

SPECIAL REPORT OF RESEARCH

Conducted in

Department of Geology  
College of Mineral Industries  
The Pennsylvania State University

THE REACTIONS  
OF  
SELECTED BITUMINOUS COALS  
WITH  
CONCENTRATED SULFURIC ACID

by

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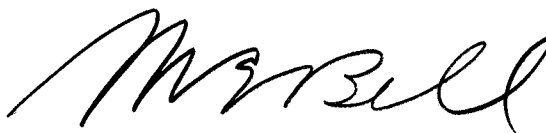
### STATEMENT OF TRANSMITTAL

Special Report SR-29 transmitted herewith has been prepared by the Coal Research Section of the Mineral Industries Experiment Station. Each of the Special Reports presents the results of a phase of one of the research projects supported by the Pennsylvania Coal Research Board or a technical discussion of related research. It is intended to present all of the important results of the Coal Board research in Special Reports, although some of the results may already have been presented in progress reports. The following is a list of Special Research Reports issued previously.

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SR-20	The Radiation Chemistry of Coal in Various Atmospheres	September 12, 1960
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SR-22	The Nature and Occurrence of Ash Forming Minerals in Anthracite	December 30, 1960

SR-23	A Phenomenological Approach to the Batch Grinding of Coals	January 20, 1961
SR-24	The Unsteady State Diffusion of Gases from Anthracite at High Temperatures	January 31, 1961
SR-25	Some Advances in X-Ray Diffractometry and Their Application to the Study of Anthracites and Carbons	February 24, 1961
SR-26	The Filtration of Coal Solutions	March 17, 1961
SR-27	A Preliminary Investigation into the Application of Coal Petrography in the Blending of Anthracite and Bituminous Coals for the Production of Metallurgical Coke	May 1, 1961
SR-28	Preparation and Properties of Activated Carbons Prepared from Nitric Acid Treatment of Bituminous Coal	August 15, 1961



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### SUMMATION OF RESULTS

An analytical procedure is devised for establishing a carbon balance in the coal-sulfuric acid reaction. The nature and distribution of various reaction products including carbon dioxide, carbon monoxide, hydrocarbons, sulfur dioxide, water, and water- and sulfuric-acid soluble carbonaceous materials is discussed. Reaction possibilities are limited.

It is concluded that oxidation is slight at 25°C and 50°C. Sulfur and oxygen are added to peripheral aliphatic groups which are oxidized at 100°C with a resulting loss in sulfur content and evolution of carbon dioxide. At 150°C the peripheral groups are eliminated with additional loss in sulfur content. The high-temperature-stable sulfur which constituted a small part of the net sulfur added at 25 and 50°C was not positively identified.

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## I. INTRODUCTION AND STATEMENT OF THE PROBLEM

Coal has been one of the most important building blocks of our industrial revolution. It has served not only as a primary fuel and as a source of coke for the reduction of iron ore, but also as an important source of industrial chemicals. The production of these chemicals has remained more of an art than a science, dependent upon the vast amount of empirical knowledge gained through years of experience. A more accurate coal model and a scientific determination and definition of its chemical properties would present ideas for the development of new processes and an improvement of the old. For years the problem of determining the structure of coal has fascinated scientific investigators. Unique problems complicate this endeavor since coal is not a pure compound, but a mixture of closely related substances. It is still impossible to draw an exact coal model.

One of the most successful means of indirectly determining coal structure has been to break it down into fragments which can be identified and then fitting these pieces together in order to visualize the parent molecules. In this respect the oxidation of coal has been most fruitful. Oxidation with sulfuric acid is particularly suited to this purpose because it is generally a mild oxidant, depending on the temperature, and yields products not far removed from the original structure. Unfortunately, in past investigations of coal using sulfuric acid a largely empirical approach was taken. The main product of the coal-sulfuric acid reaction was a useful ion

exchange material, and the study of this process followed the lines of development and production rather than basic research. Sulfur dioxide and carbon dioxide were identified as reaction products, but the amounts produced and their relation to the time and temperature of the reaction was unknown. Water- and sulfuric-acid-soluble materials as well as carbon monoxide were possible but unreported products. More knowledge of the nature and distribution of all the reaction products would indicate the course of the reaction and elucidate some chemical properties of the coal molecule. For example, the production of sulfur dioxide indicates the extent of oxidation, and the susceptibility of the molecule to attack. Carbon dioxide and carbon monoxide result from the oxidation of peripheral aliphatic side chains. Water soluble materials such as acetic and oxalic acid could be formed by the oxidation of cycloalkanes. Separation of small aromatic fragments from the main coal nucleus would result in a sulfuric acid soluble fraction.

In order to use this reaction as a tool in the determination of the chemical properties of coal, a carbon balance which would indicate the distribution of these various products had to be established. Thus, a consideration of the oxidizing and sulfonating properties of sulfuric acid at the various temperatures, together with an analysis of all products, would give an indication as to how the parent molecule was broken into fragments.

Coals originate from plant debris which become increasingly aromatic through the loss of carbon dioxide, water, and methane, as they

approach the final product. Different ranks of coal should show a corresponding difference in the effect of a reaction conducted under the same conditions. The extent of oxidation with sulfuric acid, and the resulting sulfur dioxide and carbonaceous reaction products, should change with rank. Low volatile, high volatile A, high volatile C, and sub-bituminous B coals were treated with sulfuric acid to verify this prediction.

The object of this thesis is to follow quantitatively the progress of oxidation in selected ranks of coal by analysis, the changes in amounts of all the elements and reaction products. Through a consideration of these changes the number of possible reactions will be limited and the reactions of sulfuric acid with coal will be more clearly defined.

## II. LITERATURE SURVEY

The reaction of carbons with sulfuric acid has been known from the outset of modern chemistry. In 1845 Marchard (1) noted that sulfuric acid reacts with various coals and charcoals to form sulfur dioxide, carbon dioxide, and small amounts of organic acids.

Giraud (2) observed the formation of pyromellitic acid in a 5% yield when bituminous coal was distilled with concentrated sulfuric acid.

Unfortunately, the research immediately following these initial discoveries was superficial and in some cases misleading. Dennstedt and Bunz (3) recorded a rise in temperature when coal was mixed with sulfuric acid, but did not pursue the reaction further. Pictet and Bouvier (4), while noting an increase in sulfur content, failed to identify sulfonic acid groups following treatment of coal with sulfuric acid and concluded that there were no aromatic groups present. Phillippi and Thelen (5) heated wood charcoal with concentrated sulfuric acid at 300°C and obtained 1-2% yields of pyromellitic acid. These yields were increased threefold when mercury was employed as a catalyst, the temperature raised to 290°-315°C, and the reaction time extended to six hours. They also produced "sulfonic acid carbons" by heating aliphatic bodies such as cellulose with sulfuric acid. On this basis they reached the conclusion that preformed ring systems were not necessary for the formation of the products observed, thus tacitly agreeing with the ideas of Pictet and Bouvier. When Pearson (6) reacted coal with sulfuric acid fol-

lowed by treatment with hypobromite, he observed an initial attack on peripheral aliphatic groups, and a subsequent attack on condensed cyclic systems. The residual nuclei were shown to be unchanged by all available tests. Strache and Lant (7) identified carbon monoxide among the reaction products when sulfuric acid was combined with other oxidizing agents, and the oxidizing mixture reacted with coal. They did not determine whether carbon monoxide was formed when sulfuric acid was used alone.

Up to this point the interval between successive papers was measured in decades. The information which had been amassed was entirely qualitative. However, increased interest in the structure of coal spurred more comprehensive and fruitful investigations. In 1927 Kreulen (8) carried out the first quantitative examination of the coal-sulfuric acid reaction. Coals containing 38.4, 22.8, and 15.4% volatile matter were treated with 94 - 96% sulfuric acid. Upon carbonization of the sulfonated product he ascertained that heating values, volatile matter, ash, tar yield, and phenol contents of the tar were lowered while sulfur and gas yields were raised. This indicated to him that the action of the sulfuric acid was mainly oxidizing. He later (9) calculated the heats of combustion of treated coals and found a general increase with an accompanying decrease in volatile matter. However, these values were not uniform, probably owing to reaction with constituents other than volatile matter. Preheating the coals from 125° - 150°C increased the heats of combustion of the reacted products while preheating to 175°C

decreased them.

The first general examination of the reaction was given in a Fuel Research Board Report of The British Department of Scientific and Industrial Research (10). They found that when coal was treated with concentrated sulfuric acid at temperatures to 250°C, the product after removal of the acid had base exchange properties. When treated with up to two times its weight of acid at ordinary temperatures, the coal swelled, partially disintegrated, and gradually absorbed the sulfuric acid. Heat and sulfur dioxide were evolved. The coal absorbed all of the sulfuric acid, was dry to the touch, and could be preserved indefinitely if kept dry. Gentle warming accelerated the reaction. As the temperature was raised the apparent density increased and the amount of recoverable acids decreased. The production of good base exchange products required temperatures over 100°C and a larger excess of sulfuric acid. Some low temperature cokes (480°C) reacted in the same way as coal if treated at 200°C. High temperature cokes would not give base exchange materials even when treated with oleum at 200°C. Partly hydrogenated, oxidized, and chlorinated coals gave exchange materials. The authors pointed out that there was no direct evidence that sulfonation of coal occurred. The action seemed specific in that no other oxidizing agents or mineral acids gave base exchange products. Radiographs showed only major fissures formed due to disintegration and gave no indications as to the mode of absorption. The amounts of phenols produced by caustic fusion following sulfonation were very small. It was con-

cluded that the main action of sulfuric acid is oxidizing and that there is no direct relationship between the absorption of sulfuric acid and the production of base exchange properties.

Considerable work has been done concerning the adsorption of sulfuric acid on charcoals. Zaverina and Dubinin (11) found that sulfuric acid adsorption on fine sugar charcoals gave additional oxidative activation and produced considerable change in porosity. Therefore, theoretical conclusions based on comparison of isotherms before and after activation were not possible. Brose (12) studied the adsorption isotherms of hydrochloric and sulfuric acids on five different charcoals of differing ash contents over the range of concentrations from 0.005 to 2 molar. One charcoal was demineralized and the measurements repeated. The linear equation of Ostwald,

$$f_x = af_{c-x} + b,$$

(where  $f_x$  = activity coefficient of the adsorbed solution of virtual concentration  $x$ .

$f_{c-x}$  = activity coefficient of the equilibrium solution of concentration  $c - x$ .

$a$  and  $b$  are constants) held well for the intermediate concentration. For the ash-free and low-ash charcoals the sulfuric acid curve was superimposed on the hydrochloric acid curve when the single cation activity coefficient at the virtual concentration,  $x$ , was plotted against the mean coefficient, which is defined by

$$-\log n_f^t = 0.505z^2 \sqrt{m/n}.$$

(where  $n$  = the number of cations in the molecule;  $z$  = valence;  $m$  = ionic strength). Jha and Jain (13) found the adsorption of sulfuric



acid by sugar charcoal to be discontinuous. Burshtein and Frumkin (14) found that hydrogen peroxide was formed when sulfuric acid was adsorbed on charcoal in the presence of freshly adsorbed oxygen. The maximum amount of hydrogen peroxide was reached in about ten minutes, and then decreased owing to the breakdown of hydrogen peroxide catalysed by the charcoal. The formation of hydrogen peroxide stopped when adsorption of sulfuric acid was complete.

Adsorbed sulfuric acid has been found to have interesting effects on the combustion properties of charcoal. When Frey (15) pretreated charcoal with small amounts of sulfuric acid the  $\text{CO}/\text{CO}_2$  ratio of the charcoal in combustion with oxygen increased. The overall rate was reduced ten-fold. The initial rate of oxygen adsorption was reduced one hundred-fold. The  $\text{CO}/\text{CO}_2$  ratio obtained by heating the charcoal (saturated with oxygen) in vacuum was increased. The carbon monoxide produced up to  $600^\circ\text{C}$  was from a primary reaction. Generally, acid pretreatment produced a charcoal of considerably reduced activity towards these reactions. The results were explained in terms of electromagnetic theory of catalysis where electromagnetic effects produced by impurities in the carbon were transmitted through the graphite lattice.

