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THE FORMS OF SULFUR IN COKE.

A PHYSICO-CHEMICAL STUDY OF THE SULFUR HELD BY
CARBON AT HIGH TEMPERATURES¹

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Historical

The presence of sulfur in metallurgical coke gives rise to many problems and difficulties in the uses of coke for metallurgical purposes and for that reason is an important problem from an economic point of view. It follows, therefore, that any knowledge concerning the sulfur in coke is of great direct or potential value. A complete summary of the earlier work concerning the sulfur in coke is given by Simmersbach.³

Several years ago, S. W. Parr, professor of applied chemistry at the University of Illinois, and the writer of this paper confirmed the presence of what was supposedly organic sulfur in the coke, but reached no definite conclusion as to its exact nature.⁴

¹ Published by permission of the Director, United States Bureau of Mines. Presented before the Gas and Fuel Section at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., Sept. 4 to 9, 1922.

² Physical Organic Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

³ Simmersbach, "Koks-Chemie," Berlin, 1914, pp. 162-188.

⁴ Powell and Parr, "A Study of the Forms in which Sulfur Occurs in Coal," Univ. Illinois, Eng. Exp. Station, *Bull.*, 111, 42 (1919).

Later work by the writer⁵ has indicated the quantitative variation in this "organic sulfur" at various stages of carbonization up to a temperature of 1000°.

Wibaut has pointed out that organic sulfur exists in coke, and that it occurred in quantities greater than the organic sulfur of the coal from which it had been derived.^{6,7} Recently Wibaut attempted to identify this sulfur held by charcoal at high temperatures.⁸ He concludes from his results that sulfur is chemically combined with the carbon, and he calls this compound a "carbon sulfide." Wibaut explains the lack of a stoichiometrical relationship between the carbon and the sulfur by assuming something of the nature of a surface compound, such as described by Langmuir⁹ and by Lowry and Hulett¹⁰ as existing between carbon and oxygen.

The results of Wibaut's experiments have brought to light some interesting information concerning the behavior of sulfur and charcoal, but it is not possible to draw any definite conclusions as to the exact nature of their chemical or physical relationships. In fact, the data published by him might apply equally well if the sulfur were present as carbon-sulfur compounds, as adsorbed sulfur, either free or in a combined form, or as a solid solution of either free or combined sulfur.

Several months before the appearance of Wibaut's paper the Bureau of Mines undertook an investigation of the sulfur in coke, with special reference to the carbon-sulfur complex. From previous work it was known that no ordinary method of chemical examination would indicate the nature of this complex, as it was impossible to distil or extract it in its original condition. Recourse was had, therefore, to a phase-rule study of the system to accomplish this identification.

The investigation naturally divided itself into two parts: first, a study of pure sugar charcoal containing sulfur added at high temperatures; in this case the carbon-sulfur complex could be studied without interference due to the ash constituents; and second, the study of sulfur forms in coke itself.

Experimental Part

Theoretical Study of Sulfur Held by Charcoal at High Temperatures.— It is very probable that the carbon-sulfur complex, regardless of its nature, would show a certain dissociation pressure of sulfur, or a vapor pressure of sulfur as the case might be, dependent on the temperature and perhaps on the relative concentrations of carbon and sulfur.

The possible forms in which the sulfur might occur in the carbon-sulfur complex may be narrowed down in general to three. First, it may exist as one or more chemical compounds, neither adsorbed by nor dissolved in the carbon. A second possible form would be a solid solution, either of free sulfur or of a carbon-sulfur compound, in carbon. A third possibility

⁵ Powell, *J. Ind. Eng. Chem.*, **12**, 1069 (1920).

⁶ Wibaut and Stoffel, *Rec. trav. chim.*, **38**, 132 (1919).

⁷ Wibaut, *ibid.*, **38**, 159 (1919).

⁸ Wibaut, *Verhande. Akad. Wetenschappen Amsterdam*, **30**, 86 (1921); *Rec. trav. chim.*, **41**, 153 (1922).

⁹ Langmuir, *THIS JOURNAL*, **37**, 1154 (1915); **38**, 2271 (1916).

¹⁰ Lowry and Hulett, *ibid.*, **42**, 1408 (1920).

would be adsorption of either free sulfur or of a carbon-sulfur compound on the surfaces of the carbon.

The phase rule gives a method for determining in which of these three classes the carbon-sulfur complex should be placed. In the system under study there are two components, carbon and sulfur. The three possible degrees of freedom are represented by temperature, vapor pressure (or dissociation pressure) of sulfur, and the concentration or percentage of sulfur in the charcoal. The temperature may be kept constant, in which case the relationships existing between the concentration or percentage of sulfur in the charcoal and the vapor pressure of sulfur over the complex would indicate in which of the three classes the complex occurred. In other words, isotherms could be plotted showing the vapor pressure of sulfur corresponding to every percentage of sulfur in the charcoal from zero up to the maximum amount of sulfur taken up by the charcoal. The nature of these isotherms would show whether the system was univariant or divariant, and hence the carbon-sulfur complex could be classified.

