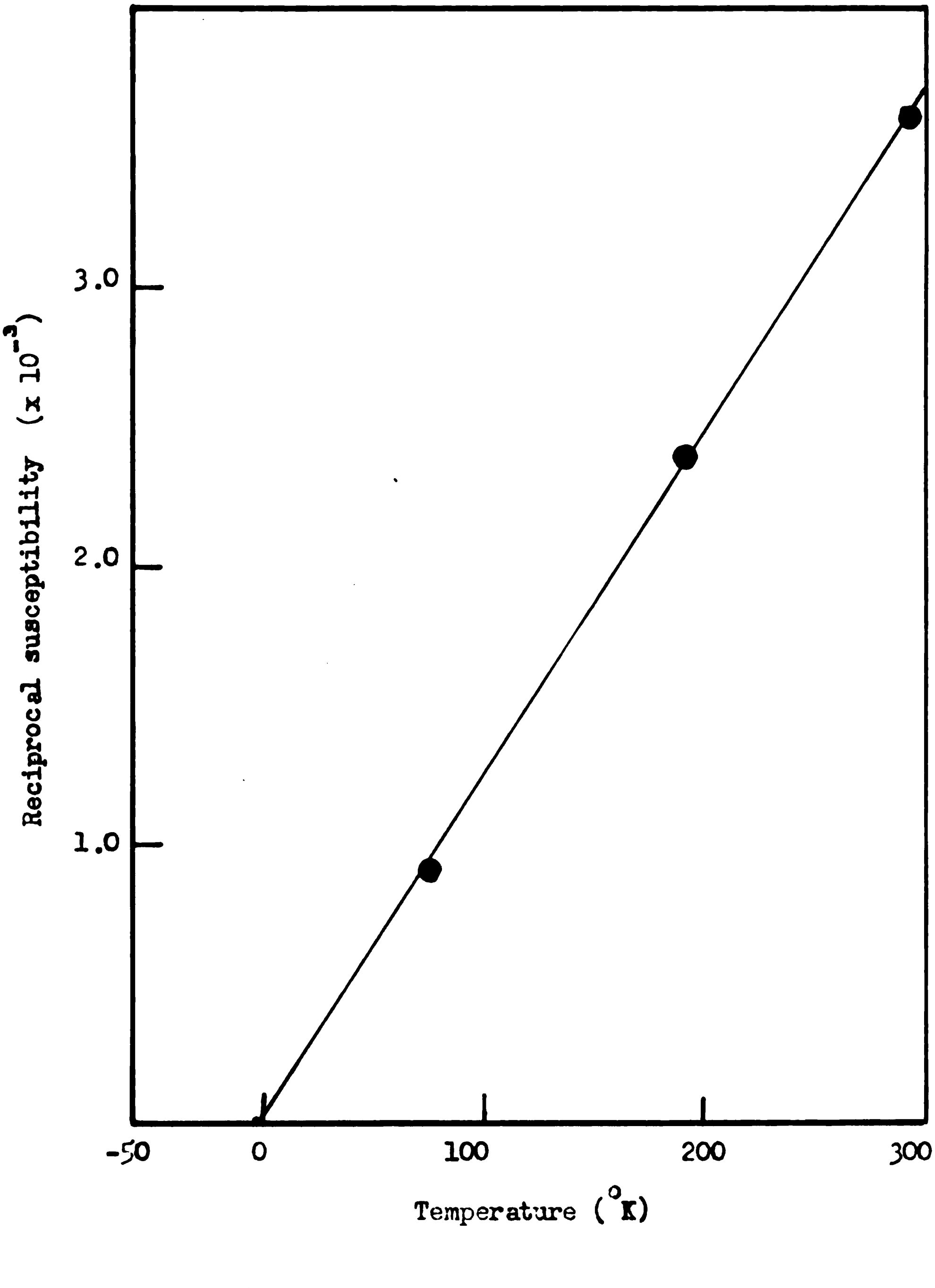


Figure 16. Reciprocal susceptibility as a function of temperature for manganese (II) sulfate adsorbed on charcoal.

in terms of the gram atomic susceptibility of manganese. The Bohr magneton number was calculated from equation (10) to be 6.04. Stoner's value[68] is 5.86. Again the magnetic properties of the adsorbed and of the pure salt were found to be essentially the same.

TABLE XXXII

GRAM SUSCEPTIBILITY OF MANGANESE (II) SULFATE ADSORBED ON CHARCOAL

Temperature °K	Charcoal $X \times 10^6$	Charcoal with Adsorbent* $X \times 10^6$	Adsorbed Manganese $X \times 10^6$
295	-0.46	+0.78	276
193		+1.41	416
76		+4.37	1075

*4.49 mg. of manganese adsorbed per gram of charcoal.

Inasmuch as it had been reported previously[67] that the magnetic moments of iron (II) and iron (III) salts adsorbed on charcoal were anomalous, a study was made of these systems which included low temperature magnetic susceptibility measurements. The charcoals used were all activated at 400°C., and the experimental techniques and treatment of data were the same as those discussed above. The results are shown in Table XXXIII. Column six gives the calculated effective Bohr magneton numbers for the adsorbed salts, and column seven lists the effective Bohr magneton numbers found by other observers from measurements on the pure salts.[68] Column eight gives the value of the constant Δ and column nine the value of the slope.

TABLE XXXIII

MAGNETIC SUSCEPTIBILITIES OF ADSORBED IRON SALTS

Adsorbate	Adsorption* Milligrams		Temperature °K	$X_{\text{Char.}}$ x 10^6	X_{Mixture} x 10^6	$\mu_{\text{Ads.}}$** Salt	μ_{Pure}** Salt	Δ Degrees	Slope
$Fe_2(SO_4)_3$	A	2.66	294	-0.471	-0.224	3.66	5.84	25	0.0298
			197.8	-0.448	-0.089				
			76.6	-0.336	+0.436				
$Fe_2(SO_4)_3$	B	2.19	300	-0.471	-0.217	4.12	5.84	10	0.0376
			192.6	-0.446	-0.004				
			70.9	-0.322	+0.486				
$FeCl_3$	C	2.47	299	-0.464	+0.109	5.73	5.80	10	0.0730
			192.3	-0.406	+0.419				
			75.5	-0.201	+1.745				
$FeCl_2$	D	1.09	298	-0.464	-0.201	5.87	5.19	23	0.0765
			193.4	-0.406	-0.037				
			78.5	-0.201	+0.679				
$FeCl_2$	E	1.67	300	-0.476	-0.100	5.55	5.19	3	0.0682
			192.7	-0.456	+0.127				
			73.9	-0.356	+1.063				

---

*Milligrams of the paramagnetic constituent adsorbed per gram of charcoal

**μ is the Bohr magneton number

The plots of reciprocal susceptibility as a function of temperature, which test the validity of the Curie-Weiss law for these samples, are given in Figures 17 through 21. Within experimental error these plots are all linear, and from the slopes of these lines the Bohr magneton numbers were calculated. The magnitude of the constant Δ, the "molecular field constant", is an indication of the magnetic environment of the paramagnetic ions.[47] For magnetically concentrated substances where the paramagnetic ions lie closely together Δ is large in absolute value, but for magnetically dilute substances where there is no mutual interaction between the magnetic species Δ is nearly zero and Curie's law is valid. The values of Δ given by Stoner[66] for iron (III) sulfate, iron (II) chloride, and iron (III) chloride are 66, -30.5, and 3, respectively. The fact that the values of Δ obtained in the present investigation tend to be less than the accepted values for the pure salts may be due to the greater distances between magnetic neighbors caused by dispersion of the salt upon the charcoal surface.