Beet (16) digested bituminous coal samples in sulfuric acid before running Kjeldahl nitrogen determinations. He found that unless prolonged boiling periods were used, Kjeldahl nitrogen values were low. This was traced to the formation of very resistant pyridine carboxylic acids. After 72 hours of digestion, 20% of the

nitrogen had not been converted into ammonium sulphate, and of this amount, about one-third was recovered as nitrogen-containing acids which gave pyridine on heating and appeared to be largely nicotinic acid.

In 1941 Gordon (17) found that organic zeolites could be made from brown coal, coal, peat, lignite, wood and other carbonaceous materials. He described the properties of sulfonated coal and peat. This discovery stirred great interest in the reaction. However, subsequent research emphasized development of the sulfonated product. Stach (18) gave a good review of ion exchange in terms of basic chemistry and physics and reviewed the effect of sulfuric acid on the ion exchange properties of coal. Jurkiewicz (19) discussed the preparation of sulfonated bituminous coals and included 56 references. A number of papers followed describing the uses of sulfonated coal in the softening of sea water (20), in the polymerization of epoxy compounds (21), in reducing the pH of furnace blacks (22), and in other potential ion exchange applications.

In spite of the attention given to developing better base exchange materials, a few bits of information appeared which helped to clarify the nature of the reaction. Drozdov and Popov (23) treated 0.25 - 0.5 mm. particles of coal with sulfuric acid containing  $\text{H}_2\text{S}^{35}\text{O}_4$  and 27% excess sulfur trioxide for three hours at 20° C, 100°C, and 200°C, and for twenty minutes at 150°C. The resulting sulfocarbon was washed with water, 10% hydrochloric acid, and again with water until it was neutral to methyl orange and then was dried

at 100°C. Preliminary experiments showed that sulfur originally in the coal was not oxidized to sulfonic acid groups. These formed from the oleum. The content of sulfonic acid groups in the sulfocarbon prepared at 100°C and 150°C was practically equal to the ion exchange capacity at pH = 7. Those prepared at 20°C exhibited a capacity smaller than their sulfonic group content, and that of those prepared at 200°C was greater. Anderson and Jonsberg (24) attempted to sulfonate a number of carbonaceous materials. Graphite could not be sulfonated and anthracite coal heated to 555°C could be sulfonated only with difficulty. Suitable materials were bituminous coal, and charcoal heated to 450°C. Capacities of the organolites as calculated from sulfur content were higher than capacities as determined from extraction. This was attributed to the presence of non-sulfonic acid groups such as sulfones.

The complex reaction leading to the production of ion exchange materials is specific to sulfuric acid in that no other mineral acids or oxidizing agents produce zeolites upon reaction with coal. However, few experiments have been carried out for the purpose of determining the reactions responsible for this effect. As a result, many conclusions deduced from these experiments concerning the structure of coal have been false or misleading. A new quantitative technique has been developed in order to examine the reaction of sulfuric acid with coal, with the objective of elucidating the nature of the reactions involved.

### III. EXPERIMENTAL PROCEDURE

#### A. Description of the Coal Samples

Representatives of alternate classes of coal in the A.S.T.M. classification from low volatile bituminous through subbituminous B were chosen for these experiments so that changes in reactivity might be related to the different ranks of coal. All samples were core drillings or channel cuts which represented the entire seam.

The coals selected and the A.S.T.M. classes to which they belong were: (1) low volatile bituminous coal from the Upper Kittanning bed, Cambria County, Pennsylvania; (2) high volatile bituminous A coal from the Pittsburgh seam, mined in Washington County, Pennsylvania; (3) Illinois high volatile C from the Sahara mine, Harrisburg, Illinois; and (4) subbituminous B from the Eagle mine of the Imperial Coal Company of Erie, Weld County, Colorado.

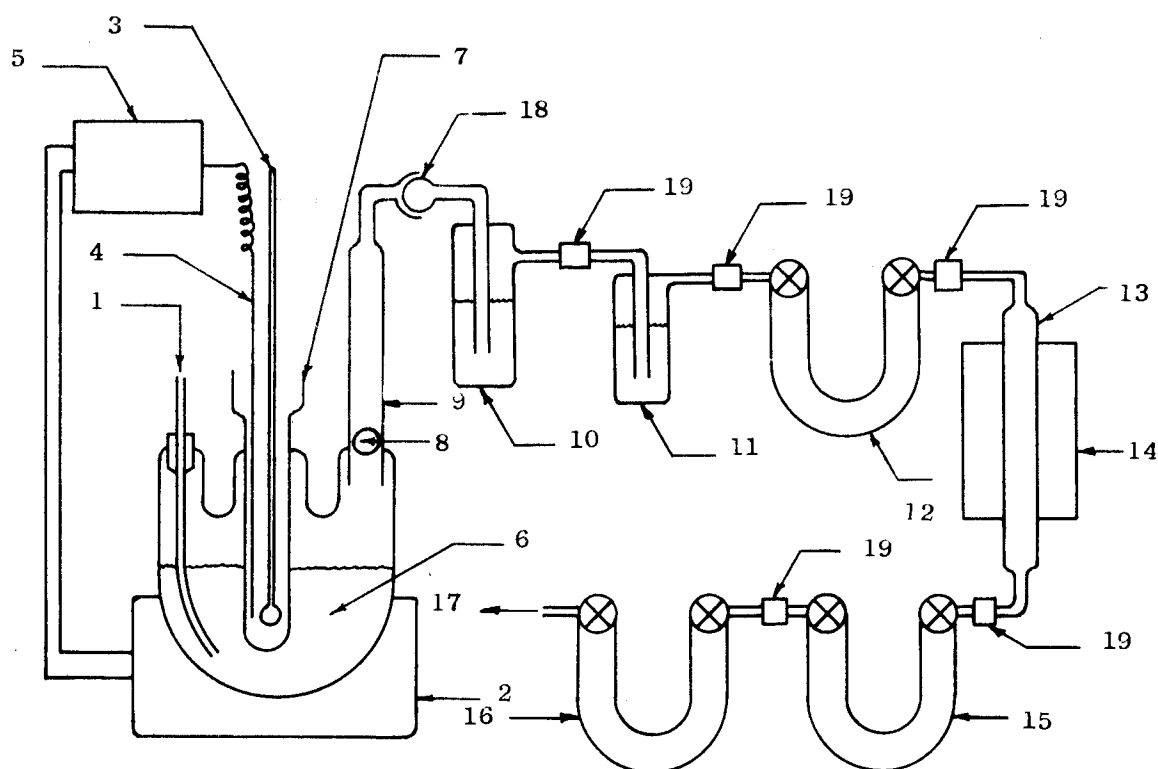
#### B. Preparation of the Raw Coal

Each gross coal sample was reduced in an Alen-Bradley shear type Mikro-Sample Mill until it passed a number 200 United States Standard sieve. The reduced samples were mixed for 48 hours in a solid-mixing apparatus and placed in weighing bottles. The weighing bottles containing the coal samples were then placed in a vacuum oven and dried to constant weight at 85°C. After drying, the vacuum oven was filled with nitrogen and the bottles were tightly stoppered in order to keep air oxidation at a minimum.

### C. Preparation of the Sulfonated Coal

A 1.0 - 3.5 g sample of dry, raw coal was placed directly from the nitrogen filled weighing bottle into a 500 ml, round-bottom, three-neck flask, and mixed with 400 ml of 98% sulfuric acid. The flask was equipped with an inlet for the passage of a stream of pure nitrogen and an outlet which was connected to a reaction train for the absorption of product gases. The nitrogen was bubbled through the coal-sulfuric acid mixture in order to provide agitation. The third neck accepted a well which contained a thermometer and thermocouple. This gave a completely closed system so that only the effect of the sulfuric acid would be noted. See Figure 1.

The sample weights were chosen between 1 and 3.5 g since this amount of coal produced gaseous products within the capacity of the absorption train. A large excess of sulfuric acid was used because it gave an even dispersion of coal without mechanical stirring. The 4 cm nitrogen pressure necessary to sweep the product gases through the various absorption traps made the use of mercury seal or other conventional stirrers impractical. When 100 to 200 ml of sulfuric acid were added the coal swelled, absorbed the sulfuric acid, and formed a gel. With the addition of 200 to 300 ml of sulfuric acid a crust formed which puffed above the surface of the reaction mixture. The addition of 400 ml of sulfuric acid gave a more even dispersion of coal although it was noted after the reaction that a small amount of coal was concentrated in the bottom of the flask. The rate of evolution of sulfur dioxide which was a measure of reaction rate was little affected by the absence of mechanical stirring as is



- |  |  |
|--|--|
| 1. Pure nitrogen inlet                         | 11. Concentrated sulfuric acid and chromic acid trap |
| 2. Heating mantle                              | 12. Caroxite trap                                    |
| 3. Thermometer                                 | 13. Cupric oxide catalyst                            |
| 4. Thermocouple                                | 14. High temperature furnace                         |
| 5. Variable relay                              | 15. Anhydron trap                                    |
| 6. Coal-sulfuric acid mixture                  | 16. Caroxite trap                                    |
| 7. Thermometer well                            | 17. Nitrogen outlet                                  |
| 8. Glass wool plug                             | 18. Ball and socket joint                            |
| 9. Anhydron trap                               | 19. Rubber connective tubes                          |
| 10. Dilute sulfuric acid and chromic acid trap |  |

Sulfonation Apparatus

Figure 1

shown in Figure 4.(see page 21).

The coal was reacted at 25°C, 50°C, 100°C, and 150°C. The temperature was controlled by means of a heating mantle and a Chromel-Alumel thermocouple connected to a West relay. A United States Bureau of Standards thermometer was used to calibrate the relay. The control was found to be accurate to  $\pm 1^\circ\text{C}$  on this thermometer.

The reaction was stopped with ice after approximately 500 hours. The resulting mixture of sulfonated coal and diluted sulfuric acid was filtered through a fritted glass thimble. The sulfonated coal was then extracted with water in a Soxhlet until free from sulfuric acid, and dried to constant weight in the same manner as the raw coal. The coal was judged free from sulfuric acid when negative tests for hydrogen and sulfate ions were obtained with litmus paper and 10% barium hydroxide respectively. A straight line relation of moles of sulfur dioxide produced versus time was obtained after about 200 hours. The reaction was carried out to 500 hours in order to verify the slope and continuity of this straight line.

#### D. Analysis of Gaseous Reaction Products

The gases evolved during the course of the reaction consisted of sulfur dioxide, carbon dioxide, carbon monoxide, and traces of hydrogen and low-molecular-weight hydrocarbons. These gases were continuously swept from the reaction flask by a stream of pure nitrogen into an absorption train where they were collected and gravimetrically

ly determined (See Figure 1). An Anhydrone trap removed water produced by the reaction. Sulfur dioxide was collected in a dilute sulfuric acid - chromic acid trap. A Caroxite trap absorbed the carbon dioxide produced. These traps effectively retained known amounts of sulfur dioxide and carbon dioxide generated in the reaction flask, and the concentrated sulfuric acid - chromic acid trap absorbed all of the water evaporated from the dilute sulfuric acid - chromic acid trap.

