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Spontaneous Combustion Studies of U.S. Coals

By Alex C. Smith and Charles P. Lazzara

UNITED STATES DEPARTMENT OF THE INTERIOR

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SPONTANEOUS COMBUSTION STUDIES OF U.S. COALS

By Alex C. Smith[1] and Charles P. Lazzara[2]

ABSTRACT

This report describes laboratory studies conducted by the Bureau of Mines on the spontaneous combustion of U.S. coals. Approximately 11 pct of U.S. underground coal mine fires are attributed to spontaneous combustion. The relative self-heating tendencies of 24 coal samples were evaluated in an adiabatic heating oven. Minimum self-heating temperatures (SHT's) in the oven ranged from 35° C for a lignite and high-volatile C bituminous (hvCb) coal, to 135° C for two low-volatile bituminous (lvb) coals. An empirical expression was determined predicting a bituminous coal's minimum SHT in the adiabatic oven based on the coal's dry ash-free oxygen content. Several factors that can affect the self-heating process were also evaluated. The self-heating tendency of a coal increased when the coal was dried and exposed to humidified air, and was dependent on the particle size and oxygen concentration of the air.

A new moderate-scale apparatus is described, in which the self-heating tendencies of larger coal samples, 3 kg, can be evaluated. The minimum SHT's of two coals were determined and the results were in good agreement with those found in the adiabatic oven. Finally, results of a test in the moderate-scale apparatus indicated a strong dependence of the self-heating rate of a low rank coal on the moisture content of the air.

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INTRODUCTION

In the United States, approximately 11 pct of underground coal mine fires are attributed to spontaneous combustion (1).[3] The incidence of such fires is expected to increase with deeper mines, the introduction of longwall mining methods, and the increased consumption of lower ranked coals. In addition, spontaneous combustion continues to be a problem in the storage and transport of coal (2). Clearly the spontaneous combustion of coal represents a significant hazard to life and property.

Spontaneous combustion occurs when the heat that is produced by the low temperature reaction of coal with oxygen is not adequately dissipated by conduction or convection, resulting in a net temperature increase in the coal mass. Under conditions that favor a high heating rate, the coal attains thermal runaway and a fire ensues. It is generally accepted that the spontaneous combustion of coal is a rank-related phenomena. Other factors include the heat-of-wetting, temperature, ventilation, oxygen concentration, particle size, impurities, geological factors, and mining practices (3-6). With the exception of the last two, these factors can be studied in the laboratory.

Generally, four methods for evaluating the spontaneous combustion potential of coals and examining the factors that can affect the spontaneous combustion process are used. These are reviewed, along with various ranking indices, by Kim (5) and Guney (7). Briefly, the methods are: (1) adiabatic and (2) isothermal calorimetry, which measure heating rates or minimum ignition temperatures; (3) oxygen sorption methods, in which ratios of various reactant and product gases are related to self-heating; and (4) temperature differential methods, which measure temperature differences between the coal and a heated bath.

In this investigation, an adiabatic heating oven was used to determine the minimum self-heating temperature (SHT), the minimum initial temperature that produced a sustained exothermic reaction, or thermal runaway, of several U.S. coals. These temperatures were then used to rank the coal's relative self-heating tendencies compared to other coals evaluated in this study. The lower the minimum SHT the higher the self-heating potential of the coal. An empirical relationship was then derived to predict the minimum SHT based on the coal's dry ash-free oxygen content. The adiabatic oven was also used to study the effect of moisture on the self-heating process, both as inherent moisture in the coal and as a constituent in the test gas, as well as its synergistic effect on the oxidation process. Finally, the effects of varying the particle size and oxygen concentration, and the effect of prior oxidation of the coal's surfaces on the coal's minimum SHT were examined.

A moderate-scale apparatus is described that enabled the study of larger coal masses under more realistic conditions. The minimum SHT's of two coals were determined, and the movement of moisture through the coal mass and its effect on the heating rates of the coal are discussed.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

ACKNOWLEDGMENT

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EXPERIMENTAL APPARATUS AND PROCEDURES

SAMPLE PREPARATION

To run a series of tests in the adiabatic heating oven, either to determine the minimum SHT or to study the effect of some experimental parameter, several kilograms of fresh coal was passed through a jaw crusher and reduced to a minus 0.95-cm size. This coal was then pulverized in a rotary mill and sieved to the appropriate sizes on a sieve shaker. The sized fractions were sealed in plastic bags and stored in an N_2 atmosphere until testing. The time required to complete the pulverizing and sieving of the coal was approximately 0.5 h. Tests described in a later section of this report indicated that this short-term exposure of the coal surfaces to air had no effect on the results of the self-heating tests.

To run a test in the moderate-scale apparatus, several kilograms of the coal was passed through a jaw crusher for reduction. The reduced material was sieved and the minus 0.64-cm fraction collected. The sample was then loaded directly into the test apparatus for drying.

ADIABATIC HEATING OVEN EXPERIMENTS

Test Apparatus

The relative self-heating tendencies of coals, and factors that affect the self-heating process, were evaluated in the adiabatic heating oven shown in figure 1. The apparatus is designed to minimize heat losses from the coal sample during the self-heating stage of the test. The present apparatus is a modification of the adiabatic calorimeter described by Kuchta (6). Previously, a stainless steel wire mesh sample basket was suspended by a wire strand in the middle of the sample oven and the test gas was circulated around the sample by a magnetically controlled fan.