It is clear from the results presented in this section that all the paramagnetic ions when adsorbed on charcoal retain their paramagnetism. Manganese (II) sulfate and cobalt (II) chloride obey the Curie-Weiss law very closely and have the same magnetic properties in the adsorbed state as they have as pure salts. Similarly both divalent and trivalent iron have essentially the same paramagnetism in the adsorbed state as in the pure salts, although in this case the limits of error are appreciably larger. These findings are in conflict with those of Bhatnagar _et al._[26] who reported that these salts became diamagnetic upon adsorption

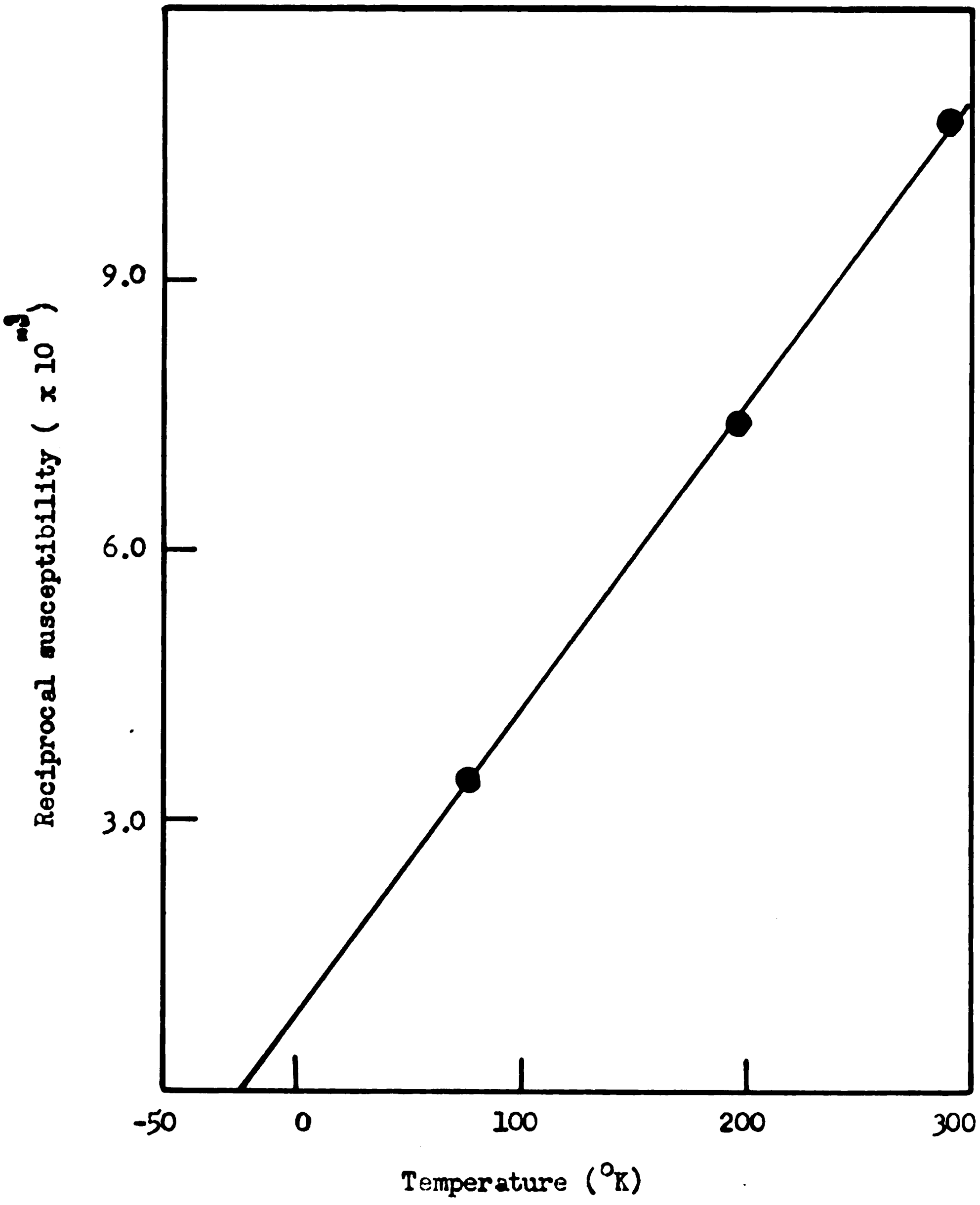


Figure 17. Reciprocal susceptibility as a function of temperature for iron (III) sulfate, sample A, adsorbed on charcoal.

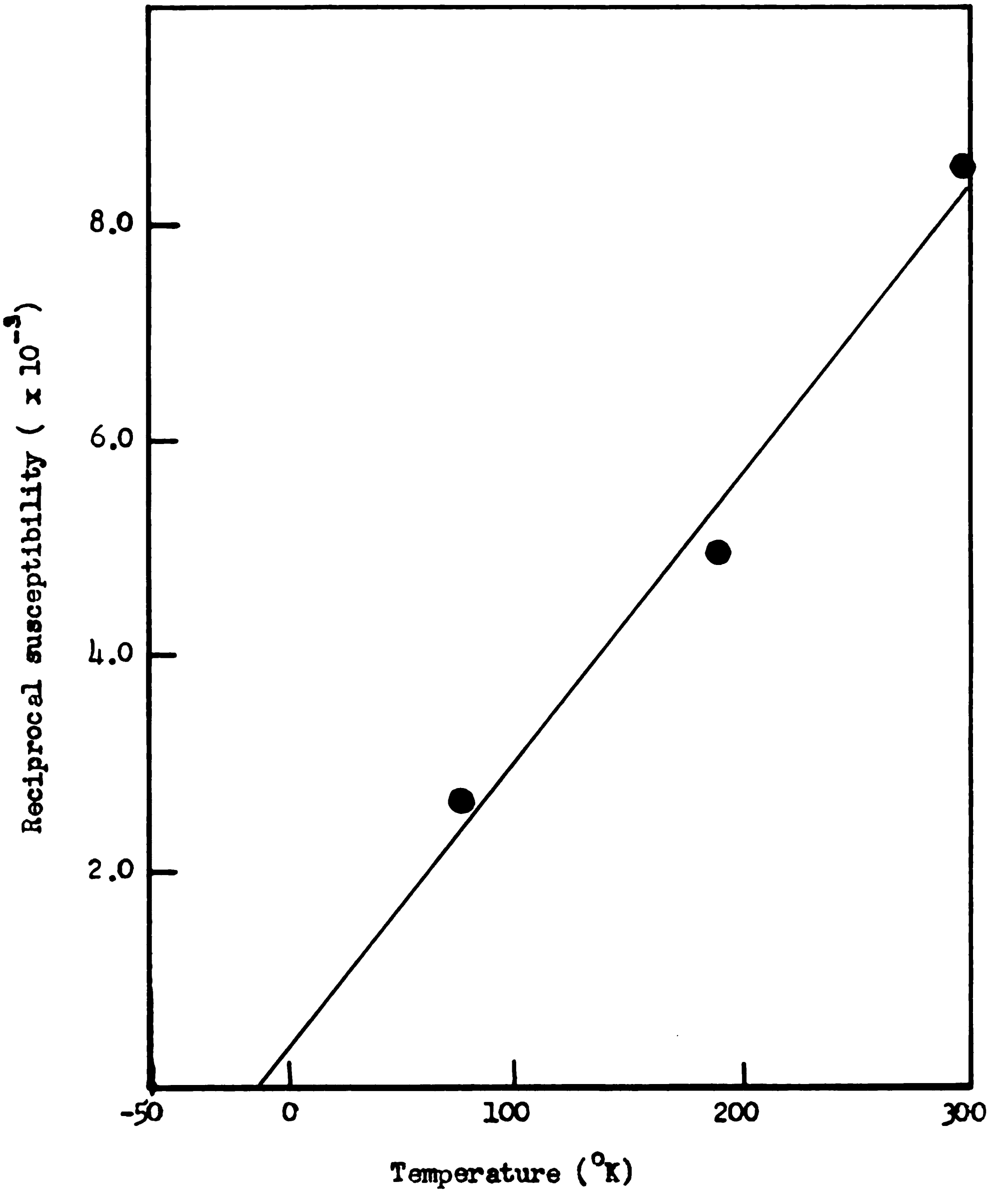


Figure 18. Reciprocal susceptibility as a function of temperature for iron (III) sulfate, sample B, adsorbed on charcoal.