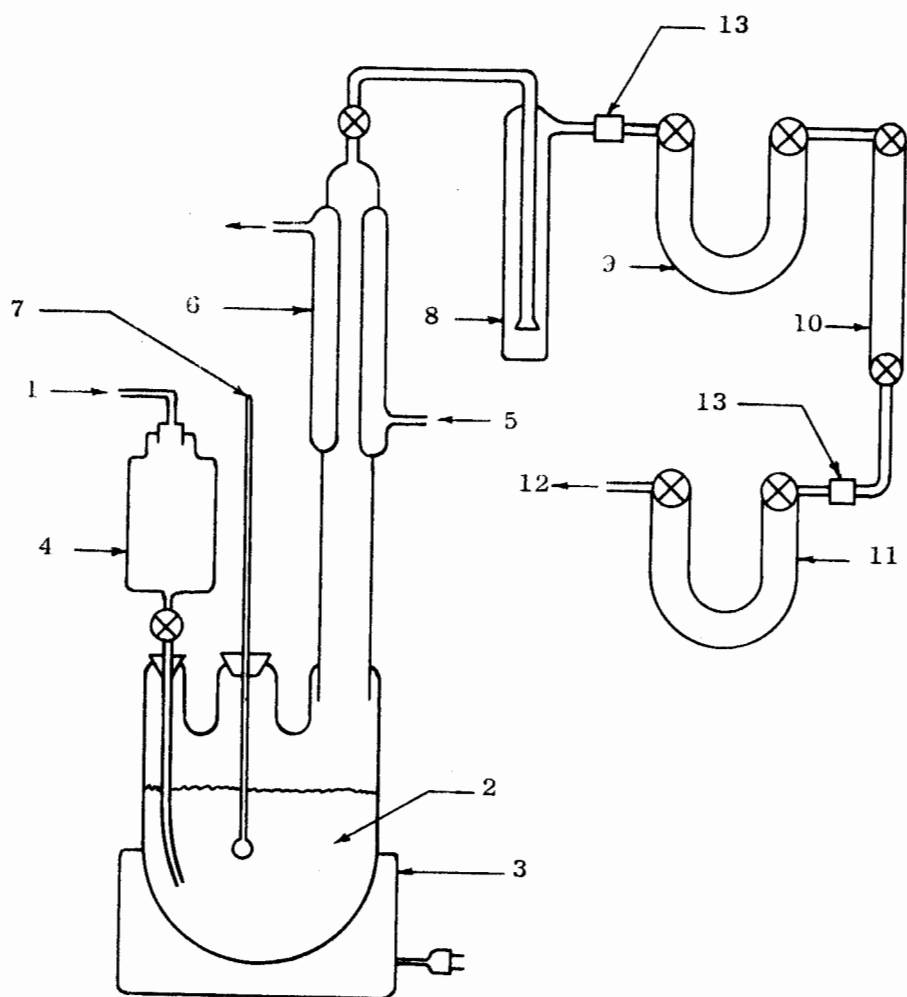
The rest of the reaction gases were oxidized over cupric oxide at 380°C and the resulting water and carbon dioxide collected in Anhydrone and Caroxite traps respectively. Negative colorimetric tests for carbon monoxide were obtained when it was passed over the oxidant, proving complete oxidation.

The measurement of these gases was repeated thrice at 100°C with Pittsburgh seam coal as a check on reproducibility, with results shown in Figure 4. (see page 21).

#### E. Analysis of Reaction Products Contained in Liquid Extracts

Both the dilute sulfuric acid filtrate and the wash water contained small amounts of carbonaceous extracts. The amounts of these materials were too small to allow a qualitative examination. However, in order to complete the carbon balance, they were quantitatively analyzed for carbon in the apparatus described in Figure 2. The carbonaceous material was oxidized by an excess of concentrated sulfuric acid and chromic acid at 250°C, and the resulting carbon





- |  |                                    |
|--|------------------------------------|
| 1. Pure nitrogen inlet                     | 7. Thermometer                     |
| 2. Concentrated sulfuric acid-chromic acid | 8. Concentrated sulfuric acid trap |
| 3. Heater                                  | 9. Anhydrous trap                  |
| 4. Dropping funnel                         | 10. Drierite trap                  |
| 5. Water inlet                             | 11. Caroxite trap                  |
| 6. Condenser                               | 12. Nitrogen outlet                |
| 13. Rubber connective tubes                |                                    |

Apparatus for the Oxidation of Liquid Soluble Products

Figure 2

dioxide collected in a Caroxite trap. A blank with a known amount of benzoic acid gave a 99% recovery of the carbon.

#### IV. RESULTS AND DISCUSSION

##### A. General Observations

As sulfuric acid was added, the coals passed through several alternations of physical appearance. At first the sulfuric acid was absorbed completely, leaving the coal swollen but dry. Further addition produced a damp, sticky gel. This was followed by a thick dispersion of coal in sulfuric acid, above the surface of which a puffy crust formed. At this stage it was possible to maintain an even dispersion by violent agitation. Finally, the addition of more sulfuric acid gave an even dispersion of coal. When 400 ml of sulfuric acid were added to about 3 g of coal, a  $4^{\circ}$  -  $6^{\circ}\text{C}$  rise in temperature and the evolution of detectable amounts of sulfur dioxide occurred. Preliminary experiments confirmed the production of water, carbon dioxide, and carbon monoxide.

The dilute sulfuric acid resulting from stopping the reaction with ice and filtering was colorless. Fractional distillation of the acid resulted in two components, one of which boiled at  $98^{\circ}$  -  $100^{\circ}\text{C}$  and smelled of acetic acid, and the other of which was a pale yellow, reconcentrated sulfuric acid. In an experiment at  $25^{\circ}\text{C}$  on Pittsburgh seam, high volatile bituminous A coal (HVA), half of the total carbon contained in the dilute sulfuric acid was shown to be acetic acid from the  $98^{\circ}$  -  $100^{\circ}\text{C}$  fraction, and half was carbonaceous material from the reconcentrated sulfuric acid. Upon cooling the latter, small amounts of colorless crystals formed. These were found to be

metal sulfates.

The water extracts resulting from washing the products in a Soxhlet extractor contained small amounts of organic materials which imparted colors ranging from straw to dark brown, depending on the quantities present. These amounts increased with the temperature of reaction and depended to a lesser extent on the time of extraction. Extraction times from 5 to 10 days were necessary to remove all the sulfuric acid, depending on the sample.

The washed product was highly hygroscopic and was dried only with difficulty. It was much harder than the original coal and was porous in appearance.

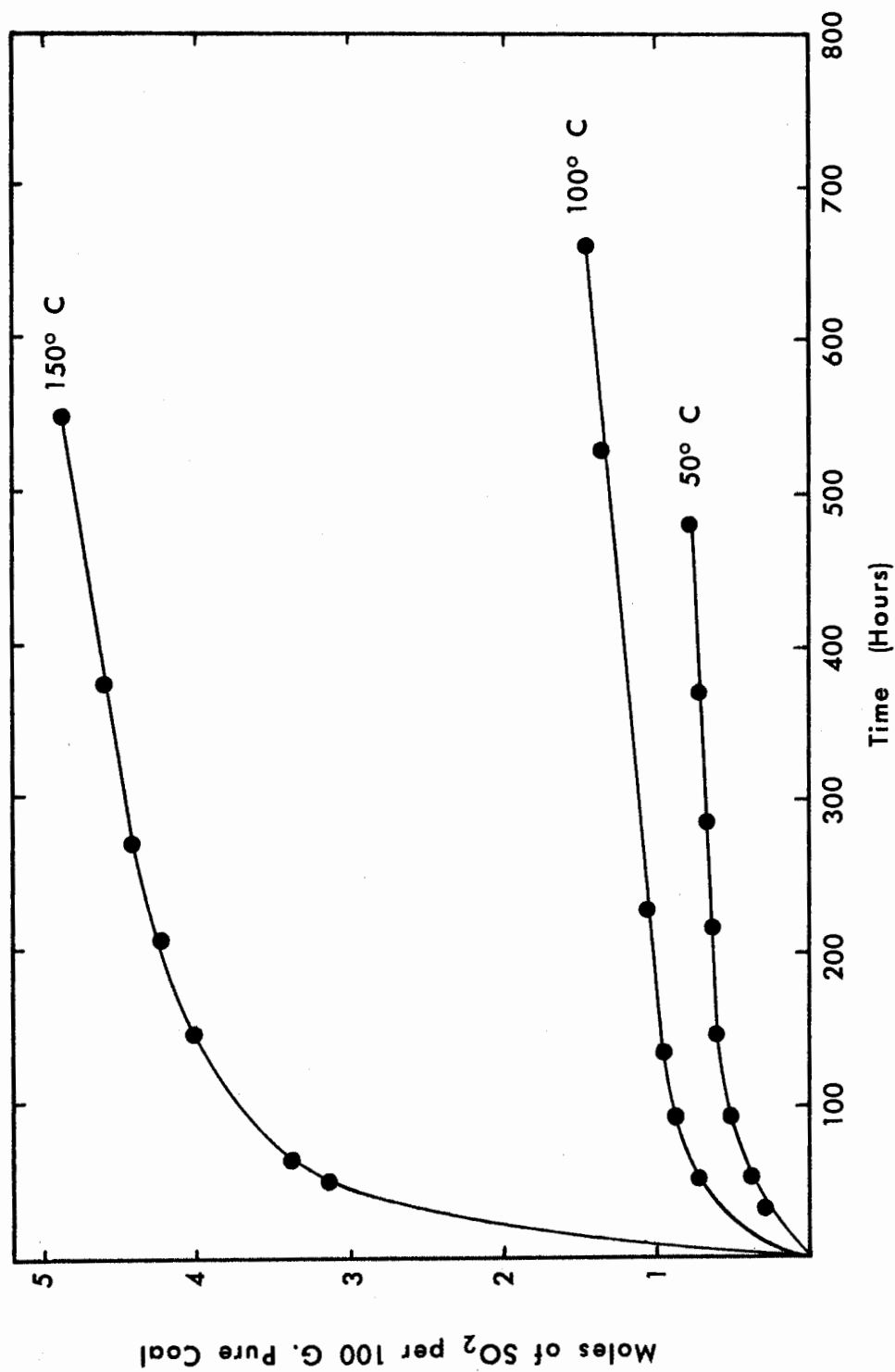
#### B. Interpretation of Elemental Analyses<sup>1</sup>

Since several reactions were run simultaneously it was impossible to stop all reactions at the same point because of the length of time necessary to process the reacted product. However, it may be seen from Figures 3, 4, 5, and 6, that the reactions level off greatly after about 250 hours, and thus the runs are similar although somewhat different in length.

Table I shows the analyses of the raw and reacted coals together with the times and temperatures of treatment. The percentages of mineral matter in the raw coals have been corrected for pyrite loss

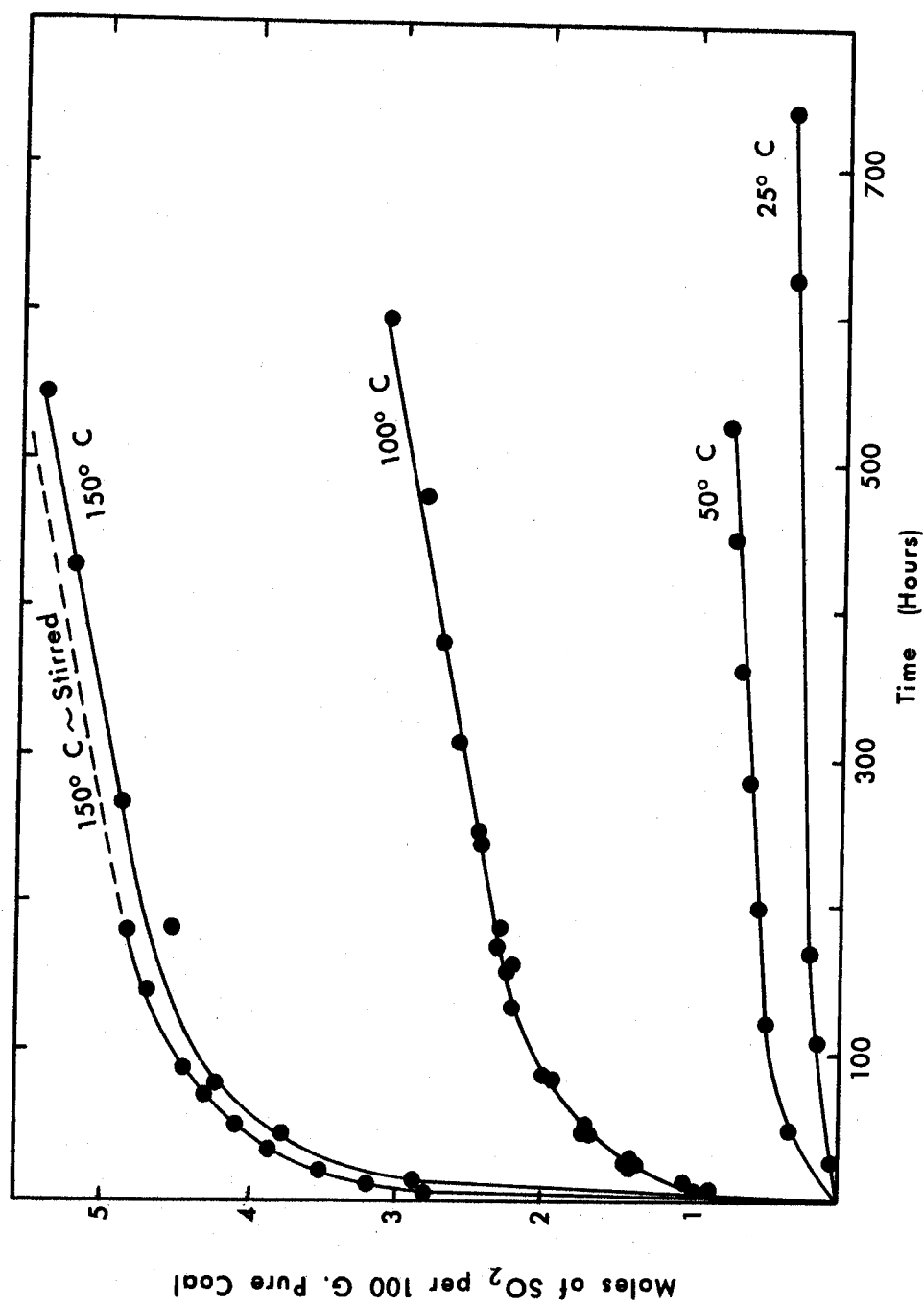
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<sup>1</sup>The analysis of the raw and sulfonated coals was carried out by Dr. Franz Pascher, Mikroanalytisches Laboratorium, 54 Buschstrasse, Bonn, Germany.