From phase-rule relationships it is well known that compounds show constant dissociation pressure at constant temperature, irrespective of the relative quantities of the compound and the solid decomposition product. The isotherm for a compound would, therefore, be a straight horizontal line. Solid solutions, if sufficiently diluted, follow Henry's law. A solid solution would, therefore, show on the isotherm as a straight slanting line. The phase-rule relationship does not hold for adsorbed substances, but the isothermal curve for substances in this condition has been found to have a characteristic shape. In general, in the case of an adsorbed substance, the concentration in the gaseous phase is an exponential function of the amount adsorbed.

The isotherm for adsorbed substances may also have a form very similar to that shown for solid solutions. The manner in which such substances are held to the surface is not entirely understood. Some investigators have explained this phenomenon by "residual valence" or "chemical adsorption." In any case, such surface attraction may exist and may very readily be confused with the phenomenon of solid solution.

Aside from the equilibria differences noted above, another factor differentiates adsorption from solution, namely the rate at which the substance is taken up or given off. In the case of adsorption, the rate, especially at first, is extremely rapid, since here we are dealing with a surface phenomenon; on the other hand, solid solutions are formed and broken up very slowly.

It may be seen from the foregoing theory that the experimental part of this portion of the investigation will consist in maintaining at a constant temperature the charcoal containing the carbon-sulfur complex, and measuring the vapor pressure of the sulfur. The sulfur will then be gradually removed from the charcoal, and the variations in the pressure

of the sulfur vapor noted; or the reverse scheme of adding sulfur to charcoal gradually, and measuring the vapor pressure of sulfur can be used.

In any case it will be necessary to measure extremely small pressures of sulfur vapor—pressures somewhere in the neighborhood of 10^{-8} atmospheres. The measurement of this vapor pressure of sulfur from the carbon-sulfur complex is analogous to the measurement of dissociation pressures of metallic sulfides. Four experimental methods and one calculation method have been proposed for this purpose,^{11,12,13} but none of these four methods is nearly sensitive enough for the measurement of the small pressures encountered in this investigation.

Methods for calculating the equilibrium constant and, therefore, the dissociation pressure from the heat of reaction have been given by Nernst and van't Hoff. However, as we do not know the heat of formation of the carbon-sulfur complex, this method could not be used in the present investigation.

Considerable work has been carried on recently in the laboratory at the Pittsburgh Experiment Station on the desulfurization of coke by hydrogen.¹⁴ At 900°, hydrogen sulfide will be formed in the hydrogen only up to a rather low concentration. This low equilibrium value points to a gaseous equilibrium between free sulfur over the coke and the hydrogen. The equilibrium value has been found to be the same when approached from either direction.

The fact that the hydrogen sulfide concentration reached a certain equilibrium value indicated that this property might be taken advantage of in measuring the small vapor pressure of the sulfur in the carbon-sulfur complex. In a system composed of hydrogen and the carbon-sulfur complex, the equilibrium relation in the gaseous phase would be as follows: $K_p = (p_{H_2}^2 \times p_{S_2})/p_{H_2S}^2$. For purposes of calculation, the pressure of hydrogen would always be one atmosphere. The formula, therefore, reduces to, $p_{S_2} = K_p \times p_{H_2S}^2$. The partial pressure of the hydrogen sulfide could be determined by analysis. The values for K_p have been determined by Preuner and Schupp.¹⁵ By interpolation and extrapolation of their results, the following values have been obtained for the different temperatures used in this investigation.

°C.	K_p	°C.	K_p
700	0.00003	900	0.00120
800	0.00018	1000	0.00600

¹¹ Wasjuclnowa, "Das Gleichgewicht Cupro-cuprisulfid," *Dissertation*, Berlin, 1909.

¹² Johnson, *Z. physik. Chem.*, **61**, 457 (1908).

¹³ Allen and Lombard, *Am. J. Sci.*, **43**, 175 (1917).

¹⁴ Ref. 5, p. 1077.

¹⁵ Preuner and Schupp, *Z. physik. Chem.*, **68**, 157 (1909).

By this procedure all the data necessary are made available for the calculation of the pressure of free sulfur vapor over the carbon-sulfur complex.

For the purpose of studying the sulfur held by carbon at high temperatures, several lots of pure sugar charcoal were made up, and sulfur was added to them.