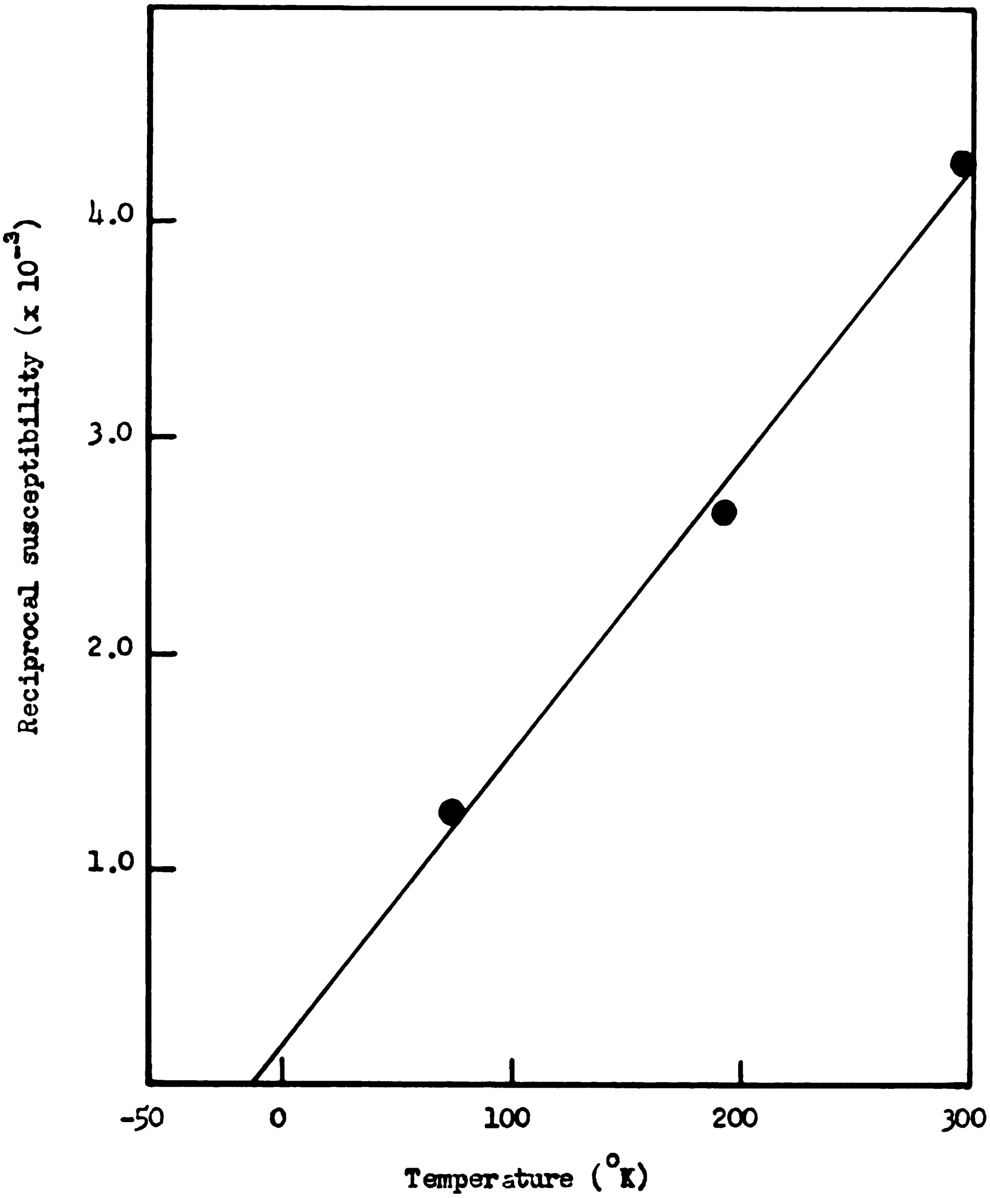


Figure 19. Reciprocal susceptibility as a function of temperature for iron (III) chloride adsorbed on charcoal.

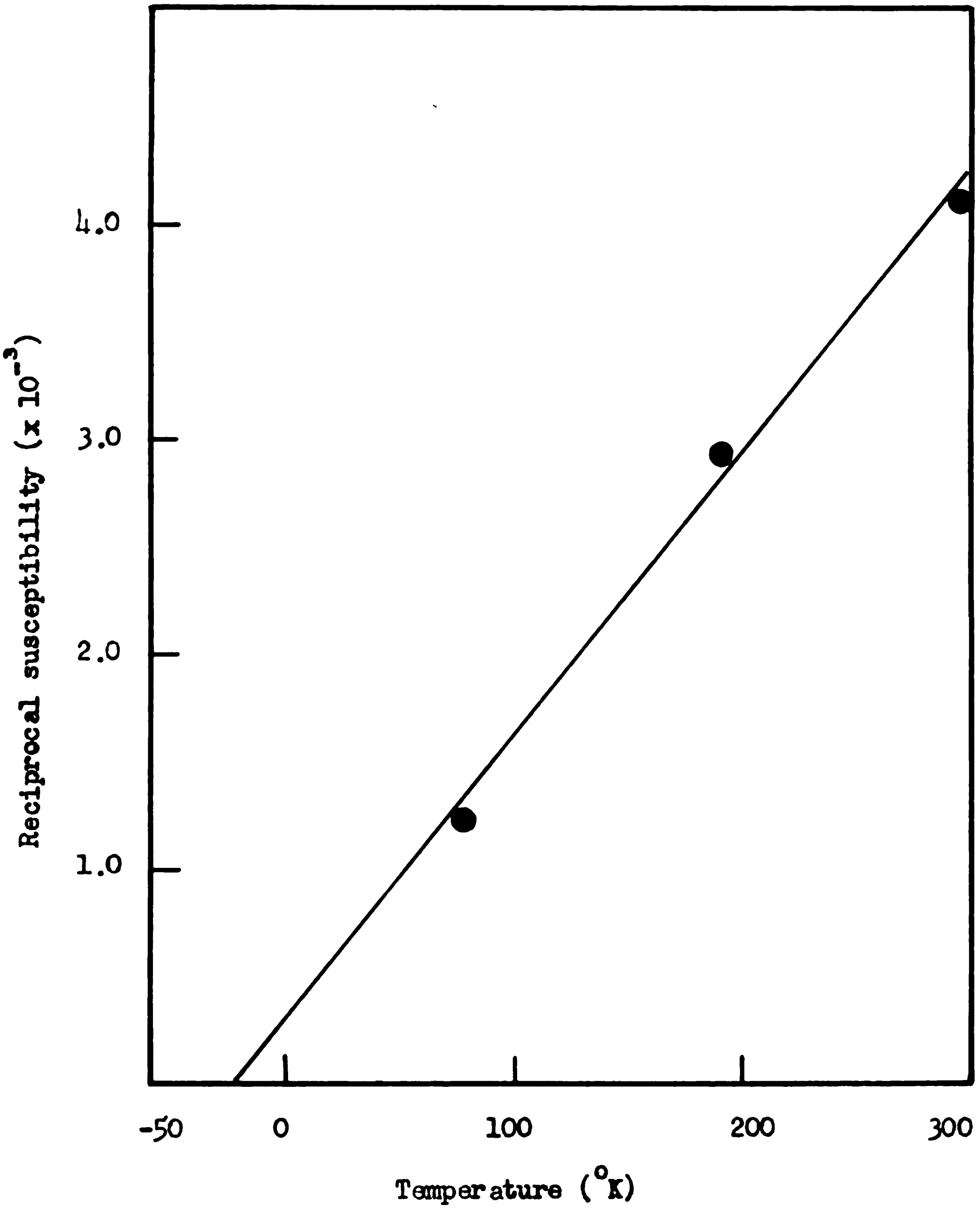


Figure 20. Reciprocal susceptibility as a function of temperature for iron (II) chloride, sample D, adsorbed on charcoal.