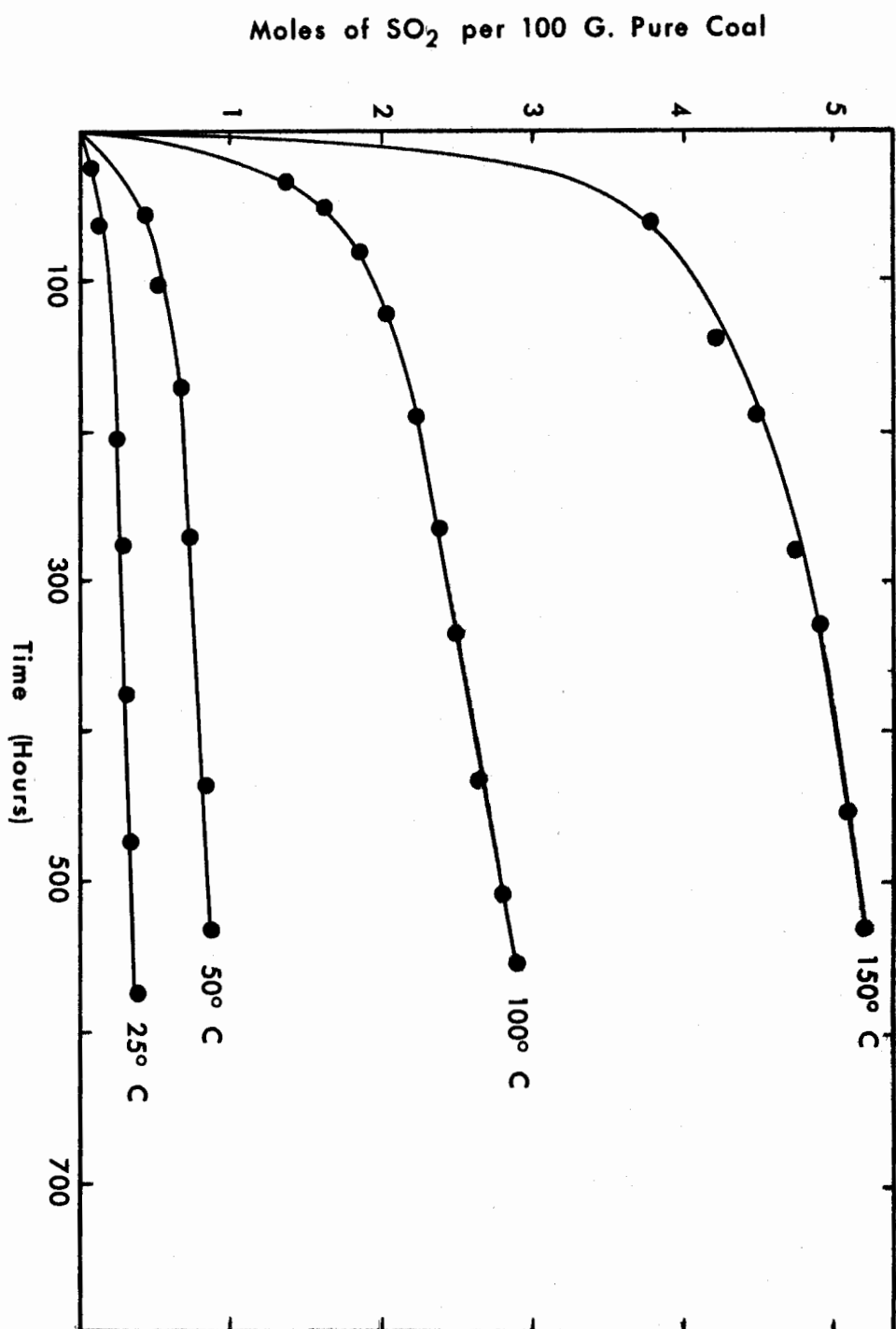
EVOLUTION OF SULFUR DIOXIDE FROM LOW VOLATILE COAL

Figure 3



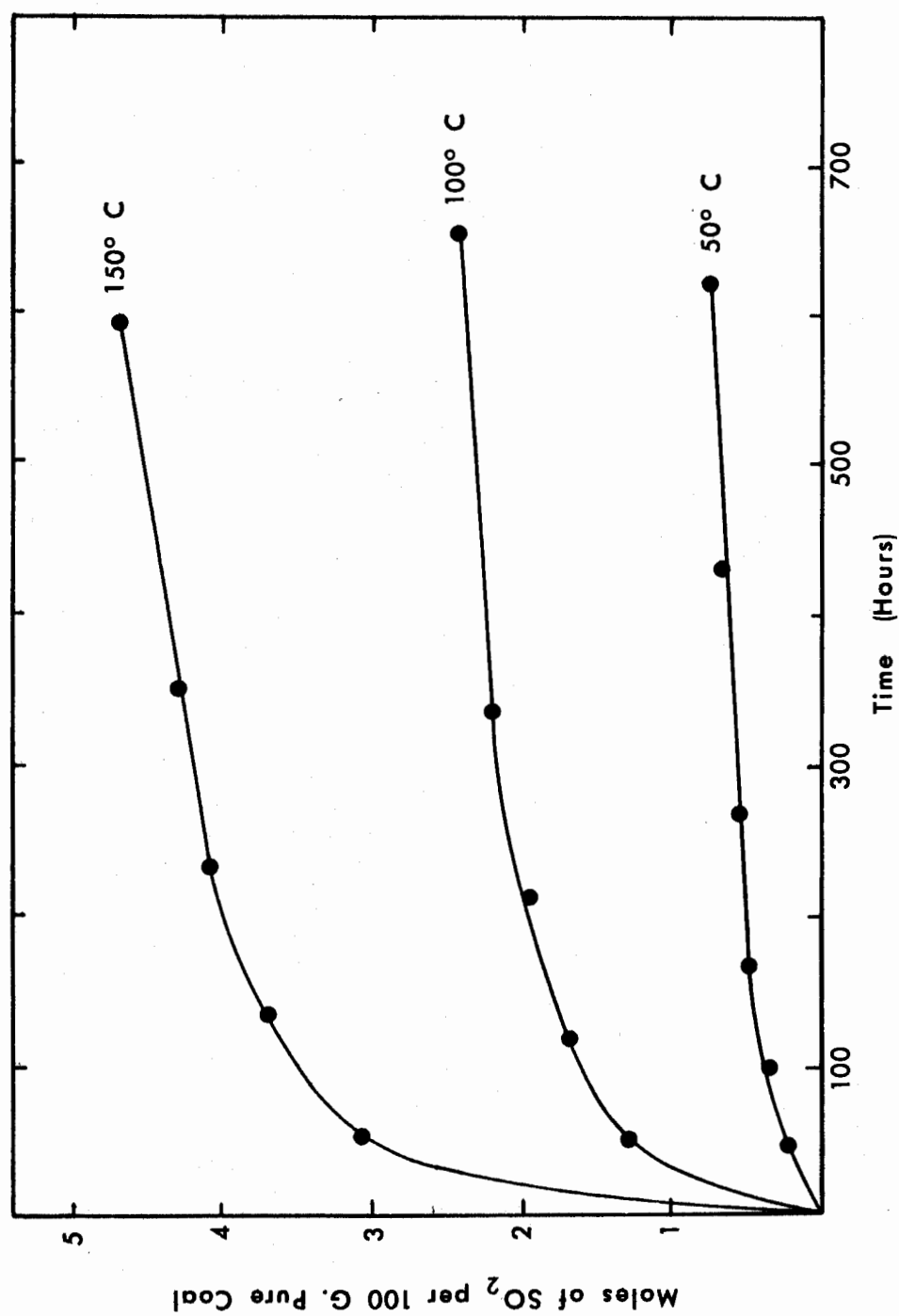
EVOLUTION OF SULFUR DIOXIDE FROM HIGH VOLATILE A COAL

Figure 4



EVOLUTION OF SULFUR DIOXIDE FROM HIGH VOLATILE C COAL

Figure 5



EVOLUTION OF SULFUR DIOXIDE FROM SUB-BITUMINOUS B COAL

Figure 6



TABLE I  
ANALYSES OF RAW AND SULFONATED COALS ON A DRY BASIS

Coal	Time (hours)	Temperature °C	Moisture* %	Ash %				Moisture - Free Basis				% O (by diff.)
				%	% C	% H	% N	% S	% O	% S	% O	
LVC	---	raw	0.1	10.4	80.5	4.1	1.8	0.2	3.0			
	480	50	15.1	6.2	63.3	3.8	0.9	7.1	18.7			
	662	100	7.6	5.4	64.4	3.0	1.1	7.0	19.1			
	531	150	10.8	4.3	60.0	2.5	1.4	3.4	28.4			
HVA	---	raw	0.0	11.0	74.0	4.9	1.7	0.5	7.9			
	747	25	6.3	6.8	60.7	3.2	1.9	5.8	21.6**			
	530	50	6.8	6.7	61.1	2.8	1.7	6.1	21.6**			
	600	100	9.5	4.9	60.4	2.4	1.0	6.2	25.1			
	548	150	14.3	5.7	58.6	2.3	1.2	4.1	28.1			
HVC	---	raw	1.4	5.7	77.1	4.9	2.1***	0.1	10.1**			
	574	25	12.7	4.2	62.1	3.3	1.6	7.3	21.5			
	532	50	10.4	3.7	63.2	4.3	1.8	7.5	19.5			
	557	100	8.6	5.3	60.7	2.2	1.8	5.3	24.7			
	558	150	12.9	4.2	62.5	3.2	2.0	3.7	24.4			
Sub-bit B	---	raw	5.3	7.8	70.4	4.7	1.6	0.1	15.4			
	623	50	5.5	3.2	61.1	3.0	2.2	6.1	24.5			
	653	100	14.0	3.7	60.9	2.5	1.6	3.9	27.5			
	594	150	13.5	4.1	59.6	1.6	1.5	2.8	30.5			

\* Removed before analysis

\*\* Direct determination

\*\*\* By difference

and loss of moisture from the clay according to the Parr (25) formula. The mineral matter of the coals was assumed to consist entirely of pyrite and clay. These corrections increase the ash content, and correspondingly decrease the oxygen, hydrogen and sulfur contents. Broadhead (26) found that sulfuric acid has no appreciable effect on pyrite below 100°C; therefore loss in weight of ash due to the pyrite was compensated for in the 25°C and 50°C runs. Since sulfuric acid is a strong dehydrating agent and reacts extensively with the mineral matter of the coal at these temperatures, the water loss due to the dehydration of the clays was not believed to have occurred during ashing. Thomas (27) found complete reaction of the pyrite at 100°C, so ash corrections were not made for runs at or above this temperature. Reaction of sulfuric acid with the mineral matter of the coal accounts for the production of the metallic sulfates mentioned earlier. All of the samples in Table I were dried for 24 hours at 100°C under vacuum in order to remove most of the moisture. Before analysis the samples were dried to constant weight. The moisture physically removed from the samples before analysis is recorded in Table I. The percentages of ash, C,H,N,S, and O, are given on a moisture-free basis.