In the present configuration, the sample is contained in a brass wire mesh basket, 7.6-cm diam by 5-cm high, which is enclosed in a stainless steel assembly. The assembly has ports in the bottom and top to allow the test gas to pass through the coal sample instead of around it. The assembly is held in place in the sample oven by two brass rods attached to a stainless steel plate secured to the top of the sample oven. These are not shown in the figure. A stainless steel cylinder, 12.1-cm diam by 10.8-cm high, surrounded by a nickel-chromium wire resistance heater that is held in place by ceramic supports, serves as the sample

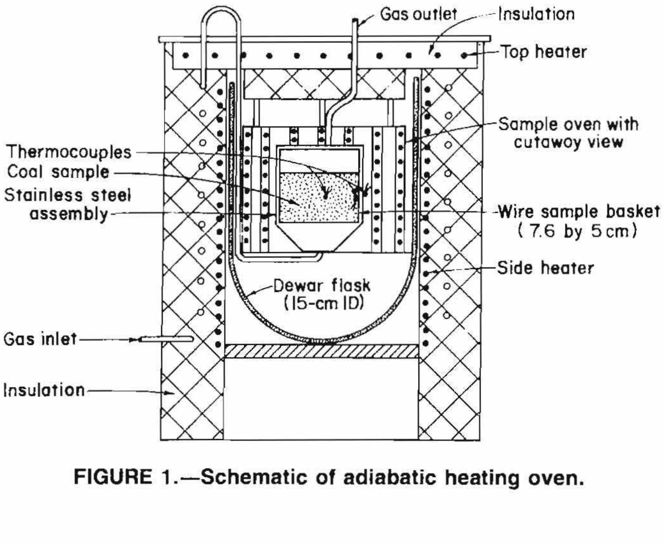

FIGURE 1.—Schematic of adiabatic heating oven.

oven. The cylinder acts as a heat shield to evenly distribute the heat produced by the hot wire. The oven is attached to a top plate, which is held in place by three brass rods extending from the top of the apparatus.

The whole oven assembly is contained in a 15-cm-ID Dewar flask that is surrounded by a 5-cm layer of perlite insulation in which another resistance-type heater is imbedded. This heater is kept near the set-point temperature throughout the test. In addition, another nickel-chromium wire resistance heater wired in parallel to the sample oven is located in the top cover of the apparatus.

Initially, the sample is heated to a selected temperature while exposed to a flow of preheated dry N_2. This is achieved using a proportional temperature controller in the set-point mode connected to a thermocouple located between the heat shield and oven walls. A pair of differential thermocouples, one located near the wall in the coal sample, and one located in the space between the sample assembly wall and sample oven cylinder, determine when an equilibrium has been reached in the apparatus and the sample has achieved the desired set-point temperature.

The temperature of the sample remains slightly less than that in the oven (ranging from 0.3° C at 40° C, to 2.0° C at 140° C), because of conductive heat losses up the stainless steel sample assembly. Stott estimates that approximately 60 pct of the heat output of the sample oven is lost from the apparatus (8). Most of the losses occur by conduction through the brass rods supporting the sample oven and through the stainless steel sample assembly, or by radiation. Figure 2 shows an example of the temperature-time traces of the differential thermocouples during the heatup period to a set-point temperature of 90° C at which the equilibrium condition was attained.

Upon reaching equilibrium condition, the preheated test gas flow is introduced to the sample. The power output to the sample oven and top heater is maintained, and control is switched to a differential proportional temperature controller, which maintains the same temperature difference as that in the equilibrium condition throughout the test. If the sample temperature increases, the change in temperature is measured by the differential pair of thermocouples located in the coal sample near the wall and the sample oven. The power output to the sample oven and top heater increases accordingly to maintain the same temperature difference. This minimizes heat losses from the coal across the sample assembly wall and through the top of the apparatus.

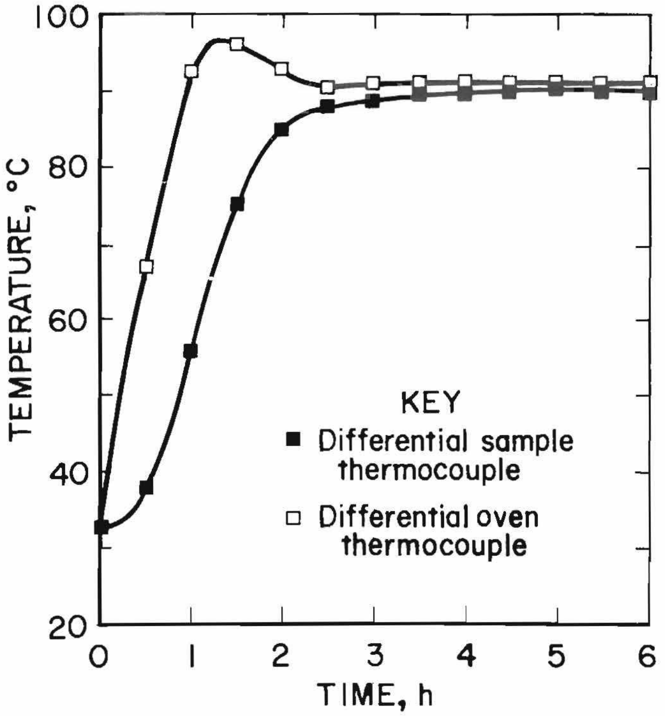

FIGURE 2.—Temperature histories of differential thermocouples during heatup period to 90° C in adiabatic heating oven.