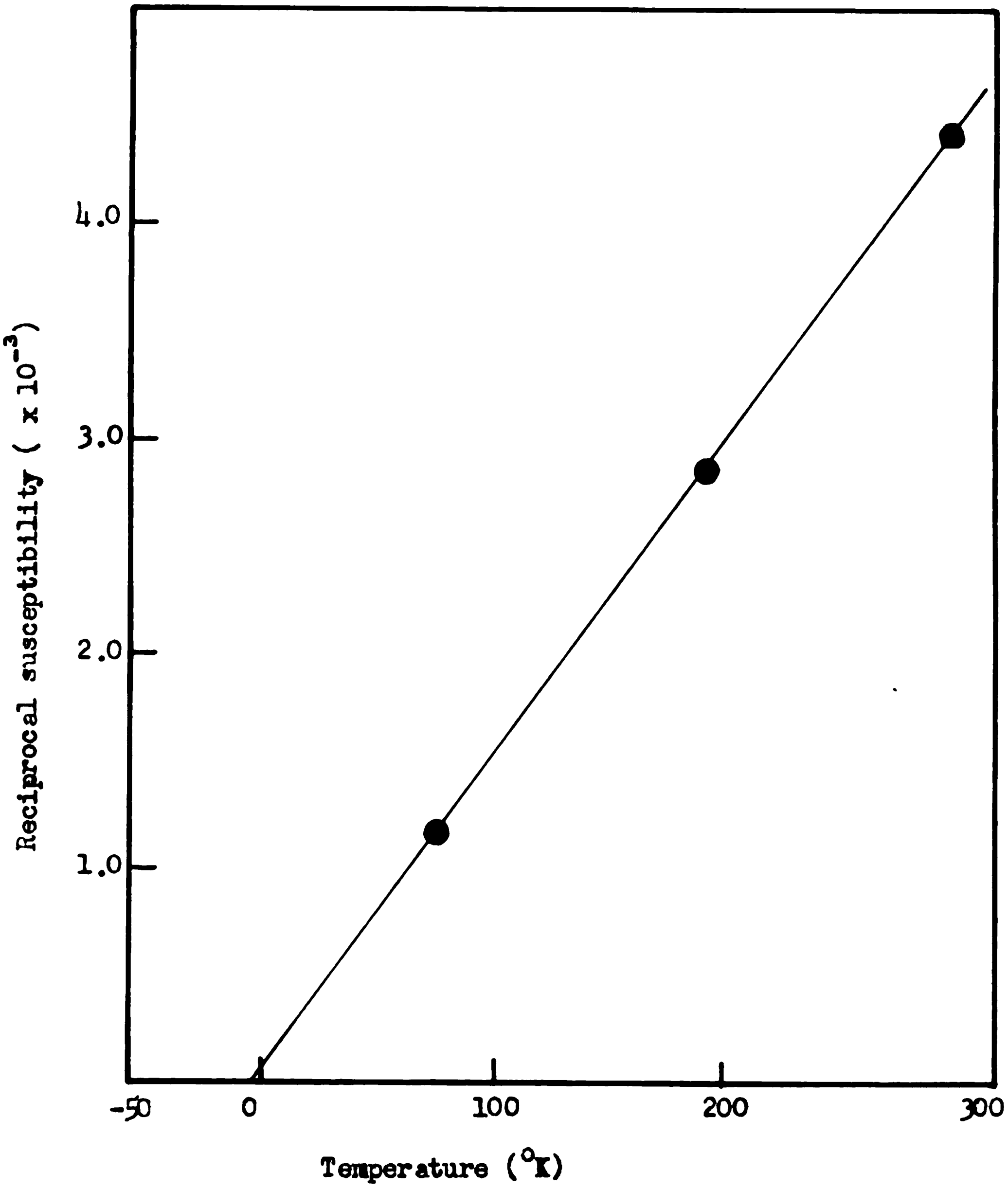


Figure 21. Reciprocal susceptibility as a function of temperature for iron (II) chloride, sample E, adsorbed on charcoal.

and that the charcoal even became more diamagnetic when salts were adsorbed. However, the charcoals used by these workers contained large amounts of paramagnetic impurities, even to the extent that the charcoals themselves possessed resultant paramagnetism, so that the validity of their results may be called into question. It may be noted that under the conditions of the present investigation there was no appearance of the so-called "super-paramagnetism" reported by Kobozev _et al._[68]

The reason for the very erratic results obtained for the iron (II) and iron (III) salts is not known. This is particularly striking in the case of the iron (II) salts for which the magnetic moments are on the average even higher than those obtained for the iron (III) salts; this is difficult to understand since iron (II) has four unpaired electrons and iron (III) has five. Thus even complete oxidation of divalent iron to the trivalent state would not entirely account for the high values obtained for iron(II). It is believed, however, that the iron remained essentially in the divalent state since precautions were taken to minimize its oxidation, and since the iron recovered by desorption from the charcoal surface was mostly divalent (see above).

The results of this investigation show that it is highly improbable that the adsorbed cations are bound to the charcoal surface by means of covalent bonds to surface carbon atoms since metal to carbon bonds of this type should reduce the magnetic susceptibility of the metal atom very markedly.[69] Furthermore the adsorption forces are much stronger than van der Waals' forces which are operative in physical adsorption as seen by the fact that the cations could not be removed from the charcoal surface even by leaching with acid. The only reasonable alternative is that these metal ions are bound to chemisorbed oxygen on the surface of the charcoal. Such bonds would have sufficient ionic character to leave the electron spins of the cation unpaired. This explanation is consistent with the ion exchange mechanism proposed by Steenberg[18] to account for the adsorption of cations on charcoals activated at low temperatures. The charcoal surface may consist of acidic carbon oxides which in the presence of water would form acidic hydroxyl groups. The cations could react with these groups liberating hydrogen ions into solution and forming essentially ionic bonds to oxygen atoms in the surface.

A MAGNETOCHEMICAL STUDY OF THE SURFACE OXIDATION OF COPPER

Introduction

The corrosion of copper has been studied very extensively and under a great variety of conditions. This is undoubtedly due to the extreme usefulness and versatility of copper, both as the pure metal and as an alloying constituent. In addition the importance of cuprous oxide as a semi-conductor has stimulated work on the interaction of oxygen with cuprous oxide and the relation between the physical properties of this material and the copper-oxygen composition. The copper-copper oxides-oxygen system is interesting from the magnetochemical viewpoint because the magnetic properties of the various phases are very different from each other: copper and cuprous oxide are diamagnetic and the susceptibilities are essentially independent of temperature, cupric oxide is paramagnetic but the susceptibility gradually decreases with decreasing temperature, and oxygen is a normal paramagnetic substance which obeys Curie's law.

The purpose of this investigation was to examine magnetochemically the surface oxidation of copper by pure oxygen at low temperatures (25 to 100°C.). From independent measurements of the extent of oxidation and from magnetic susceptibility determinations at several temperatures it was considered possible that one might ascertain which oxidation products were formed and also their quantity. Such measurements might show whether or not there was any "surface paramagnetism" associated with copper or its oxides. Finally it might be possible to detect a change in the magnetic susceptibility of the copper upon the adsorption of hydrogen or oxygen, as Selwood and co-workers recent reported for highly-dispersed nickel.[70]

Historical Survey

Methods for Determining the Thickness of the Oxide Film

A number of different methods are available for determining the extent of oxidation and the composition of the oxide film. The most important of these are summarized below.[71]

Gravimetric. The increase of weight of the sample is determined, and the amount of oxide formed can be calculated if the composition of the oxide is known. This is best suited for thick films were inaccuracies in weighings are not so important as for thin films and small weight changes.

Electron diffraction. This method is useful for examination of films 100 A. to 300 A. thick, and the compositions of the films can be determined. Electron diffraction gives no indication of film thickness and no information is obtained about the interiors of thick films.

Electrolytic. The time required for cathodic reduction of an oxide film is a measure of the amount of oxide present.[72] In the case of copper it is possible to obtain the amount of each oxide, monovalent or divalent, which is present.

Pressure decrease. From the decrease in the pressure of the oxidizing gas in a closed system the quantity of material abstracted by the metal can be calculated. This was the method used in the present investigation to obtain the total amount of oxygen adsorbed.

Composition of the Oxide

One of the basic problems in any study of oxide formation is that of determining the composition of the oxide, and for a metal such as copper where two oxides are stable under most conditions this problem is doubly important. Innumerable studies of oxide composition have been made on the copper-oxygen system over a wide range of temperatures.

Allen and Mitchell[72] stated that as far as they were aware oxygen is not dissociated on copper below 240°K. There is no oxide layer formed on copper below 240°K., and this is the critical temperature above which oxidation occurs. Up to about 200°C. and above 900°C. the oxide formed is largely cuprous oxide. At intermediate temperatures a mixture of cuprous and cupric oxides is nearly always found.

Cruzan and Miley[73] found that the essential criterion for determining whether or not cupric oxide would be present as an oxide component was the thickness of the oxide film. Cuprous oxide film thicknesses of less than 400 A. contained no cupric oxide, some of the films in the range 400 A. to 800 A. contained some cupric oxide, but all above 800 A. contained cupric oxide. Factors of secondary importance in that they control film thickness are the temperature of oxidation, the time of exposure, and the concentration of oxygen in the gas. The above authors heated copper strips in air at 240°C. They reasoned that as the film thickens diffusion through it becomes more and more difficult, and at some point cuprous oxide is expected to begin competing with the copper metal for the attacking oxygen. In the range 150°C. to 350°C. the temperature at which the films are formed has little influence on the formation of cupric oxide in the cuprous oxide films. The work of Murison[74] supports these conclusions.

Evans has stated[75] that under reversible conditions the cupric oxide phase should be present from the first and that its failure to arrive is an example of departure from thermodynamic equilibrium.

When the oxidation products of copper below about 200°C. are studied by electron diffraction it is usually reported that the presence of cupric oxide is not detected. The sensitivity of detection of cupric oxide is estimated to be one or two percent. Preston and Bircumshaw[76] reported that photographs of rings at room temperature showed only rings due to cuprous oxide, but that at 100°C. and 183°C. extra lines were occasionally observed which might have indicated the presence of cupric oxide. White and Germer[77] showed that at room temperature copper exposed to dry oxygen at a pressure of 20 mm. did not show any lines of cupric oxide.

Bound and Richards[78] studied by electron diffraction the oxidation of thin films of copper in air, and found that at 100°C. the films were completely oxidized to cuprous oxide in just under an hour. After heating the samples up to 200°C. there was no change in the transmission patterns, but at 250°C. a mixture of cuprous oxide and cupric oxide was found. Further heating at 300°C. converted the pattern completely to that of cupric oxide.