To one lot 1% of pure sulfur was added, and this mixture was slowly heated to 1000°. Analysis of the resulting product gave exactly 1% of sulfur, showing that all of the sulfur had been retained in the charcoal. To another lot 5% of sulfur was added, and this was heated in the same manner. Analysis showed 3.75% sulfur retained in the charcoal. Another lot under the same conditions gave 3.00% sulfur.

In order to determine whether the hydrogen present in charcoal had any effect on the retention of the sulfur, one lot of charcoal was roasted in order to decrease the percentage of hydrogen. Comparative analyses of 2 lots, 1 made from unroasted charcoal and the other from roasted charcoal, are given below.

	Unroasted charcoal	Roasted charcoal
Carbon.....	92.53	93.55
Hydrogen.....	0.97	0.56
Sulfur.....	3.00	3.75
Oxygen.....	3.50	2.14
	<u>100.00</u>	<u>100.00</u>

Assuming that all of the oxygen in the charcoal is united with hydrogen as water, there is left 0.53% of hydrogen in the unroasted charcoal and 0.29% hydrogen in the roasted charcoal.

From these analyses it would appear that the hydrogen did not enter into the formation of the complex, as more sulfur was taken up by the charcoal containing the least hydrogen. Later results obtained from the isotherms did not show any difference, and other results to be discussed later eliminated hydrogen from consideration, so no further attempts were made to remove the hydrogen.

The apparatus used in this investigation is shown in Fig. 1.

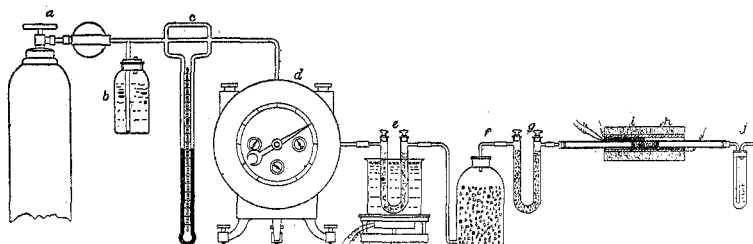


Fig. 1.—Apparatus used in a phase rule study of the carbon-sulfur complex and the sulfur in coke.

Hydrogen was obtained from the steel cylinder *a*. It first was passed through the T connection *b*, which acted as a safety valve as well as a pressure gage, then through a flow-meter, *c*, a calibrated wet-meter, *d*, and a U-tube, *e*, which contained palladium black on asbestos, to remove traces of oxygen from the hydrogen by the catalytic formation of water; this tube was immersed in a glycerol bath kept at 150° by an electric

heater. The hydrogen was then passed through the calcium chloride drying tower *f*, thence through the phosphorus pentoxide drying tube *g*, and finally as pure dry hydrogen into the fused silica tube *h*, which contained 5 g. of the charcoal under investigation, mixed with iron-free asbestos. This tube was heated by an electric furnace over about 30 cm. of its length and the temperature of the center of the tube was under observation at all times by means of the platinum-platinum-iridium thermocouple *i*. At the end of the silica tube was a bubbling tube, *j*, containing ammoniacal cadmium chloride for the absorption of hydrogen sulfide.

The method of calculating the partial pressure of sulfur vapor over the charcoal from the partial pressure of the hydrogen sulfide has been de-

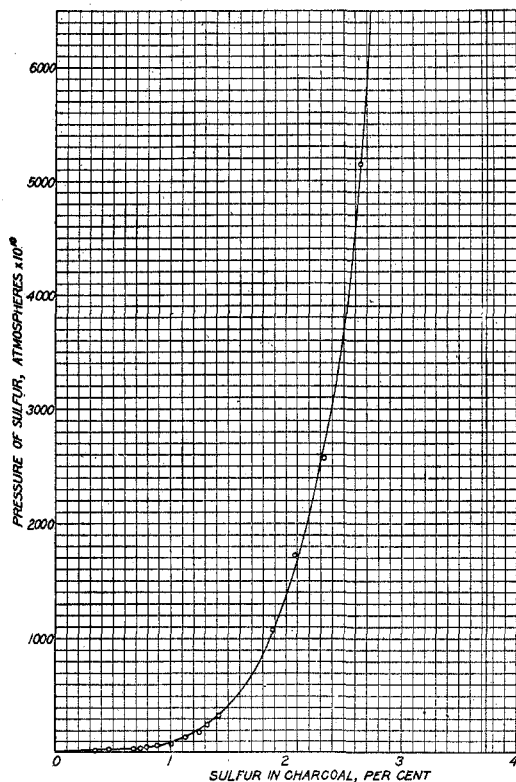


Fig. 2.—Isothermal curve at 800° showing relation between percentage of sulfur in charcoal and partial pressure of sulfur vapor over charcoal.

scribed earlier. When the original amount of sulfur in the charcoal is known, the amount removed as hydrogen sulfide during each step of the run, and the partial pressure of sulfur vapor for each step of the run, give all the necessary data for plotting the concentration-pressure isotherm.