Some heat is lost to radiation through the top and bottom of the sample assembly and to conduction up the sample assembly. Heat losses from the sample have been measured at 30° and 90° C by exposing a coal sample to a flow of dry N_2, and monitoring the sample temperature with time. The losses at 30° and 90° C were found to be -0.3° C/h and -0.5° C/h, respectively. This ensures that any temperature rise exhibited by the sample is due to a heat producing reaction and not artificial heating by the sample oven, and that at higher temperatures, the heat losses due to conduction and convection are not excessive. A thermocouple in the center of the sample is used to monitor the sample temperature during the test.

The test gas condition can be either humidified or dry by directing the flow with a series of valves. If humidified, the gas is sent through a pair of gas washers, kept at 35° C by heating tapes. The relative humidity of the gas entering the apparatus, measured by a thin film solid state sensor, is about 80 pct (4×10^{-5} g H_2O/mL air) at 35° C. The outlet gas line is equipped with O_2 and CO monitors to measure the concentrations of these gases.

Experimental Procedures

The evaluation of the self-heating tendency of a coal by the determination of the coal's minimum SHT was made using a set of standard experimental conditions. These conditions were determined to be the most stringent conditions for self-heating to occur in this apparatus. The minus 100- plus 200-mesh (74 by 150 µm) fraction of the pulverized coal was dried in an oven at 67° C with a 200-cm^3/min flow of dry N_2. A 100-g sample was placed in the apparatus and brought to a preselected initial temperature under a 200-cm^3/min flow of dry N_2. When an equilibrium was reached between the sample and sample oven at the selected initial temperature, a 200-cm^3/min flow of humidified air was passed through the sample until either a sustained exothermic reaction occurred or the sample began to cool.

A series of tests were made, each with a fresh sample, in 5° C increments, until the minimum initial temperature that produced a sustained exothermic reaction, or thermal runaway, was determined. Many factors that can affect the self-heating process, such as the effect of particle size or moisture, were also evaluated in the apparatus. The standard conditions described were used, with the exception of the parameter that was to be evaluated. The resulting temperature-time traces were then compared with traces obtained under standard test conditions. Included in this report are tests in which the particle size and O_2 concentrations were varied, and humidified and dry air and N_2 were used as test gases.

MODERATE-SCALE EXPERIMENTS

Test Apparatus

The moderate-scale spontaneous combustion apparatus permits the study of the self-heating process in a 3-kg coalbed. With a sample of this size, heat and mass transport processes occurring in the coalbed can be monitored. The apparatus, shown in figure 3, is designed to minimize heat losses from the coal and maintain accurate temperature control and measurement. The sample is contained in an aluminum cylinder, 14.6-cm diam by 40.6-cm high, with a wall thickness of 0.08 cm. The cylinder sets on a 5.1-cm transite base into which a 1.3-cm-diam hole is cut and a gas inlet tube is inserted. The aluminum cylinder is wound with a 2.5-cm-wide, 208-W fiberglass insulated electrical heating tape connected to a DC power supply. Encasing the aluminum cylinder and heating tape is a 15.2-cm diam by 40.6-cm high, 2.5-cm-thick transite cylinder and 5.1 cm of ceramic fiber insulation, inside a 32.5-cm aluminum cylinder. The top of the sample cylinder is covered with a 2.5-cm Teflon[4] fluorocarbon polymer cover that sets on top of the transite cylinder. A 0.3-cm rubber gasket forms a seal between the transite cylinder and the cover. A bifunctional temperature controller and two thermocouples located at the mid-height of the sample container, one located 0.3 cm inside the sample and one attached to the inside wall of the inner aluminum cylinder, regulate the output of the heating tape.

To bring the sample to an initial set-point temperature, and during the initial phase of the test, the temperature controller functions as an isothermal controller, monitoring the thermocouple attached to the cylinder wall and adjusting the output of the heating tape accordingly. After the initial phase of

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[4] Reference to trade names does not imply endorsement by the Bureau of Mines.