In Table II the ash values are given in grams lost per 100 g of raw coal. It is seen that the amount of ash lost increases regularly with increase in temperature and with increase in ash content of the raw coals. Two exceptions in the trend are noted, one with the Illinois high volatile bituminous C coal (HVC) at 100°C, and

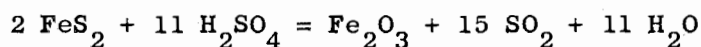
TABLE II  
GAIN OR LOSS OF ELEMENTS FROM 100 G RAW COAL

	Temperature °C	Ash g. lost	g-atoms C lost	g-atoms H lost	g-atoms N lost	g-atoms S gained	g-atoms O gained (net)	g-atoms O used in oxid. calcd. from SO <sub>2</sub>
LVC	50	2.5	0.04	+0.68	0.05	0.27	1.3	0.68
	100	4.1	0.53	0.70	0.04	0.25	1.2	1.23
	150	6.1	1.8	1.7	0.03	0.10	1.6	4.27
HVA	25	3.1	0.28	1.3	+0.04	0.20	1.1	0.34
	50	3.4	0.32	1.7	+0.02	0.20	1.1	0.74
	100	5.7	0.77	2.9	0.04	0.19	1.2	2.39
	150	6.1	1.9	3.0	0.04	0.10	1.0	4.62
HVC	25	0.55	0.04	0.73	0.01	0.28	1.0	0.33
	50	1.7	0.64	0.18	0.01	0.25	0.71	0.83
	100	+0.10	0.86	2.5	0.01	0.18	1.1	2.69
	150	1.83	1.6	1.9	0.02	0.11	0.78	4.87
Sub-bit B	50	4.5	0.46	1.5	+0.06	0.20	0.66	0.68
	100	4.0	0.60	2.1	+0.01	0.12	0.82	2.22
	150	4.8	2.2	3.5	0.03	0.06	0.43	4.24

one with the subbituminous B coal (Sub-bit. B) at 25°C. In both cases these values appear to be high, indicating an error in analysis.

An examination of Table I shows approximately the same drop in carbon content of the products regardless of the temperature of reaction. However, when these values are compared with the per cent yields and the per cent carbon remaining in the product as shown in Table III, it is seen that an increasing amount of carbon is removed as the reaction temperature is raised. A better way to look at the amounts of elements gained or lost by reaction is to calculate the weight gain or loss of each element by 100 g of coal. These weights are converted into gram atoms of each element gained or lost (see Table II). The ratio of the weights is then proportional to ratios of atoms. This will be useful in later discussion.

In comparing the gain or loss of elements it is useful to calculate the total gram atoms of oxygen used in oxidizing the coals. These values are calculated from the moles of sulfur dioxide evolved during the reaction per 100 g of dry, mineral-matter-free coal versus time shown in Figures 3, 4, 5, and 6. In the cases of reactions at or above 100°C the amount of sulfur dioxide liberated by reaction of the pyrite with sulfuric acid is compensated for, according to the reaction:



These values are given in Table II.

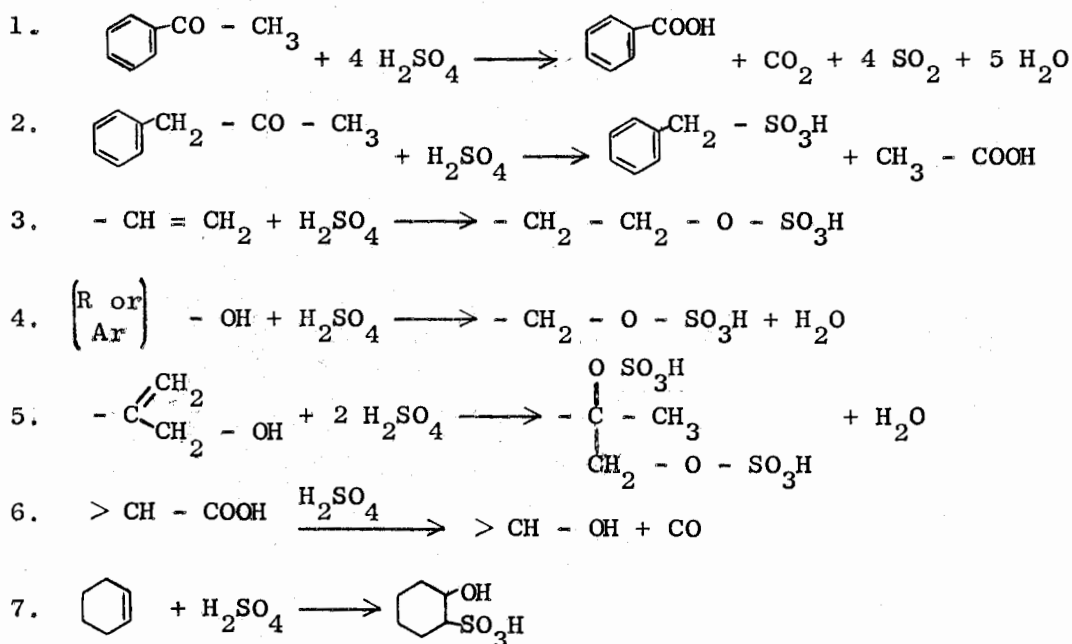
Through a consideration of the properties of sulfuric acid as an oxidizing agent, the functional groups that might conceivably be

TABLE III  
DISTRIBUTION OF CARBON IN PRODUCTS, % OF ORIGINAL CARBON OF COAL

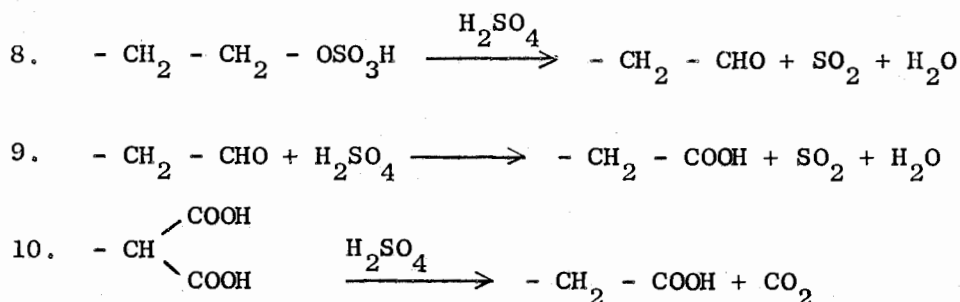
Coal	Temperature °C	% Yield	% C in Product	% C in CO <sub>2</sub>	% C as CO, Hcs.*	% C in liquid extracts	Total % C identified
LVC	50	126.4	99.2	0.6	0.3	1.2	101.3
	100	115.1	90.8	1.2	0.2	4.9	97.1
	150	99.1	73.8	13.3	0.3	13.5	100.9
HVA	25	116.4	95.2	0.1	0.1	3.6	99.0
	50	114.7	94.1	0.3	0.1	3.9	98.4
	100	107.1	87.5	4.7	0.9	7.0	101.1
	150	86.6	69.3	17.2	0.8	14.5	101.8
HVC	25	123.2	98.1	0.4	0.1	3.1	101.7
	50	109.8	90.1	1.1	0.4	8.6	100.2
	100	109.9	86.8	5.1	0.2	8.1	100.2
	150	91.6	74.3	17.8	0.4	9.3	101.8
Sub-bit B	50	106.1	92.3	0.8	0.5	5.2	98.8
	100	103.9	90.2	5.4	0.6	4.7	100.9
	150	73.1	61.9	29.3	0.7	7.8	99.7

\* Hcs. = hydrocarbons

present in coal with which it might react, and the amount of oxidation which took place, it is possible to limit the number of feasible reactions. To the best of present knowledge the following type reactions are possible at 25°C and 50°C.

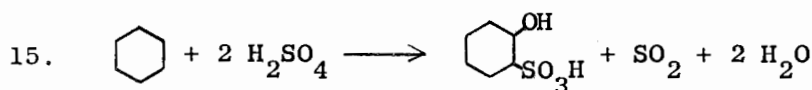
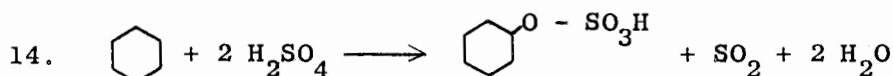
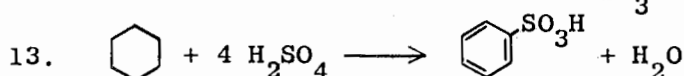
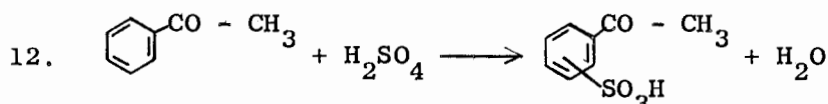
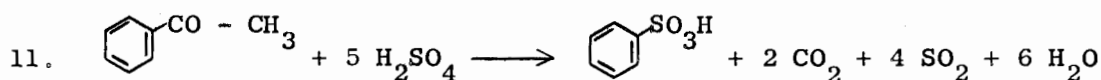


The following reactions are more likely to occur at 50°C:



Considering the small amount of carbon removed from the coals and the mild oxidizing action of sulfuric acid at these temperatures, the production of carbon monoxide and carbon dioxide probably results from primary reactions involving the coal molecule. At 100°C and higher,

the oxidative attack of sulfuric acid would be expected to eliminate a greater amount of side groups, and these in turn would be oxidized. This is evidenced in Figures 3 through 10. At these temperatures the evolution of carbon dioxide, carbon monoxide, and sulfur dioxide must be considered to be the result of secondary reactions. The initial rapid rise in moles of gaseous products evolved indicates a diversity of reactions. It may be seen from the amount of total oxidation in comparison to the amount of oxygen introduced into the coal in Table II that considerable oxidation of severed side groups must be taking place. With the advent of higher temperatures other reactions such as the following become possible:

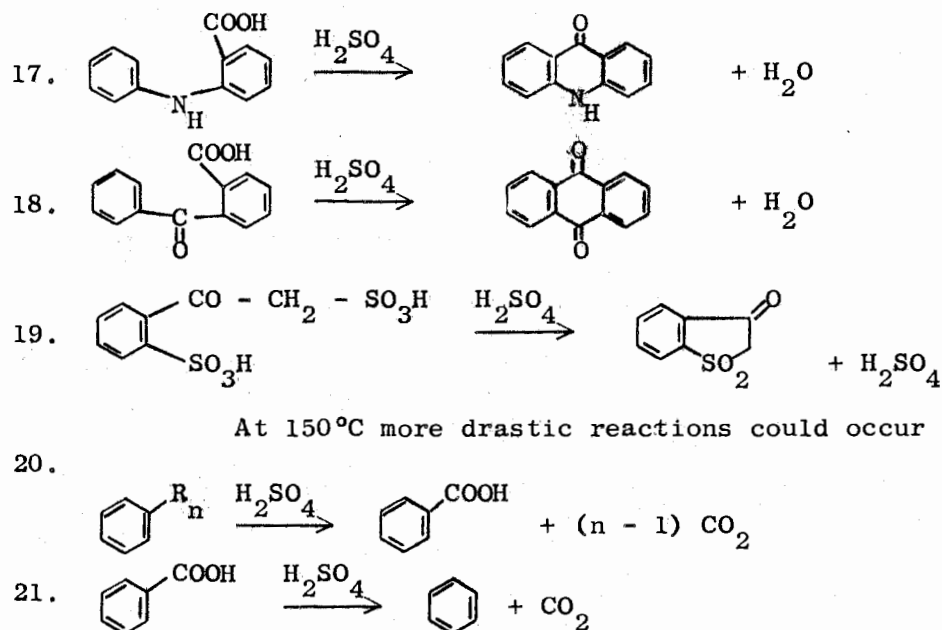


Phenols are sulfonated very readily following reaction (16).

However these structures are known to be very susceptible to oxidation and are likely to be oxidized by sulfuric acid as well as being sulfonated. No typical equations can be given for this oxidation

because of the complexity of the reactions and the wide variety of products that can result.