A typical isotherm obtained by this method is shown in Fig. 2. This charcoal contained 3.75% of sulfur, and the curve as shown extends far beyond the limits of the coördinates, finally meeting the line at the right which represents the sulfur content of the charcoal. The lower end of this isotherm, from 0 to 0.3%, is a straight line as shown by several points which could not be reproduced on the curve. From the principles laid down earlier in this paper it can be seen that this charcoal contains about 0.3% sulfur in solid solution (or surface sulfur held by "residual valence"), and the remainder is very plainly adsorbed sulfur, or an adsorbed sulfur compound. No chemical compound of sulfur, at least in an undispersed state, is present, as shown by the lack of a horizontal line. That this curve represents equilibrium conditions was proved by reversing the proc-

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ess and passing a mixture of hydrogen and hydrogen sulfide over sugar charcoal. Under these conditions the same type of curve was obtained as that shown in Fig. 2.

The exact relationships existing in that portion of isotherm representing the solid solution form of sulfur are shown in Fig. 3. The charcoal used in this run contained 1% of sulfur, and the run was made at a temperature of 700°. Under these conditions the solid solution form of sulfur was present to the extent of over 0.8%. The reasons for more sulfur in solid solution form being present in this charcoal than in the other are two. At lower temperatures it has been found that the solubility of sulfur in carbon increases. Furthermore, this charcoal had stood at a high temperature longer than the other charcoal, and the time factor is very important in the formation of this solid solution. This isotherm shows very clearly that the pressure of free sulfur is directly proportional to the concentration of sulfur in the charcoal over the range from 0 to 0.8%. This is in conformity with Henry's law.

For the sake of convenience and brevity of expression this form of sulfur is referred to throughout this paper as a "solid solution."

However, as mentioned before, this sulfur may be present on the surface held by forces unlike those associated with ordinary ad-

sorption. In either case, the practical results are the same as far as removal of the sulfur from the charcoal is concerned. Solid solutions and adsorbed substances which resemble solid solutions from their isotherms are formed and broken up very slowly. Such is the case here, as shown by the fact that about 1 week was required to obtain data shown in Fig. 3, while a similar amount of true adsorbed sulfur could be studied in 1 hour or less.

The two isotherms given here are typical of a large number that have been obtained; all show exactly the same characteristics. To sum up, the carbon-sulfur complex, at least as it occurs in charcoal, consists of sulfur in 2 forms, namely, adsorbed free sulfur or sulfur compounds, and

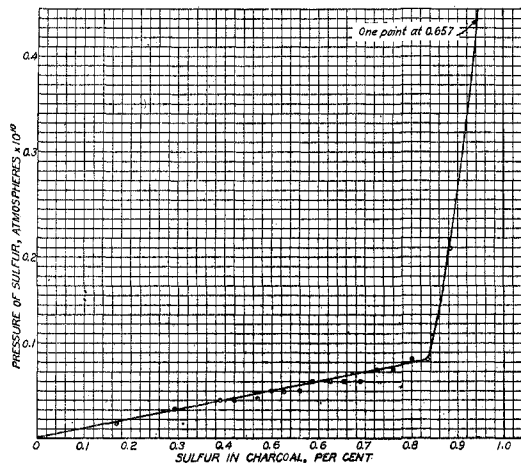


Fig. 3.—Isothermal curve at 700° showing relation between percentage of sulfur in charcoal and partial pressure of sulfur vapor over charcoal. This curve shows the solid solution portion of the isotherm in detail.

sulfur in solid solution in the carbon or held on the surface in such a manner that it is impossible to differentiate it from a solution.

In order further to identify the adsorbed sulfur, it was necessary to find out whether this was free sulfur or adsorbed combined sulfur. Two distinct lines of attack were used in this phase of the investigation: the action of solvents on the charcoal was first tried to find out whether any sulfur-containing material could be isolated by this means; cooling curves were prepared with the expectation that free sulfur, if present, would exhibit some characteristic behavior which would identify it.

Both sodium hydroxide solution and boiling aniline failed to extract free sulfur during long periods of treatment. However, this failure did not necessarily indicate the absence of free sulfur from the charcoal. Free sulfur that remains in charcoal after heating to 1000° would necessarily be very closely adsorbed, and would naturally be very resistant to the action of solvents.