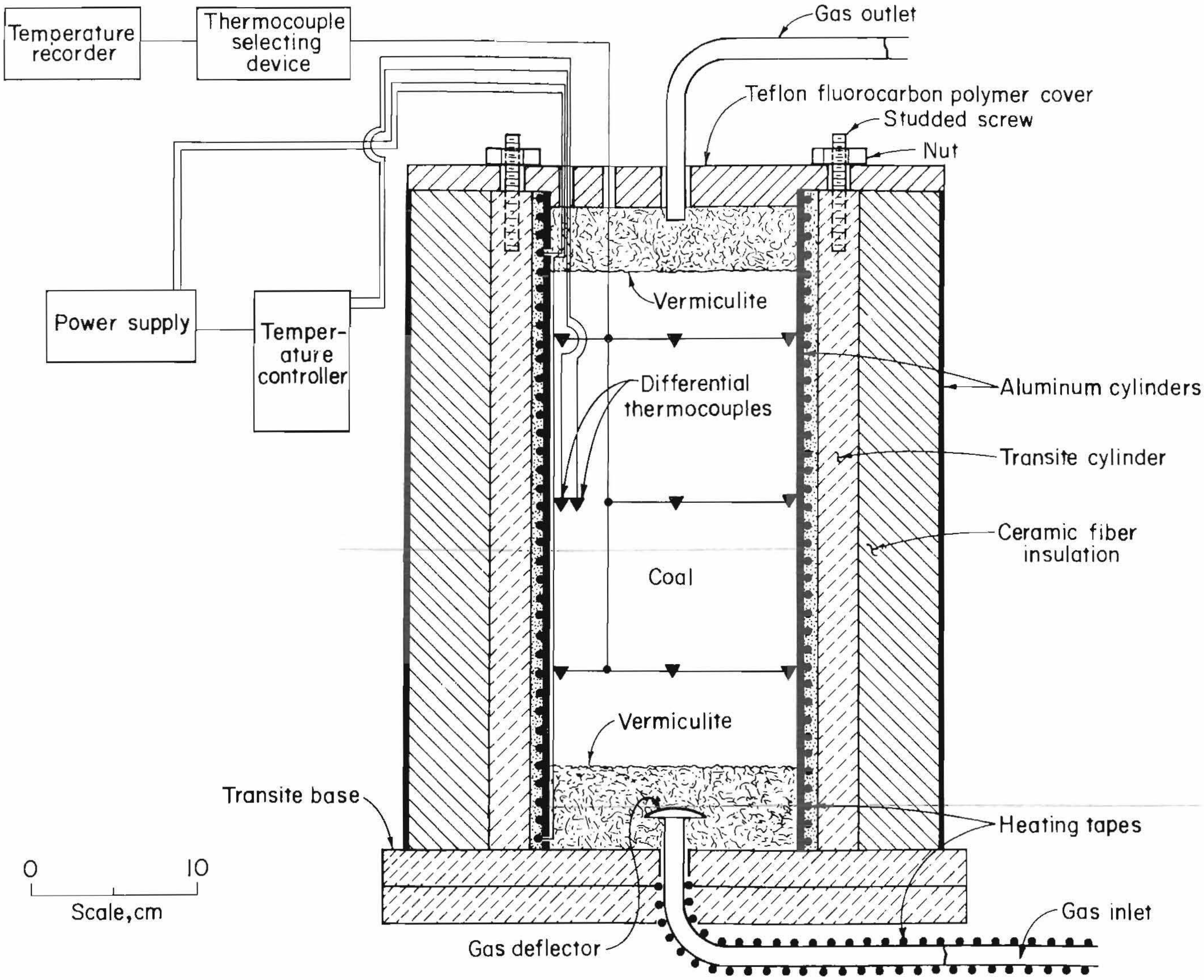

FIGURE 3.—Schematic of moderate-scale spontaneous combustion apparatus.

the test, the controller acts as a differential controller to maintain the cylinder wall temperature just below that of the sample temperature in the region where the two differential thermocouples are located.

The gas inlet line is wrapped with a heating tape to warm the inlet gas to the test temperature. A thermocouple is attached to the line to monitor the inlet air temperature. A 2.5-cm-diam deflector shield is positioned on the inlet line where the gas enters the sample container to prevent preferential flow through the middle of the sample. The inlet line configuration allows for the introduction of dry or humidified gas into the sample by a pair of three-way valves and two gas washing bottles. The gas percolates through the sample and exits the sample container through a 1.3-cm-OD gas outlet tube inserted through the cover. The outlet gas can be directed through O_2 and CO gas analyzers.

The sample temperature is monitored by an array of 15 thermocouples, five each at depths of 5.1, 15.2, and 25.4 cm in the 30.5-cm-deep sample bed. The thermocouples enter the sample container at the top of the transite cylinder. The five thermocouples at each depth are arranged one in the center of the sample and four radially 0.6 cm from the aluminum cylinder wall. The 15 thermocouples are read sequentially at 5-min intervals and the temperatures are interpolated between readings.

Experimental Procedures

To run a test in the moderate-scale apparatus, a 5-cm layer of vermiculite, an inert material, was placed in the bottom of the sample container. The freshly prepared coal sample, 61 pct minus 1/4 in plus 10 mesh, 33 pct minus 10 plus 50 mesh, and 6 pct minus 50 mesh, was then loaded into the sample container until a sample depth of 30.5 cm was reached. The thermocouples were positioned as the coal reached the previously described monitoring depths. The sample was then covered with another 3.8-cm layer of vermiculite and the cover placed on top of the container.

Because of the size of the sample, approximately 3 kg, the sample was predried in the sample container before the start of a test. To accomplish this, the sample was heated to 67° C, using the setpoint mode of the temperature controller, and dry N_2 was passed through the sample at a flow of 900 cm^3/min until the relative humidity in the outlet gas was less than 5 pct. The sample was then brought to the selected initial temperature under the same dry N_2 flow, at which time moist air was introduced to the system at a flow rate of 900 cm^3/min.

During the initial phase of the test, the temperature controller was used in the isothermal mode because of the time lag before self-heating occurred in the region of the coalbed where the differential thermocouples were located. To minimize heat losses, when a temperature rise of 0.4° C was detected at the differential thermocouple located in the coalbed, the controller was switched to the differential mode and the power output to the oven wall was increased as the sample temperature increased. The test continued until a predetermined temperature in the center of the sample was reached, at which time the air supply and power to the heating tape were shut off by an alarm circuit.