Condensation reactions are also possible, and increasing losses of hydrogen enhance this possibility.



Although there is no direct evidence for their occurrence, Thomas (27) has discussed the possibility of the reactions mentioned. Although all of them may contribute to some extent, a few stand out in importance. It will be shown that at low temperatures of 25°C and 50°C the most important reactions appear to be the addition of sulfuric acid to double bonds and the esterification of hydroxyl groups as well as the oxidative addition of sulfuric acid to reactive groups, reactions 3, 4, and 2, respectively. At these temperatures oxidation plays a minor role. At temperatures of 100°C and above,



oxidation is the predominant end result, although the other reactions probably occur as intermediate steps. Since much of the sulfur added at low temperatures is eliminated with increasing temperature, the production of stable sulfur groups such as aryl sulfonic acids must be small.

### C. Reaction Trends of the Individual Coals

1. Low volatile bituminous coal. With LV coal the run at 50°C is peculiar in that the product is the only one in which hydrogen seems to have been added (see Table II). The per cent of total carbon remaining in the product is 99.2% as shown in Table III, indicating that only 0.8 % is removed by oxidation. The gram atom ratio of hydrogen, sulfur, and oxygen added approximates to  $\text{H}_2\text{SO}_4$ ; that is, 0.6, 0.3, and 1.3 gram atoms respectively (see Table II). This suggests that addition of sulfuric acid to olefinic double bonds as illustrated in reactions 3 and 7 is the principal reaction. However, it should be borne in mind that polynuclear aromatics can react with normally substituting reagents by first adding the reagent across a double bond and then eliminating water or other small molecule at a somewhat higher temperature. This would account for the addition of hydrogen, sulfur, and most of the oxygen. A limited oxidation could occur which would produce the small amounts of carbon monoxide, carbon dioxide, sulfur dioxide, and liquid soluble extracts, which are observed. This oxidation must have taken place without loss of hydrogen. The reactions of

small contribution would correspondingly be limited to reactions 6, 9, and 10.

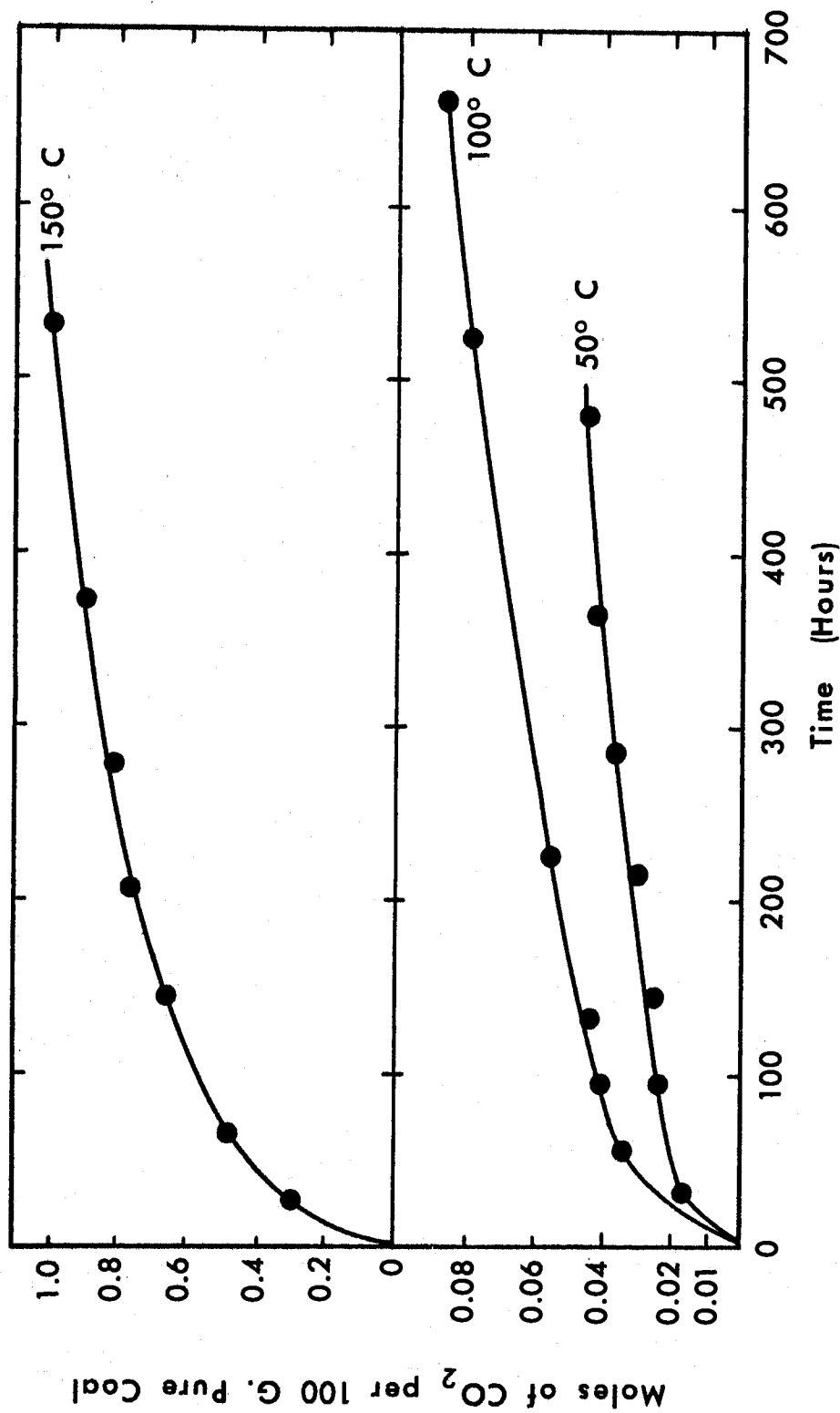
Less than twice as much total oxidation occurred with the LV coal at 100°C as compared to 50°C. About twice as much carbon dioxide was liberated. More carbon was removed from the coal, and the per cent carbon in the liquid extracts increased. Hydrogen was lost, and the amounts of sulfur and oxygen gained by the coal were lower in comparison to the run at 50°C. In general these runs are similar except that more oxidation took place at 100°C. Loss of sulfur and oxygen could be explained by reactions 8, 9, and 10.

The reaction of LV coal at 150°C is markedly different from the reactions at lower temperatures. Large amounts of sulfur dioxide and carbon dioxide are liberated. The amount of sulfur retained by the coal drops to one-third of that added at 50°C while the amount of oxygen increases. Apparently reactions similar to 8, 9, 10, 20, and 21 take place to a great extent. It is likely that a good proportion of the sulfur retained by the highly aromatic LV coal at 150°C is in the form of stable aryl sulfonic acids or oxidation resistant heterocyclics as illustrated in reactions 11, 12, 13, 16, and 19 respectively.

With stronger oxidizing conditions more reactions are possible and it is increasingly difficult to reduce reaction possibilities. Since the raw coal contains only 3.0% oxygen one would not expect the esterification of hydroxyl groups to be of great importance. The presence of 4.1% hydrogen in the raw coal indicates that most

of the side groups are paraffinic or olefinic in nature. This would explain why the coal was difficult to oxidize except at the highest temperature. The amounts of carbon dioxide, sulfur dioxide, and carbon identified in liquid extracts increases greatly at 150°C. This would be expected from a high rank coal where aromatic nuclei are connected by paraffinic or olefinic linkages and only the strongest oxidizing conditions could break them. Because of increasing hydrogen losses condensation reactions of the type 17 and 18 seem likely. Per cent yields drop off with stronger oxidizing conditions and ash loss increases regularly with increase in temperature. The production of carbon monoxide remains constant at all temperatures. Nitrogen loss is small indicating that most of it is contained in stable aromatic rings. Figure 7 shows the moles of carbon dioxide per 100 g of pure coal produced with time. The evolution of carbon dioxide is indicative of the extent of oxidation and has the same general characteristics as the plot of moles of sulfur dioxide per 100 g pure coal produced versus time (Figure 3). These graphs indicate a rapid initial reaction which becomes more pronounced with increasing temperature and which levels off at about 300 hours.

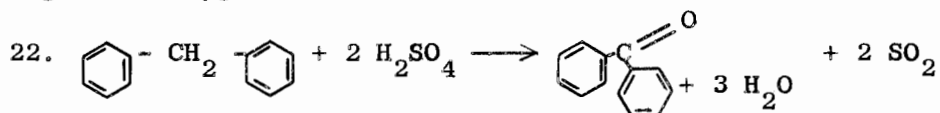
2. High Volatile Bituminous A Coal. With HVA coal at 25°C a small amount of carbon is removed as may be seen in Table III. Total oxidation, indicated by the number of moles of sulfur dioxide produced, is small, but large amounts of oxygen and sulfur are added. There is also a significant loss of hydrogen. Reaction 1 can not



EVOLUTION OF CARBON DIOXIDE FROM LOW VOLATILE COAL

Figure 7

contribute to any appreciable extent because only trace amounts of carbon dioxide are produced. Equally small amounts of carbon monoxide indicate the contribution of reactions such as 6. The fact that HVA coal has a low oxygen content reduces the possible amount of esterification of hydroxyl groups. Reaction 2 could be of major importance because most of the carbon removed from the coal is contained in the liquid extracts, and nearly half of this is found to be acetic acid. This would also explain the large loss of hydrogen. The addition of sulfuric acid to olefinic bonds or aromatic bonds of high bond order remains a possibility. Activated benzylic hydrogens such as in reaction 22 would be subject to oxidative attack, thus accounting for further loss of hydrogen and the oxidative gain of oxygen.



In addition, hydro-aromatic systems may be dehydrogenated to aromatic, and polycyclic aromatic molecules oxidized to quinonoid structures.

The reaction of HVA coal at 50°C is similar to the run at 25°C in every respect with the exception of slight additional oxidation. The percentage yields and the gain of sulfur are about the same. Very small amounts of carbon and oxygen are removed from the coal as compared to the run at 25°C. There is a correspondingly small increase in the evolution of carbon dioxide and sulfur dioxide. Apparently therefore, the same reactions occur at 50°C as occur at

25°C.