Any results that would be obtained by cooling-curve methods would be subject to the conditions existing in the case of adsorbed substances. The main condition which differs between the adsorbed state and the undispersed state is pressure. The effect of pressure on sulfur is to raise the melting point, as the transition point between orthorhombic sulfur and monoclinic sulfur. For instance, whereas monoclinic sulfur ordinarily melts at 120°, the melting point becomes 151° when the sulfur is under a pressure of 1288 atmospheres. This latter point is also the transition point between the orthorhombic and monoclinic sulfur and, therefore, becomes a triple point on the sulfur diagram.¹⁶

Later work by Smith and Carson¹⁷ has shown that these results of Tammann are considerably in error, owing to the presence of both forms of liquid sulfur in the liquid phase. From their results it is also evident that the normal freezing point of sulfur may vary over a fairly wide temperature range.

It is well known that adsorbed substances are under great pressure,¹⁸ and this pressure must vary continuously over a fairly wide range between different layers of the adsorbed material. If free sulfur were adsorbed on the surfaces of the charcoal, the pressure could vary from perhaps one hundred up to several thousand atmospheres. Under conditions such as these, slow cooling of the carbon-sulfur complex should produce a gradual freezing of the sulfur from a temperature perhaps 40° or 50° above the normal freezing point down almost to the normal freezing point. Such a condition would lead to no experimental evidence of the presence of free sulfur, as it is very improbable that the heat of solidification for the 3% of sul-

¹⁶ Tammann, *Ann. Physik*, **68**, 633 (1899).

¹⁷ Smith and Carson, *Z. physik. Chem.*, **77**, 661 (1911).

¹⁸ Harkins and Ewing, *THIS JOURNAL*, **43**, 1787 (1921).

fur in the charcoal could be detected over a temperature range of 50° or so. However, if the cooling could be carried on in such a manner that the sulfur would supercool almost down to the normal freezing point, and would then freeze in its entirety, we should expect a measurable thermal effect. The freezing of sulfur evolves 9.4 calories per g. With 10 g. of material containing 3% of sulfur, 2.8 calories would be evolved. Charcoal has a specific heat of about 0.25 calories per gram per degree. This would mean that the freezing of the sulfur would tend to raise the temperature of the charcoal about 1° . It can be seen, therefore, that the effect of the freezing of the sulfur would produce a noticeable break in the cooling curve.

A large number of cooling curves have been run on charcoal containing 3.75% sulfur in the form of the carbon-sulfur complex, and the existence of a break in the curve at or a little above the normal freezing point of sulfur has been established beyond much doubt. Consistently positive results were not obtained, nor were they expected, as the break in the cooling curve depended on the maintenance of an unstable equilibrium which was not always possible to obtain, even under carefully controlled conditions.

Very accurate cooling curves were obtained by the use of a copper-constantan thermocouple and a very sensitive potentiometer. About 10 g. of

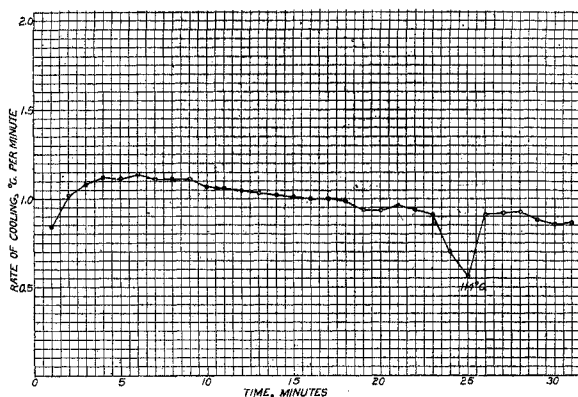


Fig. 4.—Curve showing rate of cooling of charcoal containing sulfur.

the charcoal was contained in a tube; the thermocouple junction, properly insulated, was surrounded by this charcoal. The tube was placed in an unsilvered Dewar flask containing hot glycerol. Thus, fairly slow cooling was attained, the cooling rate being such that it could be easily followed by the potentiometer. Out of six runs, one broken cooling curve was obtained, the other five being absolutely smooth. Fig. 4 shows the results obtained in the one positive run. In order to bring out the results more clearly, the curve has been drawn as a rate-of-cooling curve rather

than a true cooling curve. It may readily be seen that the rate of cooling falls off very markedly at about 114° .

Further cooling-rate tests by the use of an ordinary thermometer gave similar results. Out of about 30 carefully conducted runs, 10 gave very positive breaks over a range from 114° to 119° . Several runs gave more or less indistinct breaks, but in no case was there a distinctive break at any other point than those mentioned.

The carbon-sulfur complex existing with carbon at high temperatures, therefore, consists of adsorbed free sulfur and sulfur in solid solution. The sulfur in solid solution is probably free sulfur, although no direct proof of this has been advanced in this investigation.