In one test, the moisture content of the air was measured near the center of the coalbed. This was done using a 0.3-cm-OD stainless steel probe inserted through the top cover. The probe was equipped with a metering valve to allow an exit gas flow of 100 cm^3/min to pass over a humidity and temperature sensor located outside the sample container, which measured the relative humidity and temperature of the gas. The probe was located radially 5 cm from the sample container wall and could be moved vertically to any depth in the coal bed.

RESULTS AND DISCUSSION

ADIABATIC HEATING OVEN

Coal Analyses

The self-heating tendencies of 24 coal samples were evaluated in this investigation. Table 1 shows the rank, as-received proximate and ultimate analyses, heating values in British thermal units (Btu's) per pound and dry ash-free oxygen values of representative samples of the minus 100- plus 200-mesh fractions tested. All coals were received direct from the coal seam in lumps (10 cm) with the exception of the Lower Kittanning, No. 6, and Beulah-Zap samples (5 cm), which were from storage piles. These three coals had excessive surface moisture and the as-received values represent values corrected for air dry loss. Two samples taken from different locations in the mine were received from the No. 80, B, D, E, Lower Sunnyside, Coal Basin, and Pocahontas 3 seams, and were evaluated as separate samples, 1 and 2.

The apparent rank of the coal samples were based on the ASTM D 388 classification system (9). The heating values denoted in parentheses were computed by the following formula (10):

TABLE 1. - Analyses of coals as received

Rank[1] and seam	State	Heating value[2] Btu/lb	Proximate analysis, wt pct				Ultimate analysis, wt pct					
			Moisture	Volatile matter	Fixed carbon	Ash	Hydrogen (H)	Carbon (C)	Nitrogen (N)	Sulfur (S)	Oxygen (O)	Dry ash-free oxygen
Lignite (lig):												
Beulah-Zap........	ND	7,458	27.3	29.9	31.8	11.0	6.0	43.4	0.5	3.9	35.2	17.7
Lehigh bed........	ND	6,287	42.6	32.8	19.5	5.2	7.1	37.9	.6	.5	48.6	20.7
hvCb coal:												
F.................	CO	11,561	11.4	40.9	45.3	2.4	6.0	66.4	1.4	.3	23.4	15.5
No. 6.............	IL	11,914	2.2	41.8	42.7	13.2	5.3	65.5	1.2	4.2	10.6	10.4
No. 80-1..........	WY	11,236	7.6	38.3	44.1	10.0	5.4	64.3	1.5	.4	18.4	14.2
No. 80-2..........	WY	11,353	11.0	39.5	43.9	5.6	5.9	65.2	1.6	.7	21.0	13.5
hvAb coal:												
B-1...............	CO	(13,029)	2.8	38.3	49.6	9.3	5.5	72.0	1.4	.5	11.2	9.9
B-2...............	CO	(13,920)	3.9	40.1	53.8	2.2	5.7	77.4	1.6	.5	12.5	9.6
Clarion...........	OH	(12,888)	4.8	43.0	44.4	7.7	5.6	70.0	1.2	3.5	12.0	8.8
D-1...............	UT	(13,734)	2.1	43.9	47.8	6.2	5.8	75.5	1.5	.5	10.6	9.5
D-2...............	UT	(13,480)	2.7	44.2	47.3	5.8	5.8	74.3	1.4	.4	12.4	10.9
E-1...............	CO	(13,784)	3.9	39.7	54.6	1.8	5.8	76.5	1.3	.7	13.9	11.0
E-2...............	CO	(13,823)	3.2	40.5	54.4	1.9	5.7	76.9	1.5	.7	13.2	10.9
Lower Kittanning..	PA	11,055	1.0	31.7	44.9	22.4	4.6	62.4	1.0	3.9	5.9	6.5
Lower Sunnyside-1.	UT	(13,318)	3.2	36.2	54.2	6.4	5.4	74.3	1.5	.5	11.8	9.9
Lower Sunnyside-2.	UT	(14,097)	2.3	38.6	56.2	2.9	5.6	78.6	1.5	.4	11.0	9.4
Pittsburgh........	PA	13,947	1.7	38.8	53.9	5.6	5.4	78.0	1.6	1.3	8.2	7.2
mvb coal:												
Coal Basin-1......	CO	(14,616)	.7	22.0	70.4	6.9	4.8	82.6	1.8	.7	3.3	2.9
Coal Basin-2......	CO	(14,350)	.9	21.6	69.5	8.0	4.8	81.0	1.5	.5	4.2	3.7
lvb coal:												
Blue Creek........	AL	14,276	1.1	19.2	72.7	7.1	4.5	82.0	1.7	.5	4.3	3.6
Mary Lee..........	AL	14,381	1.3	20.2	71.3	7.3	4.7	82.2	1.7	.6	3.5	2.6
Pocahontas 3-1....	VA	14,419	.9	18.7	73.2	7.3	4.2	82.6	1.3	1.7	2.9	2.3
Pocahontas 3-2....	VA	13,279	.6	17.6	67.5	14.3	3.9	77.0	1.1	1.1	2.6	2.5
Anthracite (an):												
Anthracite........	PA	12,860	1.7	4.7	84.7	8.9	2.1	83.9	1.1	.6	3.5	2.3

[1] Rank based on ASTM D 388 classification system (9)--hvCb, high-volatile C bituminous; hvAb, high-volatile A bituminous; mvb, medium-volatile bituminous; and lvb, low-volatile bituminous.