The composition of the oxide reported by Dankov and Ignatov formed by heating massive copper in air was essentially different from that reported by Bound and Richards, however. The Russian investigators[79] used three mm. electrolytic copper plate, and at 200°C. found diffraction lines of both cupric oxide and cuprous oxide. Heating for 25 minutes under these conditions produced the maximum amount of cupric oxide, and for both shorter and longer heating times many of the cupric oxide lines dropped out altogether. After heating for 150 minutes not a single line of cupric oxide was left. Evidently the outer layer of cupric oxide in the film reached a maximum when heated for 25 minutes. The authors considered that these data were evidence for a mechanism of oxide growth in which the diffusion of copper ions from metal to adsorbed oxygen layer was the slow step.

Anderson[80] has emphasized the fact that cuprous oxide is a phase of potentially variable composition, and that the composition of a surface oxide on a copper film may or may not be $Cu_2O_{1.000}$. This point will be considered further when the mechanism of oxidation is discussed.

Mechanism of Oxidation

The mechanism by which the oxidation of copper proceeds, as interpreted from oxidation rate studies, was found to be determined largely by the temperature of oxidation and the thickness of the oxide layer. At temperatures not exceeding a few hundred degrees Centigrade the oxidation follows a logarithmic rate law[81] and the slow step in the oxidation is the diffusion of ions across the electrostatic space charge set up within the thin film.[82] At temperatures above 700°C. copper oxidises according to a parabolic rate law[83] of the form

$$x^2 = 2At$$

where X = film thickness

A = constant

t = time.

The rate-determining step in this type of oxidation is the diffusion of copper from the metal to the oxide-oxygen interface.[84] At intermediate temperatures the oxidation defies generalisation and it is possible to find theoretical and experimental verification for various laws.[82]

Dell, Stone, and Tiley[83] have made calorimetric studies of the adsorption of oxygen by copper at 20°C. They found that for the first uptake of oxygen by granulated copper the heat of adsorption was very high, about 110 kcal. per mole. The heat of adsorption rapidly fell to about 82 kcal. per mole which is the heat of oxidation of copper to cuprous oxide. Later it leveled off to 55 kcal. per mole, which is the heat of adsorption of oxygen on cuprous oxide.[85] In between these two clear-cut steps the heat of adsorption gradually decreased from 82 to 55 kcal. per mole indicating that in this intermediate region both processes were taking place. Thus oxidation of the metal was soon arrested and that process was replaced by adsorption in the oxide layer.

There is considerable evidence that pure water vapor and pure steam have little effect on the oxidation of copper up to 800°C. at atmospheric pressure.[71] Campbell and Thomas[86] used an oxygen pressure of 150 mm. and a water vapor pressure of 15 mm. at 100°C. and found that presence of the water vapor retarded the rate of reaction slightly. In similar studies by Preston and Bircumshaw[76] treatment of copper with steam for one hour at 100°C. gave cuprous oxide and a second phase which was thought to be cupric oxide. The action of water vapor in these systems is difficult to explain.

Activation of Metallic Copper

The activation of copper by repeated oxidation followed with reduction by hydrogen has been ascribed to an increase in the surface area.[87] Reduction is evidently not simply a reversal of the process of oxidation. As the oxide is reduced by hydrogen, a layer of metallic copper is first formed around the oxide. Hydrogen then diffuses through the metal to the oxide, and water is produced at such high pressures that its escape causes cracks and blistering of the surface.[88] Repetition of this oxidation-reduction cycle gives highly active surfaces. Reduction with carbon monoxide does not produce this effect, but gives a smooth surface of very low activity.

Adsorption of Oxygen on Copper Oxides

Oxygen is adsorbed on cuprous oxide at a measurable rate at room temperature, and the process possesses an activation energy. Garner, Stone, and Tiley[88] found the heat of adsorption at room temperature to be about 55 kcal. per mole, which was independent of the thickness of the oxide layer. Disappearance of oxygen continued even after 100 hours.

Garner, Gray, and Stone reported that at 200°C. the oxidation of cuprous oxide to cupric oxide was appreciable, but not very fast.[89] Although at room temperature the adsorption of oxygen on cuprous oxide is fairly rapid, the rate of desorption under vacuum is very slow. At room temperature the adsorbed oxygen neither evaporates nor does it contribute materially to the oxidation of cuprous oxide, but the adsorbed oxygen is stable on the surface for at least 24 hours. When the authors allowed the adsorbate to react with carbon monoxide and collected the resulting carbon dioxide, they found that only half of the oxygen which was adsorbed could be removed. Thus about half of the oxygen is "mobile" and the other half unreactive.

Measurements of the semi-conductivity of cuprous oxide shed some light on the interaction of oxygen with this oxide. LeBlanc and Sachse[90] found at 20°C. a specific conductance of 10^{-9} mho per cm., which changed to 10^{-6} mho per cm. when 0.1% oxygen was present. These observations have since been confirmed by many investigators. The semiconductivity of cuprous oxide is a minimum for the pure, oxygen-free material, but the conductivity increases rapidly with the addition of oxygen to a definite limit. Zhuse and Kurtschatow[91] found that the conductivity of cuprous oxide with but 0.6% cupric oxide was very little different from that of pure cupric oxide.

From the temperature coefficient of conductivity in the range 25 to 250°C. the activation energy for the conductivity process has been determined.[89] For a cuprous oxide surface free from adsorbed oxygen the activation energy is 5.8 kcal per mole; on the adsorption of oxygen this value falls to 4.96 kcal per mole. Conductivity was found to be due to positive hole conduction. It is possible that in the presence of oxygen conductivity is a surface phenomenon, while for the pure oxide the conducting ions lie embedded in the material.

Garner, Stone, and Tiley[85] have reported that no appreciable amount of oxygen is adsorbed by cupric oxide.

Magnetochemistry of Copper-Oxygen Systems

Although the ground state of the copper atom is a doublet S state[92] metallic copper is not paramagnetic but diamagnetic. Stoner[66] has pointed out that for the metals copper, silver, and gold, all of which are diamagnetic, the numerical value of the atomic susceptibility is less for the metal than for the ions. This clearly shows that there is a paramagnetic contribution from the electrons.

Selwood and Dallas[27] have reported an interesting attempt to prepare metallic copper in the paramagnetic state. Low concentrations of cupric oxide on an inert support had shown characteristics of high dispersion over the catalyst support. It was thought that by reducing the cupric oxide to metallic copper the metal atoms would be far enough apart that they would exhibit paramagnetism. The metallic copper proved to be diamagnetic, however. The conclusion was that the tendency for cohesion is so strong that even when the surface of the support is largely unoccupied by copper atoms they must still aggregate together quite strongly.

The gram susceptibility of pure copper metal has been determined by a large number of investigators, and the agreement among various authors is quite satisfactory. The mean value given in the International Critical Tables[93] for 18°C. is -0.086×10^{-6}. Most values given in the literature range from -0.080 to -0.090×10^{-6} at room temperature. The susceptibility of pure copper changes little, if any, with temperature; changes in diamagnetism of five or ten percent are sometimes reported between room temperature and 75°K.[94]

Montgomery[95] has found that copper crystals at room temperature show no magnetic anisotropy. The mean value of the susceptibility found was -0.085×10^{-6}.

The susceptibility of copper was found to be independent of particle size in a study by Bhatnagar and co-workers.[96] Copper pulverized to 0.2 microns had the susceptibility -0.081×10^{-6}. Earlier Rao[97] reported that as particle size decreased the susceptibility increased, but these results may have been due to lack of proper precautions for excluding oxygen.

Some interesting studies have revealed that the magnetic susceptibility of bulk metallic copper is a function of the stress to which the sample has been subjected. Hutchinson and Reekie[94] found that at

room temperature the susceptibility of annealed copper was -0.086×10^{-6} but after cold-working it became -0.074×10^{-6}. The samples had different temperature coefficients as well, but at high enough temperatures (about 700 °K.) the susceptibilities became about equal. Similar results have been reported by others.[98,99]

Of the reported values for the magnetic susceptibility of cuprous oxide at room temperature, that of Bhatnagar and Mitra,[100] -0.188×10^{-6}, is probably the most reliable. Samples prepared by reduction of Fehling's solution and by electrolysis give the same results. Other satisfactory values reported are -0.18×10^{-6} by Klemm and Schuth,[101] and -0.185×10^{-6} by Khanna.[102] Due to the difficulty of removing traces of paramagnetic cupric compounds from the samples, many investigators have reported that cuprous oxide is paramagnetic.[93] No determinations of the susceptibility of cuprous oxide below room temperature have come to the attention of the present writer.