The Sulfur of Coke.—The forms of sulfur in the coke were determined by using the same methods as were used for charcoal. In the case of coke,

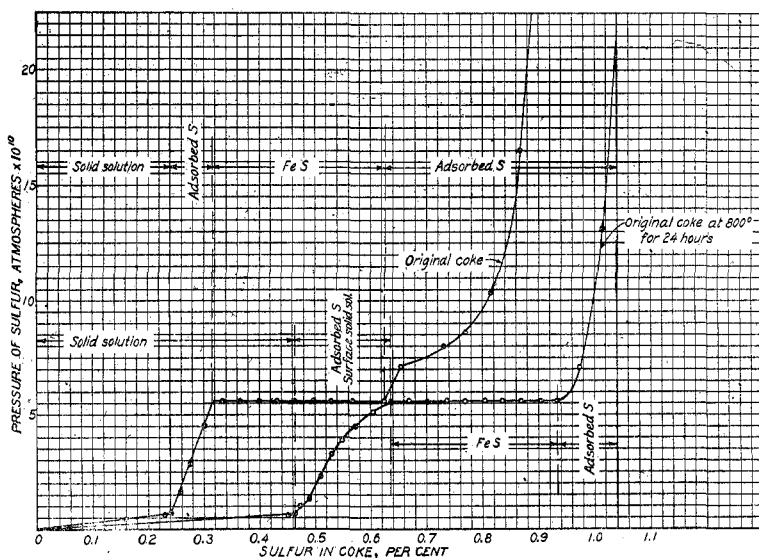


Fig. 5.—Isothermal curves at 800° showing relation between percentage of sulfur in coke made in laboratory by quick heating and the partial pressure of sulfur vapor over the coke.

however, metallic sulfides entered into the problem. Sulfates have been found in coke in small quantities, but their presence is due to oxidation of sulfides while the coke is cooling in the air. Under high-temperature reducing conditions no sulfates were found during the present investigation.

If isotherms were run on coke, therefore, we should expect straight horizontal lines over the portions of the curve represented by the metallic sulfides, since these are definite chemical compounds. Ferrous sulfide has long been known as a constituent of coke, while calcium and magnesium sulfides are also present, usually in very small quantity.

The first coke to be considered was one made in the laboratory by the usual method for the determination of volatile matter. The resulting isotherm is shown in Fig. 5, Curve 1. It may be seen that this curve is similar to those obtained from charcoal, with the exception that the middle portion of the curve consists of a straight horizontal line, indicative of a compound. This is ferrous sulfide, as experiments described later will show.

The solid-solution form of sulfur was present in this coke to the extent of only 0.24%. In order to investigate the effect of long heating, a sample of the coke was allowed to remain for 24 hours at a temperature of 800°. The isotherm for this coke is shown in Curve 2. The slow conversion of the adsorbed sulfur into solid-solution sulfur is shown in a very positive manner. The solid-solution form has been increased from 0.24 to 0.46% and, furthermore, there has been a "piling-up" effect of the sulfur at or directly under the surface of the coke, as shown by the increased length of the curve lying between the solid solution and ferrous sulfide. The amount of ferrous sulfide in the coke has not changed, as was to be expected.

The next sample of coke studied was one obtained from a standard by-product coke oven. An isotherm of this coke at 700° is shown in Fig. 6. Isotherms of the same coke were also obtained at 800°, 900° and 1000°.

At each of these four temperatures the coke has about the same composition. This coke contains no adsorbed sulfur, with the possible exception of a small quantity having a vapor pressure less than the decomposition pressure of the ferrous sulfide, but greater than the vapor pressure of the sulfur in solid solution. The composition of this coke is typical of every commercial coke studied.

The absence of adsorbed sulfur in coke made by the usual process of slow heating, say over a period of 18 hours, is most reasonably explained as follows. All coals contain organic sulfur in fairly large quantities, and this organic sulfur is uniformly distributed throughout the coal substance. By heating the organic sulfur compounds quickly, they would be decomposed with great rapidity, and the decomposition products would tend to pass out of the mass. The time factor would be so small that a comparatively

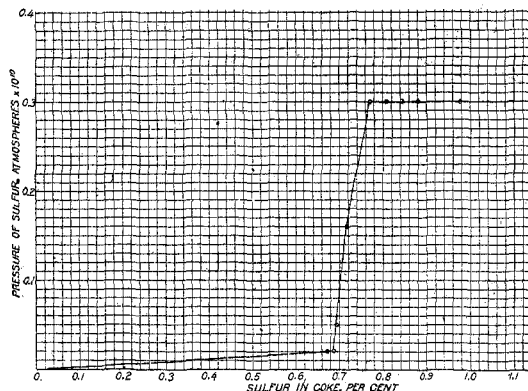


Fig. 6.—Isothermal curve at 700° showing relation between percentage of sulfur in a metallurgical coke and partial pressure of sulfur vapor over the coke.

small percentage would be retained as a solid solution in the coke carbon or carbonaceous material, a larger quantity would be held back as adsorbed sulfur at the surface, while the remainder would pass out with the volatile matter. With slow heating rates, however, more opportunity would be given for solution of the decomposition products and the sulfur which was adsorbed would have more opportunity to be dissolved in the coke carbon during the long heating time.