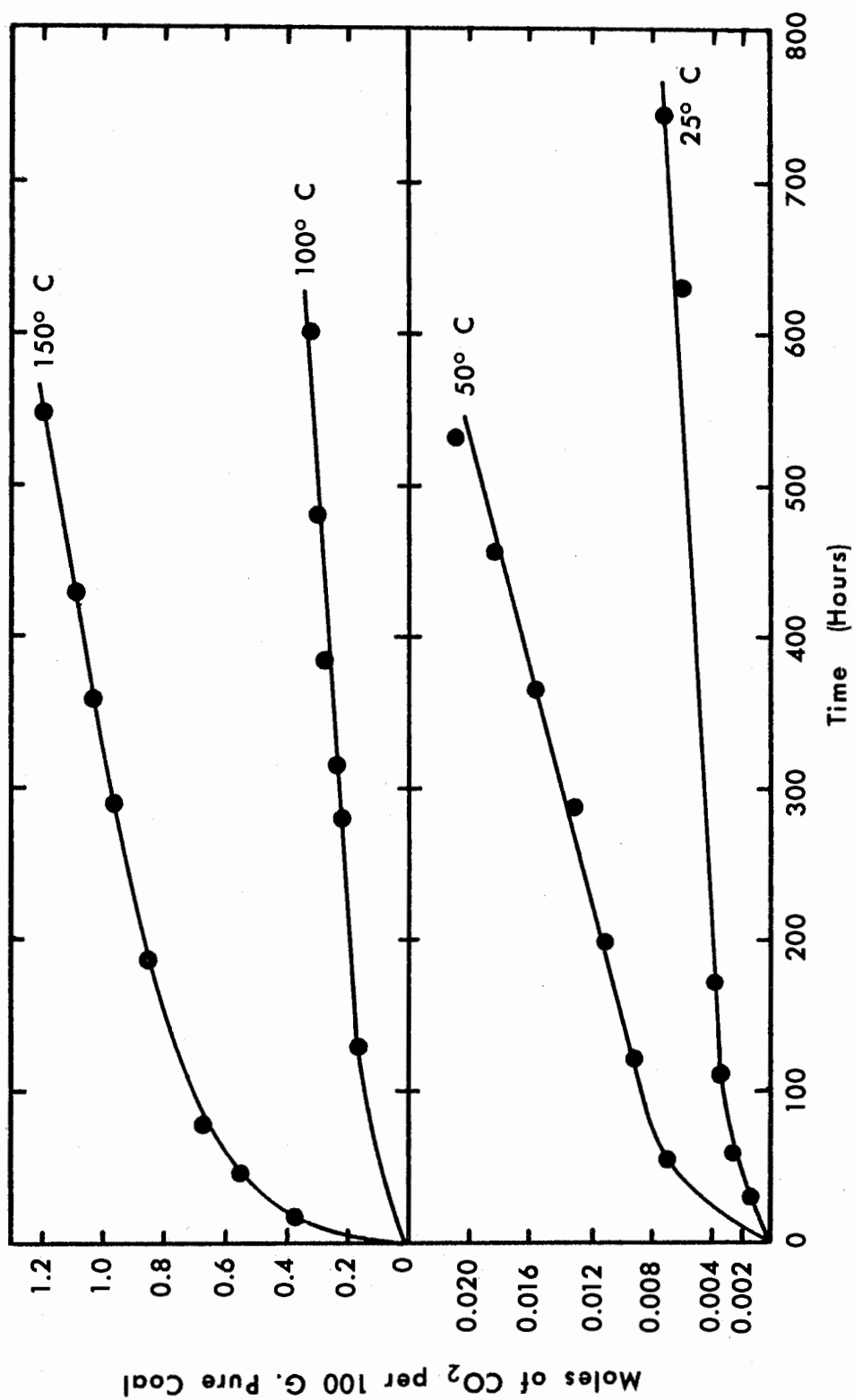
In the case of HVA coal at 100°C there is a dramatic increase in total oxidation over the amount at lower temperatures. The amount of oxygen gained increases while the amount of sulfur added decreases. The values of carbon and hydrogen lost and of carbon retained in liquid extracts are all double those at 50°C. It appears that sulfur is lost with the oxidation of side groups as in reaction 8. The amount of carbon monoxide and hydrocarbons produced increases perhaps due to secondary reactions. A large increase in ash loss is observed since the coal contains over 1% pyrite. Condensation reactions with an accompanying loss of hydrogen are possible. However, since they also involve a loss of oxygen, they may not be extensive at this temperature. Another large increase in total oxidation is observed with the HVA coal at 150°C. Here the amount of oxygen retained by the product drops. This is most likely due to a strenuous type of oxidation as in reactions 20 and 21. The amounts of carbon dioxide and water soluble products rise greatly. The sulfur which was added at 25°C and 50°C is largely eliminated. In this case the oxidative properties of sulfuric acid are clearly predominant.

In general the reaction trend with temperature is clear. Large additions of sulfonic acid and sulfate groups take place at 25°C and 50°C accompanied by slight oxidation. Some sulfur is lost at 100°C and extensive oxidation of side groups takes place. The highly oxidized peripheral groups are eliminated at 150°C together

with a large part of the sulfur which had been added to the coal. Percentage yields and carbon retained by the product drop off accordingly. The evolution of sulfur dioxide as shown in Figure 4 and carbon dioxide as shown in Figure 8 reflects this trend. These graphs show a rapid initial reaction which becomes more pronounced as the temperature is raised. Hydrogen losses follow the extent of oxidation. Very little nitrogen is lost, supporting the hypothesis that most of the nitrogen of coal exists in stabilized cyclic structures. Ash losses show a relatively large increase at 100°C, the temperature at which pyrite is destroyed. This is expected because the raw coal contained over 1% pyrite.

3. High Volatile Bituminous C Coal. With HVC coal at 25°C very little carbon is removed from the coal. More carbon dioxide is evolved than with HVA coal at 25°C, enhancing the possibility of a small contribution from reaction 1. A larger contribution from reaction 2 is likely because 86% of the carbon lost appears in the liquid extracts. Esterification of hydroxyl groups is more probable than in the case of HVA coal because the raw HVC coal contains rather more oxygen as may be seen in Table I. The addition of sulfuric acid to double bonds is also possible.

The HVC coal gains the same amount of sulfur at 50°C as at 25°C, probably according to the same reactions. However, oxygen is lost. This could be due to reactions such as 10. It is also possible that reaction 2 is promoted to the same extent that the product from reactions 3 and 4 is destroyed via reaction 8. An in-



EVOLUTION OF CARBON DIOXIDE FROM HIGH VOLATILE A COAL

Figure 8



crease in total oxidation, liquid soluble products, and amount of carbon removed from the coal, accentuates this possibility.

In the reaction of HVC coal at 100°C, a large rise in total oxidation is noted. There is a corresponding increase in the amount of oxygen gained by the coal. The amount of liquid extracts decreases. This would be expected from a low rank coal because the peripheral groups are more easily oxidized to form carbon dioxide. However, the general indication is that the side groups are oxidized, but not eliminated. This is evidenced by the fact that a relatively small additional amount of carbon is removed from the coal in comparison to the reaction at 50°C. Sulfur is removed from the coal, most likely through reaction 8.

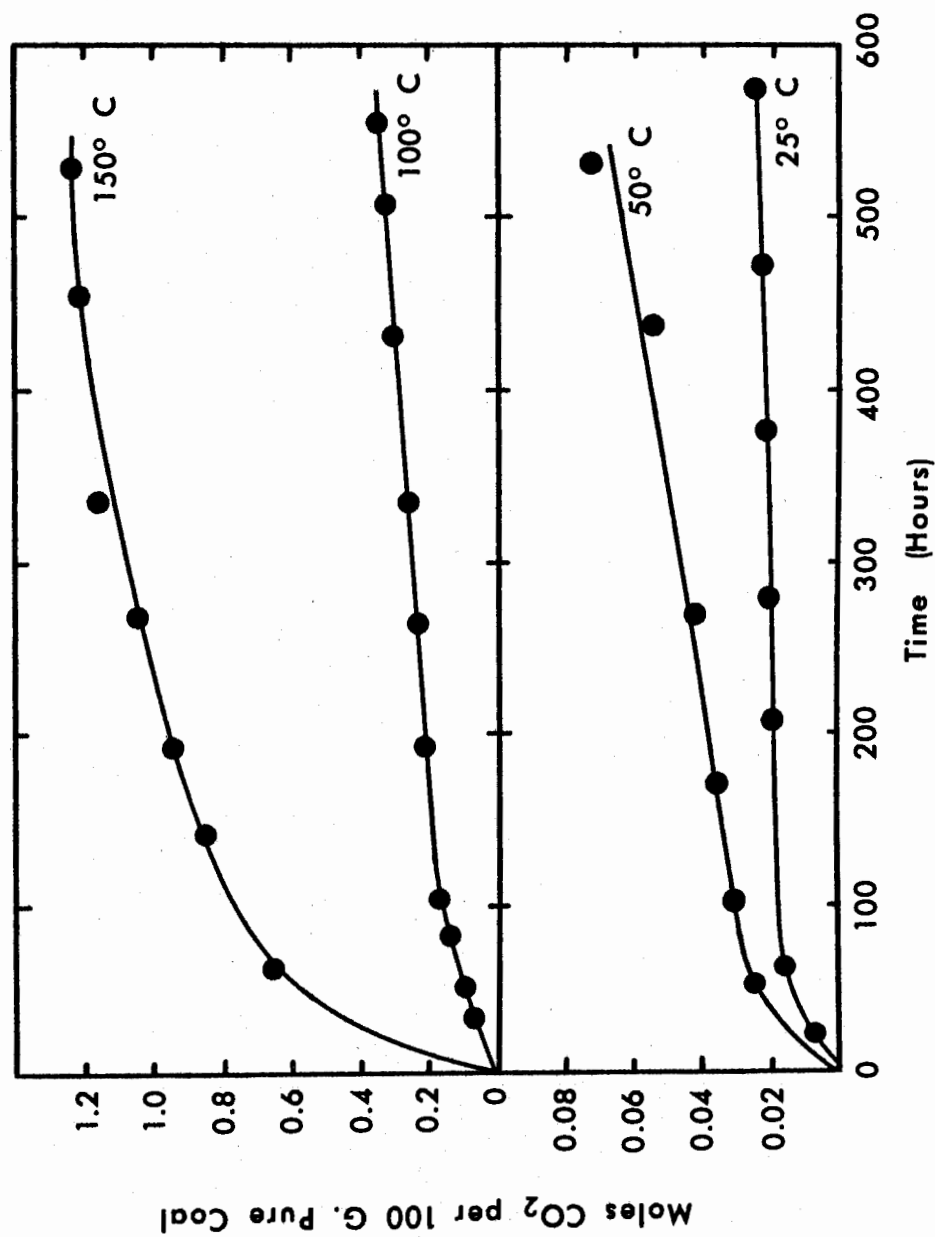
Upon reaction at 150°C, the HVC coal undergoes a large total oxidation. Oxygen content of the product is reduced compared to that at 100°C and there is considerably more carbon removed from the coal. This indicates the oxidative splitting-off of peripheral groups. The sulphur which was added at lower temperatures is largely eliminated, suggesting that it was attached to eliminated groups or was oxidized as in reaction 8.

Consideration of all of these factors suggests a probable sequence of reactions. Sulfur is added at 25°C according to some or all of reactions 2, 3, and 4, with a small contribution from reaction 1. Generally the same reactions occur at 50°C, but reactions 1 and 2 are of somewhat more importance. Reaction 8 probably takes place to some extent. At 100°C considerable oxidation of the side groups

takes place and sulfur is removed. There is additional attack on the more susceptible liquid soluble extracts. Severe oxidation of the coal occurs at 150°C resulting in almost complete removal of the sulfur which was added at lower temperatures. Additional oxidation lowers the yield of liquid extracts. Loss of nitrogen is small and somewhat lower than with the other coals; in spite of the fact that the raw HVC coal contains a larger amount of nitrogen. The loss of hydrogen is irregular and difficult to explain.

Figure 9 shows the moles of  $\text{CO}_2$  per 100 g pure coal evolved with time. Slightly more  $\text{CO}_2$  is evolved at each temperature than in the case of HVA coal, but in general the curves are similar. Ash loss is small. This is expected since the raw coal contained little ash.

4. Subbituminous B Coal. With sub-bit. B coal at 50°C, 7.7% of the carbon is removed from the coal (see Table III). One would expect oxidative attack on a low rank coal even under mild conditions, owing to its more highly phenolic nature. Most of the carbon which is removed is found in the liquid extracts. Only small amounts of carbon dioxide are evolved indicating that the main course of oxidation is to cleave reactive peripheral groups. Sulfur and oxygen are both added to the coal. Because of the paraffinic nature of subbituminous coal and the large amounts of functional groups as evidenced by the 14.3% oxygen in the raw coal, any of reactions 1 through 10 could occur. The reactions producing carbon dioxide, carbon monoxide, and