[2] Numbers in parentheses computed from elemental composition of coal; see text (p. 9) for formula.

$$
\begin{aligned}
Q^* = {} & 0.3578[\text{pct } C^*] \\
& + 1.1357[\text{pct } H^*] \\
& - 0.0845[\text{pct } O^*] \\
& + 0.0594[\text{pct } N^*] \\
& + 0.1119[\text{pct } S^*] \\
& - 0.974,
\end{aligned}
$$

where the asterisks denote values on a dry basis, Q denotes the heating value in kJ/g, and C, H, O, N, and S denote the elemental compositions of the coal. The values in the table are expressed as Btu/lb by the conversion factor, 430.66 Btu × g/kJ × lb, and corrected for moisture. The remaining heating values were determined experimentally by bomb calorimetry.

The coals are listed in ascending order according to their apparent rank. In general, the heating value and fixed carbon contents of the coals increased with increasing rank, while the moisture, hydrogen, and dry ash-free oxygen contents decreased with increasing rank. Most of the coals had low sulfur contents, with the exception of the Beulah-Zap, Clarion, No. 6, and Lower Kittanning samples, which exceeded 3.0 wt pct. The Lower Kittanning sample had an unusually high ash content and correspondingly low heating value (as received).

Evaluation of Self-Heating Tendencies

Minimum Self-Heating Temperatures

The minimum self-heating temperatures (SHT's) of the coal samples were determined in the adiabatic heating oven. Figure 4 shows typical temperature-time traces of tests to determine the minimum SHT of the Clarion seam coal. At a starting temperature of 70° C, there was a rise in the coal sample temperature to 80° C in about 6 h after exposure to the humidified airflow. The temperature then leveled off and eventually the sample cooled. In another test, with a fresh sample at an initial temperature of 75° C, the sample temperature increased steadily, reaching thermal runaway in just over 30 h. The effect of increasing the initial temperature is seen in the remaining two curves. From initial temperatures of 80° and 90° C, the samples self-heated in shorter time periods, about 11 and 4 h, respectively. Thus, the minimum SHT of this coal was 75° C.

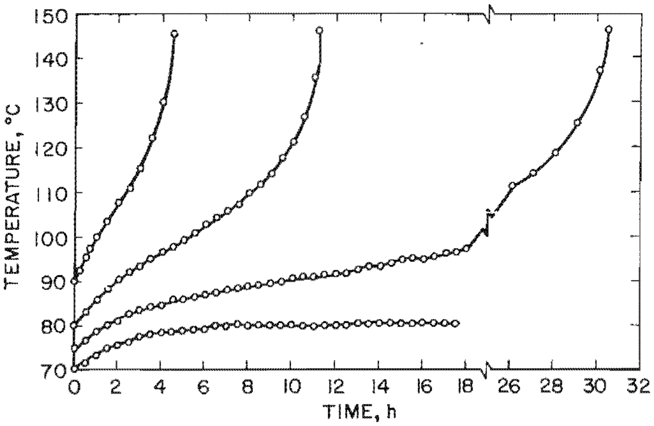

FIGURE 4.—Temperature histories in self-heating tests with Clarion coal at initial temperatures of 70°, 75°, 80°, and 90° C.

The minimum SHT's were determined for 24 coal samples and are listed in table 2. The temperatures ranged from 35° C for the No. 80-1 (hvCb) sample and the Lehigh sample (a lignite coal) to 135° C for the Mary Lee and Blue Creek (lvb) coal samples. The minimum SHT of the anthracite coal was greater than 140° C, beyond the limits of the adiabatic heating oven.

There were small variations in the minimum SHT's of five out of the seven seams represented by more than one sample. The largest difference was 10° C between the D seam samples, while the Lower Sunnyside, B, Pocahontas No. 3, and No. 80 seam samples differed by 5° C. The E and Coal Basin seam samples showed no difference in their minimum SHT's.

The temperatures reported for the No. 80-2 and Pittsburgh samples in table 2 may differ from the temperatures reported as the minimum SHT's in later sections on the studies of factors that can affect the self-heating process. This is because in the studies on various factors, fresh batches of samples were prepared and the minimum SHT of the coal was determined for each batch. That value

TABLE 2. -- Minimum self-heating temperatures and relative self-heating tendencies of coals evaluated in adiabatic heating oven

Seam	Apparent rank[1]	Minimum SHT, °C	Seam	Apparent rank[1]	Minimum SHT, °C
High:			Medium--Con.		
Lehigh bed..........	lig	35	Lower Sunnyside-2...	hvAb	80
No. 80-1............	hvCb	35	Lower Sunnyside-1...	hvAb	85
No. 80-2............	hvCb	40	D-1.................	hvAb	90
F...................	hvCb	45	Pittsburgh..........	hvAb	90
Beulah-Zap..........	lig	60	Lower Kittanning....	hvAb	100
E-1.................	hvAb	65	Low:		
E-2.................	hvAb	65	Pocahontas 3-2......	lvb	110
Medium:			Pocahontas 3-1......	lvb	115
B-1.................	hvAb	70	Coal Basin-1........	mvb	120
No.6................	hvCb	70	Coal Basin-2........	mvb	120
B-2.................	hvAb	75	Blue Creek..........	lvb	135
Clarion.............	hvAb	75	Mary Lee............	lvb	135
D-2.................	hvAb	80	Anthracite..........	an	> 140

[1] See table 1. SHT Self-heating temperature.

ranged from 40° to 45° C for the No. 80-2 sample and from 90° to 95° C for the Pittsburgh sample, a maximum difference of 5° C in each case.