After the runs had been made on this coke the residue was treated with hydrochloric acid to decompose any metallic sulfides which might remain. The results showed 0.03% sulfur present, presumably as calcium and magnesium sulfides, as tests have shown that these sulfides have no measurable decomposition pressure, even by the very sensitive method used in this investigation. This form of sulfur is represented on the isotherm as giving zero pressure of sulfur, at the extreme bottom of the curve.

A curious fact brought out by these isotherms lay in the differences between the quantities of ferrous sulfide in the hot coke and coke at room temperature. In the coke described, the isotherms indicated about 0.34% of sulfur present as ferrous sulfide. The original coke, by treatment with hydrochloric acid and evolution of hydrogen sulfide, showed 0.23% of sulfur as metallic sulfides. Subtracting the 0.03% of sulfur which is in the form of calcium and magnesium sulfides, this leaves 0.20% sulfur present as ferrous sulfide in the cold coke. The decomposition of ferrous sulfide in coke was noted by the writer in another paper,⁵ but at that time it was thought that this decomposition took place during the coking process itself. It now appears that ferrous sulfide decomposes during the cooling of the coke. Analyses of this coke cooled at different rates, for ferrous sulfide by the evolution method, gave the following results.

Sulfur as ferrous sulfide in coke by different treatments

	%
Coke at 700° to 1000° (isotherm method).....	0.34
Coke as it came from the plant.....	0.20
Coke heated to 850°, quenched very quickly.....	0.24
Coke heated to 850°, quenched after cooling to about 500°.....	0.07
Coke heated to 850°, cooled very slowly.....	0.01

These results showed that one of two things was happening during the cooling of the coke; first, that the ferrous sulfide decomposed during the cooling process; or second, that the ferrous sulfide was adsorbed or dissolved during the cooling in such a manner that the boiling hydrochloric acid did not decompose it. That the first of these theories was correct and that the ferrous sulfide actually decomposed was shown in the following experiment.

The coke referred to above, in its original condition without any heat treatment, was boiled with hydrochloric acid. The sulfur present as iron sulfide was found to be 0.20%; that as sulfate, 0.00%, and 0.75% of soluble iron was found; another sample of the same coke was heated to a red heat, allowed to cool slowly and similarly analyzed; the results were 0.01, 0.03 and 0.75%, respectively. As the acid soluble iron is the same in each case, whereas the sulfur present as sulfide has been caused to decrease to almost zero by the cooling process, this shows that ferrous sulfide is decomposed during the cooling of the coke.

In order to study the nature of this decomposition of ferrous sulfide, a high sulfur gas coke was used for further experiments. Samples of this coke were treated in the manner just described for the metallurgical coke. The original coke showed 0.64% of sulfur as iron sulfide, 0.00% as sulfates, and 1.93% of soluble iron; while after it had been heated, cooled slowly and similarly analyzed, the results were 0.01%, 0.03% and 1.80%, respectively. In this case there was a slight decrease in the amount of acid-soluble iron due to the heat treatment, but this decrease is negligible compared with the almost complete disappearance of sulfur combined as ferrous sulfide.

The next problem was to determine the fate of this sulfur, formerly combined with the iron in the form of ferrous sulfide, in the coke after the slow cooling. For this purpose an isotherm at 800° was run on the slowly cooled coke after it had been subjected to the acid treatment. As the acid treatment had removed practically all of the iron formerly combined as ferrous sulfide, the isotherm should indicate the form in which the sulfur existed in the slowly cooled coke without any possibility of reformation of ferrous sulfide during the heating of the material. The result of this test was clearly indicative of the presence of adsorbed sulfur. That the coke does not possess as great adsorbing power for free sulfur as the charcoal mentioned earlier in this paper was shown by the steepness of the adsorption curve. In fact, the sulfur was held so loosely by the coke that a considerable part of it collected as a yellowish-white deposit in the cool ends of the tube before the temperature could be raised to 800° for the passage of the hydrogen.