EVOLUTION OF CARBON DIOXIDE FROM HIGH VOLATILE C COAL

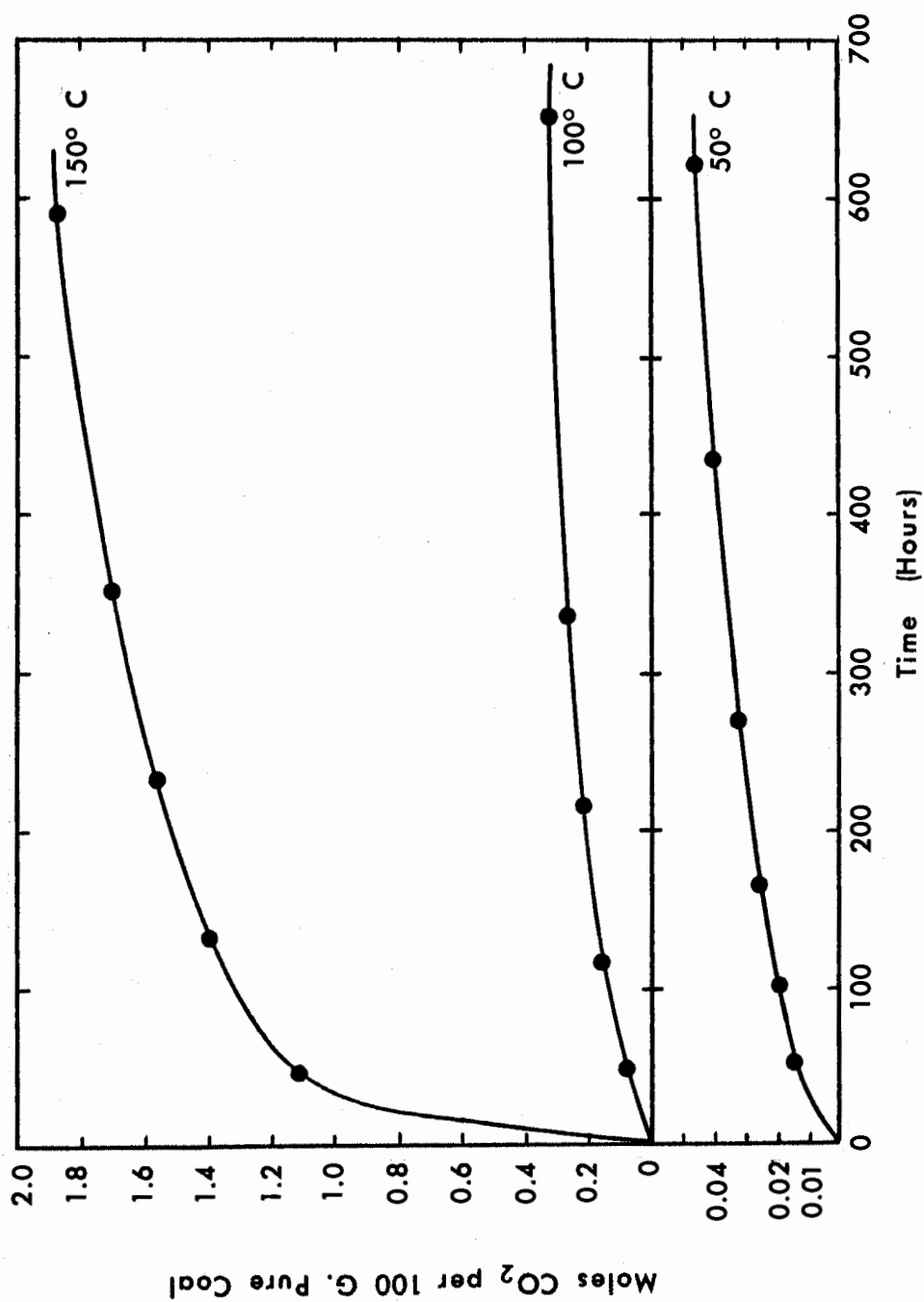
Figure 9

sulfur dioxide, are thought to be of lesser importance because these gases are not produced to a great extent in the reaction.

Little additional carbon is removed from the sub-bit. B coal at 100°C as compared to the reaction at 50°C. However, the coal gains more oxygen and the amounts of carbon dioxide and sulfur dioxide evolved rise markedly. The quantity of liquid extracts decreases, indicating an oxidative attack to produce carbon dioxide. Sulfur is lost, probably owing to the severing of peripheral groups as well as to reactions such as 8. Loss of hydrogen increases, indicating condensations or the elimination of side chains which react further.

When the temperature is raised to 150°C, the reaction of sub-bit. B with sulfuric acid evolves large amounts of sulfur dioxide and carbon dioxide. Less oxygen is gained than at lower temperatures, indicating the oxidative removal of highly oxidized side chains. A large proportion of the sulfur which had been added was removed.

Nitrogen loss with sub-bit. B at various reaction temperatures is small. This indicates that nitrogen is bound up in stabilized cyclic structures even in the low rank coals. The amounts of liquid soluble products do not increase greatly with temperature. This is to be expected since the peripheral groups eliminated from sub-bituminous coal should be more susceptible to oxidation. This susceptibility is confirmed by a large increase in the evolution of carbon dioxide at temperatures of 100°C and 150°C as shown in Figure 10. The large amounts of oxygen in the raw coal increase the pos-



EVOLUTION OF CARBON DIOXIDE FROM SUB-BITUMINOUS B COAL

Figure 10

sibility of sulfuric acid reacting with hydroxyl groups at 50°C. Higher temperatures promote the oxidative removal of sulfur. Production of carbon monoxide remains constant.

#### D. General Reaction Trends

The total amount of oxidation that takes place at 100°C and 150°C, as indicated by the moles of sulfur dioxide evolved in Figures 3 to 6, is similar for the high volatile bituminous and sub-bituminous coals. One would expect a trend towards higher oxidation with decreasing rank; however the higher oxygen content of lower rank coals may make a lower stoichiometric consumption of oxygen necessary for the conversion to acidic products. The total oxidation that takes place at 50°C and 25°C is about the same regardless of the rank of coal. The LV coal is oxidized less at 100°C and 150°C than any of the other coals because it is highly aromatic in nature and more resistant to the attack of a mild oxidant such as sulfuric acid.

For the HVA, HVC and sub-bit. B coals, the same trend appears in the addition of oxygen and sulfur. At 25°C large amounts of sulfur and oxygen are added to the coals. This is thought to be due to the addition of sulfuric acid to double bonds, the esterification of hydroxyl groups by sulfuric acid, and/or the oxidative addition of sulfuric acid to reactive groups such as in reaction 2. The likelihood of the latter two reactions increases in going from higher rank to lower rank coals. A small amount of oxidation accompanies

all reactions at 25°C. At 50°C the amount of sulfur gained by the coals is about the same as at 25°C; however oxygen is eliminated from the coals. The mild oxidizing action of sulfuric acid would not be expected to attack groups to which sulfuric acid would add. However, certain reactive groups could be destroyed with an accompanying loss of oxygen and hydrogen as exemplified in reaction 10. Reaction 8, which destroys sulfuric acid esters, does not seem to be prevalent at this temperature. At 100°C an increase in oxygen and a decrease in sulfur is observed. At this temperature conditions are strong enough to oxidize peripheral groups, but not severe enough to break them off. A sequence of reactions such as 8 followed by 9 seems likely, with additional oxidation of groups not containing sulfur. At 150°C much of the sulfur and some of the oxygen which had been added to the coals is lost. Sulfur could be lost along with the elimination of peripheral groups or by oxidation as before. The sulfonation of peripheral aromatic groups does not seem likely because these would probably contain oxidized side groups which would deactivate the ring. Apparently extensive sulfonation of the main coal nucleus does not occur since much of the sulfur is eliminated at 150°C and sulfonic acid groups attached to aromatic rings should be stable. LV coal presents a somewhat different situation. Because of the small amount of oxygen contained in the raw coal, the most probable reaction at 50°C is the addition of sulfuric acid to olefinic groups. Some of the sulfur and oxygen added in this manner could be removed oxidatively at

100°C by reactions such as 8. However, the main body of the coal molecule remains resistant to oxidation. At 150°C the aliphatic portion of the coal is attacked, oxygen is added and two-thirds of the sulfur which had been added is lost. Thus most of the sulfur must have been added to olefinic groups although the possibility of aromatic sulfonation reactions remains.

The mineral matter of the coals reacts in increasing amounts with sulfuric acid as the temperature is raised. Coals with a large amount of mineral matter react to a greater degree. Metallic sulfates are produced as a result of these reactions.

The distribution of carbon in the products of the coal-sulfuric acid reaction is important in following the course of the reaction. The carbon contained in the raw coal is identified in the products to an accuracy of  $\pm 2\%$  (see Table II). The carbon contained in the liquid extracts shows a general increase with increase in reaction temperature. One expects increasing susceptibility of the liquid extracts to oxidative attack in going from high to low rank coals. This effect is particularly evident with the HVC and sub-bit. B coals. The liquid extracts at 100°C and 150°C, where extensive oxidation occurs, are in low amounts. Generally the amount of liquid extracts obtained at 50°C, where less oxidation occurs, increases in going from low to high rank coals. However, some oxidation occurs even at this temperature with sub-bit. B coal.

Oxidation of carbon monoxide and hydrocarbon gases over hot



copper oxide produces small amounts of water and carbon dioxide. Carbon monoxide is colorimetrically proved to constitute part of these gases. It is noteworthy, however, that in each case more water is produced than can be accounted for even if the entire amount of carbon contained in the tail gas were present as methane. This discrepancy may be explained by the presence of molecular hydrogen sealed in the pores of the coals, assuming that sulfuric acid reacts to open these pores. This aspect of the research was not pursued further because of its small contribution to the overall coal-sulfuric reaction. The amounts of carbon dioxide produced from carbon monoxide and hydrocarbons were too small to graph.

The amounts of carbon dioxide evolved increase with temperature and with decreasing coal rank. These values together with the moles of sulfur dioxide evolved are related to the total oxidation which took place. Figures 3 to 10 show the moles of sulfur dioxide and carbon dioxide evolved per 100 g of pure coal versus time. The curves rise rapidly until about 250 hours are reached. At this point they level off into a straight line. It is not possible to interpret these curves in terms of a specific reaction type since several reactions probably take place simultaneously to varying degrees.

The amount of nitrogen lost is small in all cases. This supports the hypothesis of Beet (16) that the nitrogen of the coal is contained in stable cyclic structures which are not attacked by

sulfuric acid.

The amounts of hydrogen lost by the HVC coal show no particular trend with temperature. However, a general loss of hydrogen is observed with the other coals as the temperature is raised. The lower rank coals lose the most hydrogen. This also is related to the susceptibility of the lower rank coals to oxidation.

A striking similarity is seen between the reaction of HVA coal and HVC coal. The moles of sulfur dioxide produced at 25°C, 50°C, 100°C and 150°C, which are indicative of the total oxidation, are virtually identical. The HVC coal produces more carbon dioxide at each temperature, probably because of an oxidative attack on the severed peripheral groups. The addition of oxygen and sulfur to the HVC coal follows the same trend as with the HVA coal, but to a slightly more pronounced extent.

The observation of Pictet and Bouvier (4) that the principal reaction of sulfonic acid is oxidation, is confirmed at temperatures above 100°C. This is probably not the case at lower temperatures as previously demonstrated.

The observed attack of sulfuric acid on peripheral groups agrees with the conclusions of Pearson (6). Further attack on aliphatic cyclic system, as illustrated in reactions 13, 14, and 15, probably did not occur at 100°C since sulfur was eliminated at this temperature. These reactions could have occurred as intermediate steps at 150°C, but the products resulting were eventually destroyed by oxidation.

The contribution of aryl sulfonic acid groups is limited to the total amount of sulfur gained by the coals upon reaction with sulfuric acid. At 150°C the amount of sulfur that remains attached to the coal structure is fairly small. This agrees with the findings of the British Department of Scientific and Industrial Research (10) and of Anderson and Jønsberg (24).

## V. CONCLUSIONS

1. The coals used in these experiments react with sulfuric acid at 25°C, 50°C, 100°C, and 150°C to produce a solid product, carbon dioxide, sulfur dioxide, water, acetic acid, liquid soluble carbonaceous products, and small amounts of carbon monoxide, low molecular weight hydrocarbons, and molecular hydrogen.
2. The amount of sulfur dioxide produced is a measure of the amount of total oxidation.
3. At 25°C and 50°C the oxidative effects of sulfuric acid are small. Sulfur is probably introduced by addition of sulfuric acid to olefins or to reactive aromatic systems, the esterification of hydroxyl groups and/or the sulfonation of active peripheral groups (such as methyl ketones) to give alkyl sulphonic acids.
4. At 100°C there is oxidation of peripheral groups and at 150°C these groups are further oxidized, producing carbon dioxide. Oxidation is the principal reaction at or above 100°C. Much of the sulfur which is introduced at lower temperatures is eliminated because of the oxidation of sulfur-containing groups or the carbon framework to which they are attached. One would not expect oxidation of aryl sulfonic acids under these conditions; however there is no direct evidence to indicate the nature of the groups in which the high-temperature-stable sulfur is contained.
5. The carbon atoms removed from the coal during reaction are ac-

counted for in the products. The gain or loss of all elements present in the coals during reaction is quantitatively traced. Through a comparison of the above data with the possible reactions, the number of feasible reactions with each coal at each temperature is limited.

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