The results of the tests in the adiabatic heating oven agree favorably with the concept that the self-heating tendencies of coals increase with decreasing rank. The lower ranked lignite and hvCb coals had minimum SHT's in the range of 35° to 70° C, the hvAb coals fell in the range of 65° to 100° C, while the higher ranked mvb and lvb coals and the anthracite coal had minimum SHT's greater than 100° C. It is proposed that coals with minimum adiabatic heating oven SHT's < 70° C be considered as having a high spontaneous combustion potential, those that fell in the range 70° to 100° C as having a medium risk, and coals that had minimum SHT's > 100° C as having a low spontaneous combustion potential when compared with other coals. It must be noted however, that these were laboratory tests and the resulting minimum SHT's are a relative measure of the self-heating tendency of the coal alone and do not consider other important contributing factors associated with the spontaneous combustion process in actual mining or storage conditions.

The temperature-time traces for several coals starting at their minimum SHT's are shown in figure 5. The heating curves exhibited similar characteristics; a large initial heating rate, a decrease in the rate before passing through an inflection point, and an exponential rise in temperature from the inflection point until the end of the test. The time to reach thermal runaway varied but this parameter depends on how close the

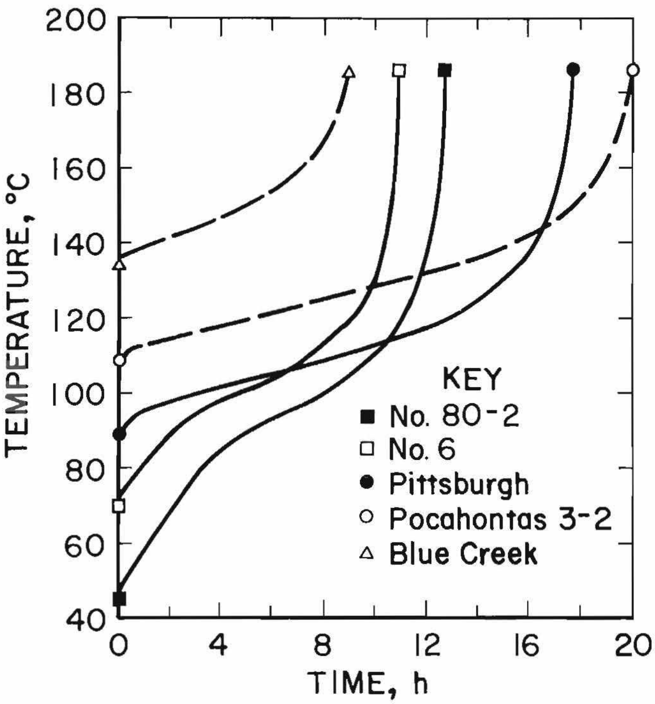

FIGURE 5.—Temperature histories for various coals at their minimum SHT's.

initial temperature, which is changed in 5° C increments, is to the actual minimum SHT of the coal sample. For example, the minimum SHT of a coal sample whose real minimum SHT is 61° C is determined to be 65° C, just as a sample whose real minimum SHT is 64° C. However, the first sample will reach thermal runaway in a shorter time based on its greater reactivity. The time to reach thermal runaway is used in determining the relative reactivity of two samples whose minimum SHT's are the same in the adiabatic heating oven. It is also important in the studies on factors that can affect the self-heating process, in which the effect may not be large enough to change the minimum SHT by the necessary 5° C.

O_2 and CO concentration profiles of the outlet gas were recorded for several of the tests. Figure 6*A* shows a plot of concentrations of these gases as a function of time for Pittsburgh coal at an initial temperature of 90° C. The sample temperature trace is included in the plot as a reference. Since N_2 was being passed through the sample prior to the start of the tests, there was an initial rise in the O_2 concentration as it replaced the N_2 in the gas lines.