Further proof that the sulfur formerly combined with iron as ferrous sulfide was present in the slowly cooled coke as free sulfur was furnished by extraction with solvents. When the slowly cooled coke was extracted with pure, redistilled carbon disulfide, a yellowish substance was left after evaporating the solvent. This substance was recrystallized from benzene. Under the petrographic microscope the substance was shown to consist of monoclinic crystals. The substance melted rather sharply at 118° and on further heating turned dark red. It burned with a blue flame, and gave off the odor of sulfur dioxide. These observations point

most decidedly to the presence of free sulfur in coke treated in this manner.

The next problem to be solved involved a more exact study of the nature of this decomposition of ferrous sulfide which resulted in the formation of free sulfur. We have undeniable proof that the decomposition of the ferrous sulfide in the coke is an oxidation process proceeding with great rapidity over certain temperature ranges. Coke was cooled in covered porcelain crucibles in a muffle, the door of which was closed. These conditions were unfavorable for oxidation. The acid extracts from coke so cooled were invariably yellow, and investigation showed this to be due to ferric iron. The acid extracts from coke not so treated contained ferrous iron and were almost colorless. Furthermore, coke heated to a red heat in an atmosphere of hydrogen and then cooled very slowly in the same atmosphere had a content of ferrous sulfide (cold) almost equal to that shown by the isotherm. This shows that under reducing conditions, decomposition of ferrous sulfide does not occur no matter how slowly the coke may be cooled. From these observations it appears that the decomposition of the ferrous sulfide in coke cooled very slowly is according to the reaction, $4\text{FeS} + 3\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 4\text{S}$. It is well known that this reaction occurs in the revivification of fouled gas-purifying material, but to the best of the writer's knowledge it has never previously been recognized as occurring in the ferrous sulfide of coke. It is our plan to study this very interesting reaction further, in order to establish definitely the proper temperature conditions for its maximum oxidation velocity. Experiments to determine this temperature have indicated that at about 500° the oxidation is extremely rapid, even when the coke has limited access to the air. At lower temperatures the rate falls off until at 300° it is scarcely noticeable. At temperatures higher than 500° , the carbonaceous matter of the coke tends to combine with oxygen, so that at temperatures much higher than 500° the action consists more in combustion of the coke than a selective oxidation of the ferrous sulfide.

Mention has already been made of the work done in the Pittsburgh Experiment Station on the desulfurization of coke by hydrogen. It was found that coke made in the laboratory by quick heating could be desulfurized almost completely by this method. When the process was tried out in a regulation coke-oven, however, only about 20% of the sulfur could be removed from the coke, even by very long treatment with coke-oven gas which contained 50% of hydrogen. The reason for the difference is shown by the isotherms for the two kinds of coke. Coke made by quick heating contains a large percentage of adsorbed sulfur, which is very easily removed by the hydrogen. In coke-oven coke, however, the sulfur form having the highest decomposition pressure is ferrous sulfide, which would be decomposed by the hydrogen with more difficulty.

Summary and Conclusions

1. A phase-rule study of the system involving the carbon-sulfur complex existing with carbon at high temperatures has brought out the fact that this sulfur occurs in 2 forms, (a) adsorbed free sulfur, and (b) sulfur in solid solution in the carbon or held on the surface of the carbon in such a manner that it is impossible by any known means to differentiate it from a solid solution.

2. Coke made in the laboratory by heating coal rapidly contains sulfur in 3 forms, (a) adsorbed free sulfur, (b) sulfur in solid solution in the carbonaceous mass, or held on the surface in such a form as to exhibit all the properties of a solution, and (c) ferrous sulfide together with much smaller quantities of calcium and magnesium sulfides. When this coke is kept at a red heat for several hours the adsorbed sulfur slowly passes into solid solutions.

3. Coke made by the usual commercial process of carbonization over a comparatively long period contains, before it is cooled, but 2 forms, (a) sulfur in solid solution or held on the surface in such a manner as to resemble a solid solution in all of its properties and (b) ferrous sulfide with smaller quantities of other metallic sulfides, the adsorbed sulfur mentioned above being missing or present in appreciable quantities.

4. When coke cools, even with limited access to the air, oxidation of ferrous sulfide occurs. This is due to the reaction, $4\text{FeS} + 3\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 4\text{S}$.

When the coke is quenched, as in ordinary coke manufacture, this decomposition of ferrous sulfide is not complete, due to the speed with which the temperature of the coke is carried below that for effective oxidation. However, coke held at a temperature in the neighborhood of 500° , even with limited access of air, shows almost complete oxidation of the contained ferrous sulfide.

5. When hydrogen, or hydrogen-containing gas, is passed through red hot coke in a coking chamber, the sulfur removed as hydrogen sulfide comes from the decomposition of ferrous sulfide, because this compound has the highest dissociation pressure of any sulfur form in the coke.

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