Several different values for the magnetic susceptibility of cupric oxide at room temperature have been reported, and they are only in general agreement. Chéneveau[103] found $+3.6 \times 10^{-6}$, Birch[104] reported $+3.04 \times 10^{-6}$ at 10°C., and Ishiwara[105] found $+3.20 \times 10^{-6}$ at 20.3°C. Ishiwara seems to have made the only measurements on the pure compound at low temperatures, and his results are given in Table XXXIV. The temperature dependence of susceptibility for cupric oxide is very unusual.

Selwood and co-workers have studied the susceptibility of cupric oxide supported on magnesia, rutile, and alumina.[27,106] From magnetic

TABLE XXXIV

GRAM SUSCEPTIBILITY OF CUPRIC OXIDE AS A FUNCTION OF TEMPERATURE

Temperature °C.	Gram Susceptibility X x 10^6
-20.3	+3.20
- 2.7	3.14
-30.5	3.07
-45.9	2.95
-65.0	2.77
-84.0	2.63
-98.2	2.55
-113.1	2.42
-128.4	2.34
-149.7	2.28
-167.9	2.17

measurements made between room temperature and 90°K. they concluded that the cupric oxide obeys the Curie-Weiss law, and has a magnetic moment corresponding to one unpaired electron.

Hommel[107] studied the magnetic properties of copper oxidised to cuprous oxide at 950°C. to 1000°C. When the oxide was exposed to air at high temperatures it was diamagnetic at room temperature, but became paramagnetic at very low temperatures. When the oxide had been vacuum-tempered at high temperatures it was found to be paramagnetic at room temperature but diamagnetic at low temperatures. Hommel was not able to find any correlation between the magnetic susceptibility and semiconductivity of cuprous oxide with varying oxygen content.

Experimental Procedures

The vacuum system constructed for this investigation is depicted in Figure 22. The distinguishing feature of this vacuum system was that from the two-stage diffusion pumps to the manifold, tubing of 20 mm. diameter or greater was used; this construction permits of high pumping speeds. The single exception to this was the right-angle stopcock isolating the manifold from the pumping system; the bore of this stopcock was 15 mm. The McLeod gauge used was capable of measuring pressures as low as 1×10^{-8} mm. The pumping system consisted of a two-stage mercury diffusion pump* backed by a mechanical pump.** The manifold of the vacuum system was made from 22 mm. Pyrex tubing, and storage flasks were constructed from round-bottom flasks, two of them having volumes of two liters and the other having a volume of one liter. The manometer used for measuring pressure changes was made from seven mm. Pyrex tubing and was equipped with a one meter scale. The susceptibility tube could be attached to the vacuum system through a standard taper ground joint, and between that joint and the manifold was sealed a coarse sintered glass filter so that the contents of the susceptibility tube would not escape into the manifold when the tube was being evacuated.

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*H. S. Martin and Company, Evanston, Ill., Model M-40130-1.

**Kinney Manufacturing Company, Boston, Mass., Type CVD-3431.

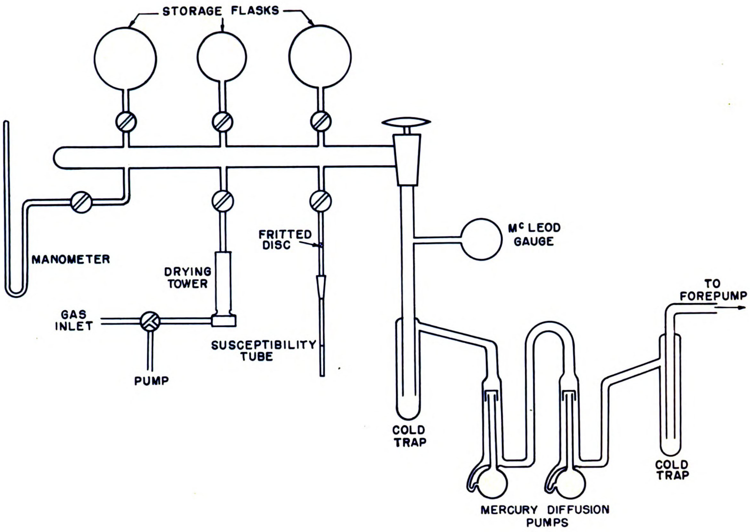

Figure 22. Vacuum System

The volume of the manifold was determined in the following manner. The volume of the one liter storage flask was determined before it was attached to the manifold by weighing the amount of water required to fill it. That weight of water was 1093 g. which at 23°C. occupied a volume of 1095 cc. This flask was then sealed to the manifold, the whole system was evacuated, and helium introduced to the manifold but not to the flask. The pressure of helium was read on the manometer and then the stopcock to the storage flask was opened and the pressure again read. From the ideal gas law the volume of the manifold enclosed entirely by stopcocks was found to be 164 cc. In a similar manner the volume of the susceptibility tube filled with sample plus the tubing connecting the susceptibility tube to its stopcock was found to be seven cc. The small correction for the change in volume of the vacuum system due to the rise and fall of the mercury column in the manometer was made where necessary.

Finely divided metallic copper was prepared by reduction of a copper sulfate solution with hydrazine, according to the method of Garner, *et al.*[85]

In 300 ml. of demineralized water was dissolved 45.9 g. of copper sulfate pentahydrate,* and to this was added 64% hydrazine hydrate** until the evolution of hydrogen ceased. A muddy-brown copper suspension was formed. The copper metal was separated from the liquid by

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*Mallinckrodt Chemical Works, Analytical Reagent grade.

**Mathieson Chemical Co., technical grade.

centrifugation and the product was washed with demineralized water six times. The copper was then washed once with absolute alcohol and filtered through a sintered glass filter. It was finally put into a weighing bottle and exposed to the drying action of anhydrous calcium chloride in a desiccator for one day. The weight of product obtained was about ten grams.

Complete elimination of all oxidation products on the surface of the copper was insured by the following treatment. The copper was put into the susceptibility tube and the tube and sample were attached to the vacuum system. The sample was heated by a heater consisting of Nichrome heating wire wound at half-inch intervals around a Pyrex tube 0.6 inches in diameter and seven inches long; the heating wire was covered with asbestos paper and then wound with heat-resistant tape. The copper sample was initially heated under vacuum to a temperature of 200°C. For 48 hours the pressure was maintained at 10^{-5} mm. and then for a period of about three weeks the sample was alternately exposed to hydrogen at atmospheric pressure and then evacuated to a very low pressure. At the end of this time the sample was no longer able to take up hydrogen and the reduction was complete. The reduced copper was then evacuated at a pressure of 10^{-5} mm. for 48 hours. The sample, which had been at 200°C. during all these operations, was then cooled to room temperature and helium was admitted as the supporting atmosphere.

Preliminary magnetic susceptibility measurements on this product indicated the presence of a ferromagnetic contaminant. The copper was then removed from the susceptibility tube and washed thoroughly with 10% hydrochloric acid, then several times with demineralized water, and finally was dried 15 minutes at 110°C. This copper was put into the susceptibility tube and the reduction treatment again given the sample until it was no longer able to take up hydrogen. It was then evacuated to 10^{-6} mm. and isolated from the manifold of the vacuum system by a stopcock. Oxygen which was taken from a cylinder and passed over anhydrous calcium sulfate was then introduced into the manifold until atmospheric pressure was reached. The oxygen pressure was read with the manometer and the stopcock to the susceptibility tube opened to allow contact between oxygen and the sample. After a suitable time of contact, usually 24 hours or longer, the oxygen pressure was again read from the manometer. The amount of oxygen adsorbed by the sample was calculated from the change in pressure after correction was made for the expansion of oxygen from 164 cc. to 171 cc. No attempt was made to control the temperature precisely since room temperature did not vary more than one or two degrees Centigrade during the course of an adsorption determination. When the oxygen had been in contact with the sample for a suitable length of time the sample was evacuated to 10^{-4} or 10^{-6} mm. and helium was introduced as the supporting atmosphere preliminary to the susceptibility measurements.

Cuprous oxide was prepared by the following method.[100] Twenty grams of copper sulfate pentahydrate,* and 40 g. of C. P. grade sodium

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*Mallinckrodt Chemical Works, Analytical Reagent grade.

potassium tartrate,* were dissolved in 400 ml. of demineralized water. Then C. P. sodium hydroxide solution was added until the pH of the copper solution was approximately nine. To the clear solution was added 25 g. of dextrose and the solution was heated to boiling. It was kept near the boiling point for 30 minutes during which time it was stirred continuously. A finely-grained, bright red precipitate of cuprous oxide settled out. The supernatant liquid was decanted from the precipitate and the cuprous oxide was washed several times with demineralized water. It was then transferred to a weighing bottle and dried in a vacuum desiccator overnight.

The magnetic susceptibility of the cuprous oxide sample so prepared was -0.162×10^{-6} measured at room temperature, compared with the literature value[100] of -0.188×10^{-6}. Cuprous oxide has the ability to adsorb paramagnetic oxygen tenaciously, and probably that was why this sample was less diamagnetic than would be expected for the pure material. The work of Garner, et al.[89] showed that this adsorbed oxygen is stable to evacuation at room temperature but that it can be removed by baking in a vacuum at 160°C. This procedure was tried on several cuprous oxide samples, but in every case the sample changed in color from bright red to black or dark blue indicating that some cuprous oxide had been oxidized to the black cupric oxide.

An alternative method for removing the adsorbed oxygen from cuprous oxide[108] was to treat the sample with carbon monoxide; the reaction,

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*J. T. Baker Chemical Co., C. P. grade.

which involves oxidation of carbon monoxide to carbon dioxide, was said to be completed in about 30 minutes at room temperature. Treatment of a cuprous oxide sample with carbon monoxide at room temperature did not cause an appreciable change in the magnetic susceptibility of the sample, however, so treatment at 100°C. was tried. The sample was evacuated to 10^{-6} mm. at room temperature, carbon monoxide from a cylinder[*] was introduced until a pressure of 200 mm. was reached, and then the temperature was raised to 100°C. The reaction was allowed to proceed for three hours, then the carbon dioxide was removed by evacuation and the sample was cooled to room temperature. The magnetic susceptibility of this sample is recorded in the following section. A copper analysis of this sample was performed by the standard iodometric procedure;[51] the average of three determinations showed that the cuprous oxide sample contained 85.16 ± 0.06% copper. The theoretical copper assay for cuprous oxide is 88.82%. The low value found for the copper analysis is most likely due to the presence of hydrated water.

Cupric oxide was prepared by boiling a solution of cupric sulfate which had been made alkaline. In 500 ml. of demineralized water was dissolved 25 g. of copper sulfate pentahydrate. To this was added two grams of sodium fluoride to prevent the precipitation or occlusion of any traces of ferromagnetic iron present. Cupric hydroxide was precipitated by adding sodium hydroxide solution until the copper solution was distinctly alkaline. The solution was then boiled and stirred

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[*] Matheson Co., Inc., Joliet, Ill.

continuously for 30 minutes until the precipitate turned black and began to coagulate. The cupric oxide was filtered by centrifugation and it was washed five times with demineralized water. It was then collected on a watch glass, dried for 2.5 hours at 135°C., and ground in an agate mortar.

Preliminary determinations of the magnetic susceptibility of this sample showed it to have a susceptibility of $+3.75 \times 10^{-6}$, compared with the value of $+3.20 \times 10^{-6}$ given by Ishiwara.[108] Richards[109] found that during its preparation cupric oxide was able to adsorb large quantities of gases, particularly nitrogen and oxygen, but that a satisfactory way to remove these gases was to heat the sample to 300°C. for one hour. Therefore this sample of cupric oxide was placed in a covered silica crucible and heated to 300°C. for one hour in a muffle furnace.*

The sample was then returned to the susceptibility tube and heated at 100°C. for 2.5 hours at a pressure of approximately 1×10^{-5} mm. After the magnetic susceptibility of this sample was determined approximately 0.4 g. samples were weighed and dissolved in dilute sulfuric acid. These were analyzed iodometrically in the same manner as were the samples of cuprous oxide and the average of three analyses gave $78.53 \pm 0.09\%$ copper. The theoretical copper assay for cupric oxide is 79.89% and the low value obtained was most likely due to water of hydration or incompletely decomposed cupric hydroxide.

The procedures for making magnetic susceptibility measurements were the same as those described in Part I of this paper.

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*Blue M Electric Co., Chicago, Ill., Model M 10-A.

Results and Discussion

The magnetic susceptibilities of metallic copper samples which had been repeatedly oxidized and reduced were always essentially the same regardless of how often this cycle was repeated. The magnetic susceptibilities of several samples of granulated metallic copper as functions of maximum field strength and determined at three different temperatures are given in Table XXXV. The values at the highest field strength are the most reliable because the changes in weight were greatest and because the effect of ferromagnetic impurities on the susceptibilities was the least.

TABLE XXXV

GRAM SUSCEPTIBILITY OF COPPER AS A FUNCTION OF FIELD STRENGTH AND TEMPERATURE

Temperature °K.	Field Strength		
	7,360 Oersteds	9,060 Oersteds	10,470 Oersteds
		$X \times 10^6$	
298	-0.096	-0.087	-0.085
	.083	.082	.080
	.084	.081	.080
	.085	.084	.082
	.070	.075	.075
	.070	.075	.077
	.084	.087	.087
		Average	-0.081 ± 0.003
192	-0.077	-0.079	-0.081
75	-0.076	-0.075	-0.077
	.066	.074	.073
	.079	.082	.082
		Average	-0.077 ± 0.003

The magnetic susceptibility values obtained for cuprous oxide are shown in Table XXXVI. It is possible that some or all of the temperature dependence of susceptibility for cuprous oxide may be due to adsorbed oxygen.

TABLE XXXVI

MAGNETIC SUSCEPTIBILITY OF CUPROUS OXIDE AS A FUNCTION OF FIELD STRENGTH AND TEMPERATURE

Field Strength Oersteds	Temperature 297°K.	192°K.	75°K.
	Susceptibility $\chi \times 10^6$		
7,360	-0.191	-0.184	-0.166
9,060	-0.195	-0.187	-0.169
10,470	-0.196	-0.188	-0.168

The magnetic susceptibility of cupric oxide is shown in Table XXXVII. The values obtained at room temperature are in accord with those of Ishiwara[108] (see Table XXXIV) but at low temperatures Ishiwara's values are somewhat lower.

The magnetic susceptibilities of several samples of copper which had been oxidized to various extents were determined at two or three temperatures. The resulting mixtures contained in general metallic copper, cuprous oxide, cupric oxide, and oxygen. The gram susceptibilities of the mixtures could therefore be expressed by the sum of the susceptibilities of each constituent multiplied by the weight fraction of that constituent present, that is,

TABLE XXXVII

MAGNETIC SUSCEPTIBILITY OF CUPRIC OXIDE AS A FUNCTION OF FIELD STRENGTH AND TEMPERATURE

Field Strength Oersteds	Temperature 300°K.	195°K.	76°K.
	Susceptibility $X \times 10^6$		
4,780	+3.21	+2.85	+2.24
7,360	+3.24	+2.81	+2.32
9,060	+3.25	+2.81	+2.30
10,470	+3.22	+2.82	+2.29
Average	+3.23	+2.82	+2.29

$$X_{mixture} = P_{Cu} X_{Cu} + P_{Cu_2O} X_{Cu_2O} + P_{CuO} X_{CuO} + P_{O_2} X_{O_2} \qquad (13)$$

where P = weight fraction. If the susceptibility of each component is known then there are apparently four unknown factors in equation (13), namely, the weight fraction of each component. Actually there are only three unknown factors since the sum of the weight fractions must equal unity. Since one of the unknown weight fractions can be calculated from equation (13) if all the others are known and the susceptibility of the mixture is known, two additional measurements must be made on the system to solve the equation completely. These measurements were of the total amount of oxygen adsorbed and of the magnetic susceptibility of the mixtures at 75°K.

The weight fractions of each component in the oxidized copper system were calculated by a method of successive approximations. From the susceptibility values of the mixture at two temperatures the amounts of oxygen and cupric oxide present were calculated, assuming that the weight fraction of copper was unity and that the contribution of cuprous oxide to the susceptibility of the mixture was negligible. Then by subtracting from the total amount of oxygen present the amount calculated to be present as adsorbed oxygen and as cupric oxide the amount of cuprous oxide was calculated; the sum of the weight fractions of these components was subtracted from unity to give the weight fraction of copper. Then taking into account the contribution of copper and cuprous oxide to the susceptibility of the mixture the amounts of adsorbed oxygen and cupric oxide were re-calculated. Then the amounts of copper and cuprous oxide were again calculated, and if different from those obtained earlier the cycle of calculations was again repeated. The magnetic susceptibility of oxygen as a function of temperature is given by Selwood.[47] The results of these measurements are presented in Table XXVIII. The last column of Table XXVIII is the susceptibility of the mixture calculated from the weight fractions and susceptibilities of the components (equation (13)).

Samples 1 through 5 of Table XXVIII represent the oxidation of a fresh copper surface. For all the other samples the starting material was copper which had already reacted with a known amount of oxygen; these samples were first evacuated and then equilibrated with oxygen to allow the adsorption of additional amounts of oxygen. The oxidation of all these samples except numbers 10 and 11 was carried out at room temperature, but the two samples were oxidized at 100°C. Copper was first

TABLE XXXVIII

MAGNETIC SUSCEPTIBILITIES OF PARTIALLY OXIDIZED COPPER SYSTEMS

Sample	Temperature °K.	$X_{Mixture}$ x 10^6	Total Oxygen %	Weight Fraction				ΣPX x 10^6
				Copper	Oxygen x 10^6	Cupric Oxide	Cuprous Oxide	
1	298	-0.067	0.072	1.00	1.28	0.0043	0.00	-0.067
	196	-0.067						-0.067
	75	-0.062						-0.062
2	298	-0.071	0.080	1.00	3.0	0.0025	0.0027	-0.071
	196	-0.070						-0.069
	75	-0.059						-0.059
3	298	-0.059	0.128	1.00	8.8	0.0025	0.006	-0.059
	196	-0.046						-0.055
	75	-0.032						-0.032
4	298	-0.059	0.081	1.00	9.4	0.0030	0.0011	-0.059
	75	-0.029						-0.029
5	298	-0.072	0.20	0.99	3.1	0.0029	0.013	-0.072
	196	-0.073						-0.070
	75	-0.060						-0.059
6	298	-0.071	0.43	0.98	2.1	0.0040	0.031	-0.071
	75	-0.062						-0.062
7	298	-0.066	0.64	0.95	3.0	0.0056	0.048	-0.066
	75	-0.056						-0.056
8	298	-0.068	0.85	0.93	4.5	0.0049	0.067	-0.068
	75	-0.053						-0.053
9	298	-0.069	0.965	0.92	4.2	0.0052	0.078	-0.069
	75	-0.055						-0.055
10	298	-0.024	1.60	0.87	14.5	0.0180	0.112	-0.025
	75	+0.011						+0.011
11	298	-0.009	2.20	0.81	17.4	0.0231	0.155	-0.009
	75	+0.032						+0.032

reduced with hydrogen at 100°C.; sample 10 represents the oxidation of the clean copper surface, and sample 11 represents an addition of the oxide layer started by sample 10.

For each of the partially oxidized copper samples there proved to be a unique solution to equation (13), indicating that all the factors contributing to the magnetic susceptibility have been accounted for. In those cases where susceptibility measurements were made at 196°K, it was possible to calculate what the susceptibility of the mixture should be, and agreement was within the experimental error. Since the magnetic susceptibilities of the mixtures can be accounted for in a satisfactory manner from the susceptibilities of the known constituents of the mixture, there is no apparent surface magnetism nor change in the susceptibility of the copper upon the adsorption of oxygen.

The treatment of the magnetic susceptibility data presented here appears to be a satisfactory way to analyze the products resulting from the oxidation of copper without recourse to chemical methods. Particularly interesting is the sensitivity of this method to small amounts of adsorbed oxygen. This would seem to be of interest in the study of cuprous oxide semi-conductors where small amounts of oxygen are very important. The accuracy of the determination of the components of the mixture is estimated to be about 10%, so that this method is most useful in low concentration ranges. The limit to the accuracy is in the magnetic susceptibility determinations which are accurate to about three percent. The sources of error are chiefly the lack of uniform packing of the samples in the susceptibility tube and the inability to get completely uniform and reproducible samples.

The composition of the oxidized film on the surface of copper, as shown in Table XXXVIII, is interesting. It seems that certain amounts of oxygen and of cupric oxide were built up on the surface rather readily at room temperature, but as the oxidation proceeded the growth of the oxide layer was due mostly to cuprous oxide while the amounts of adsorbed oxygen and cupric oxide did not increase very much. In fact the amount of cupric oxide present hardly changed at all. However, comparison of samples 9 and 11, which were oxidized at room temperature and at 100°C., respectively, shows that while oxidation at 100°C. approximately doubled the amount of cuprous oxide present, the amount of cupric oxide and of adsorbed oxygen increased approximately four-fold. Thus oxidation at the higher temperature appears to have favored the fixation of oxygen as cupric oxide and as adsorbed oxygen.

Summary

A study has been made of the nature of the surface of activated charcoal, of the manner in which electrolytes are adsorbed by charcoal, and of the reaction at room temperature between oxygen and metallic copper.

The structure of the surface of activated charcoal is still largely unknown, even though charcoal has a great many well-known uses as an adsorbent. A review of the literature showed that the capacity of a charcoal to adsorb electrolytes from aqueous solution can be varied by suitable changes in the temperature of activation of the charcoal. Charcoal activated in air at 800°C. has the greatest affinity for acids and anions, while charcoal activated at 400°C. has the maximum ability to adsorb bases and cations. The latter type of charcoal has been of chief interest in the present investigation.

Ash-free charcoals were prepared from pure sugar and activated under controlled conditions. Analyses for the elements present were performed and the adsorption of iodine by the charcoals was measured under standard conditions. The charcoals were further characterized by their abilities to adsorb acids and bases. The magnetic susceptibilities of a number of charcoals activated under different conditions were determined both at room temperature and also at 192°K. and 75°K. It was found possible by the magnetic measurements to determine the amount of oxygen adsorbed physically on the charcoal surface, since molecular oxygen is

paramagnetic. The dependence of the magnetic susceptibility of charcoal on temperature was attributed to this physically adsorbed oxygen, while the magnitude of the susceptibility at room temperature was believed to be determined largely by the amount and kind of surface carbon oxides. Charcoal free from oxygen was prepared and it was found to be more diamagnetic than oxygen-containing charcoal and its susceptibility was independent of temperature.

Other methods of studying the nature of the surface carbon oxides of charcoal included direct chemical oxidation of the charcoal surface with sodium metaperiodate, which oxidation yielded carbon dioxide. The infrared absorption spectra of several charcoals prepared as mulls were obtained, but in the region from two to seven microns only one charcoal, which contained 25% oxygen, showed any absorption bands; those were in the regions of carbonyl and of ethylenic carbon-to-carbon absorption. Studies were made of the reaction at room temperature of charcoal with water enriched in the oxygen isotope O^{18}. The water reacted with the charcoals to form surface oxides which were removed from the charcoals at high temperatures as carbon dioxide and carbon monoxide.

In a study of the nature of the adsorbed phase when electrolytes are adsorbed on charcoal, the magnetic susceptibilities were determined of salts of iron, cobalt, and manganese adsorbed on charcoal. The magnetic susceptibilities of these salts were found to be the same in the adsorbed state as they are in the pure crystals. From magnetic measurements at low temperatures, these salts in the adsorbed state were found to obey the Curie-Weiss law for paramagnetic substances. It was concluded from these results that the salts were held on the charcoal surface by bonds between metal and oxygen atoms, not directly by bonds with carbon atoms. An adsorption process was postulated in terms of an ion exchange reaction in which hydrogen ions are removed from charcoal to the aqueous solution.

The surface oxidation of granulated metallic copper was studied at room temperature and at 100° C. by the method of magnetic susceptibilities. It was found that the reaction could be accounted for magnetically by the formation of cuprous oxide, cupric oxide, and by the presence of physically adsorbed oxygen. From independent determination of the total amount of oxygen adsorbed and from magnetic measurements at room temperature, 192° K., and 75° K. the amounts of each of the constituents present was calculated. The gram susceptibilities of cuprous oxide and cupric oxide were also determined at the three temperatures.

APPENDIX

Qualitative Analysis of Charcoal Ash

Two samples of commercial sugar charcoal (Eimer and Amend) were ignited to determine ash content. Weights of charcoal taken were 1.5637 and 1.4929 g., and the ash contents were 0.0678 and 0.0652 g. giving, respectively, 4.34 and 4.36% ash.

The ash was difficultly soluble in cold water and the solution had a basic reaction to litmus. It was almost completely soluble in both dilute nitric and dilute hydrochloric acids. No precipitate was formed with ammonium chloride solution, nor with hydrogen sulfide in either acidic or basic solution. This indicated the absence of all ions of Groups I, II, and III of the qualitative analysis scheme.

A precipitate was formed with ammonium carbonate in basic solution. Barium and strontium were found to be absent, and magnesium and calcium present, using the chromate-sulfate-oxalate procedure for Group IV cations. Flame tests were used which showed the presence of sodium and the absence of potassium. A precipitate of chloride was not formed with silver nitrate, but a voluminous precipitate of sulfate was formed when barium chloride solution was added.

Special tests for iron (II) and iron (III) were made with ammonium thiocyanate, potassium ferricyanide, and potassium ferrocyanide. There was no evidence of any trace of iron present, although the presence of a small amount of ferromagnetic impurity was indicated by magnetic measurements.

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