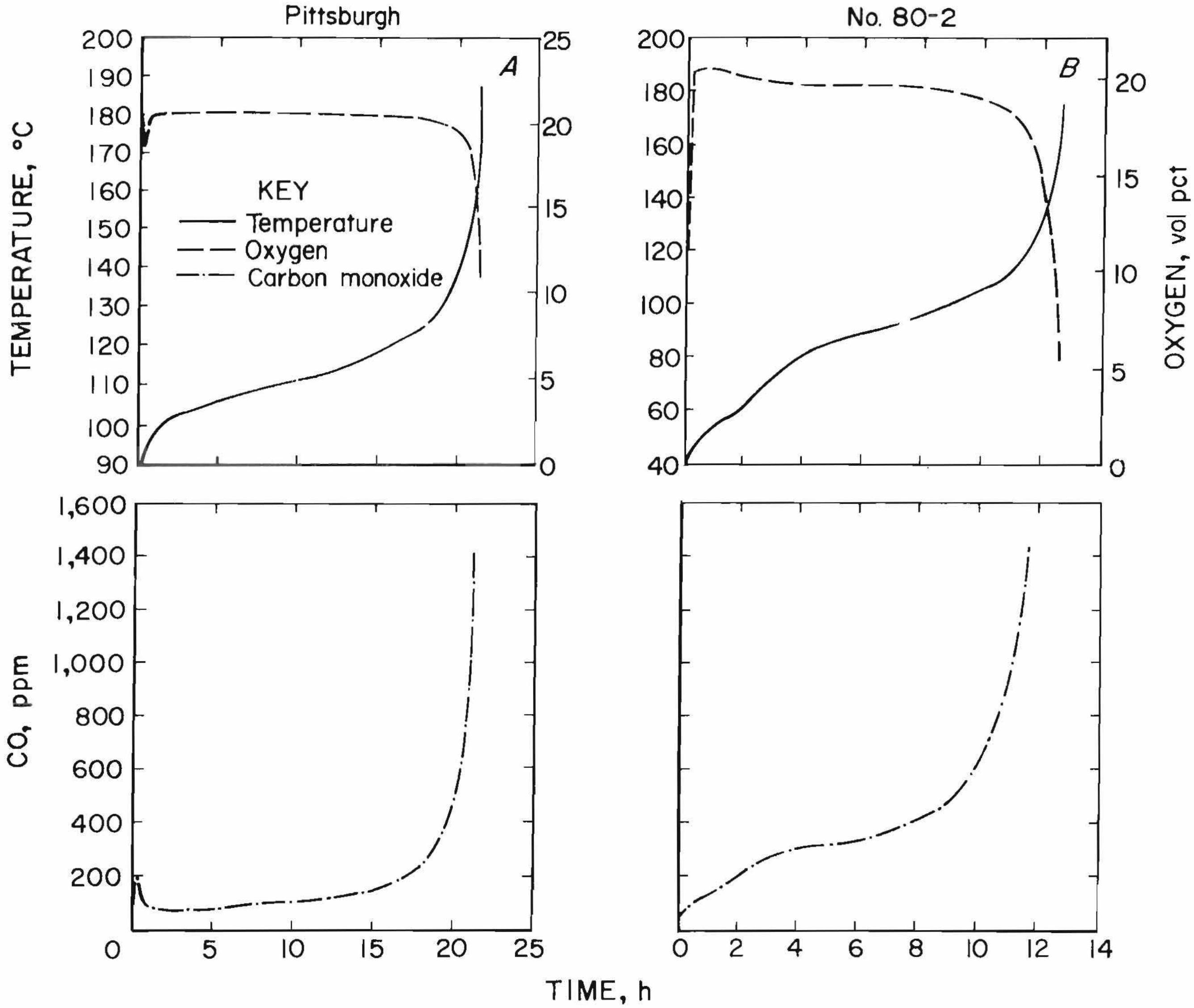

FIGURE 6.—O_2 and CO concentration profiles in self-heating tests of *A*, Pittsburgh coal, initial temperature, 90° C, and *B*, No. 80-2 coal, initial temperature, 40° C.

Within 10 min from the start of the test, this concentration was above 20 pct. Between 20 and 30 min into the test, there was a relatively steep increase in CO and a corresponding dip in the O_2 concentrations. This phenomenon was short-lived and corresponded to the sharp rise in temperature at the start of the test. After about 15 h, the O_2 concentration began to decrease exponentially while the CO concentration increased exponentially, roughly corresponding to the rate of temperature rise in the sample.

Figure 6*B* is a plot of O_2 and CO for a lower rank coal, No. 80-2, from an initial temperature of 40° C. Similar curves to those in figure 6*A* were found for the O_2 and CO concentrations, with the exception of the CO peak and O_2 dip in the initial phase of the test. In both cases, the outlet O_2 concentration remained above 15 pct until late into the test, assuring an adequate supply of oxidizer for the reaction with coal until high temperatures are reached.

Prediction of Minimum Self-Heating Temperatures

The prediction of the minimum SHT of a coal sample allows the assignment of the relative self-heating risk or potential of a coal without the need for detailed laboratory experiments. In addition, the basis of the prediction may provide some insights into the self-heating process. In general, the minimum SHT's of the coals increase with increasing rank, which is related to the chemical composition of the coal. A multiple linear regression analysis was conducted using the experimental minimum SHT of the coal as the dependent variable and the chemical constituents, both in the dry and dry ash-free states, as determined by the proximate and ultimate analyses, and the moisture content of the coal, as the independent variables. The analysis did not include the lignite samples because of their high moisture values relative to the other samples. Also excluded were the E-2 and Coal Basin-2 samples because of their similar composition to the E-1 and Coal Basin-1 samples, respectively. The anthracite sample was not included since the minimum SHT was not determined. In total, the analysis included 19 bituminous coal samples.

The computational method used in the regression analysis was a forward stepwise regression procedure based on the method given by Draper (<u>11</u>). The computer software used in the analysis is described by BBN Research Systems (<u>12</u>). The procedure involved inserting variables into the model in an order determined by using the partial correlation coefficient as a measure of importance. After the introduction of a variable into the model, an examination of the contribution made by each variable in the model was made using the F-test, and any variable making a nonsignificant contribution was removed. The process continued until no variables were added to or removed from the model.

The resulting model showed a correlation of the minimum SHT with the oxygen content of the coal. The best fit was with the dry ash-free (DAF) oxygen:

$$\mathrm{SHT_{min}},\ ^\circ\mathrm{C} = 139.74 - 6.57 \times [\mathrm{O,\ pct\ (DAF)}].$$

The resulting line had a correlation coefficient of 0.934, with a standard deviation of regression of 10.53 and an average relative error of 10.6 pct. The minimum SHT's predicted by this model are shown in table 3. A plot of the predicted versus the experimental minimum SHT's is shown in figure 7. The largest relative errors were in the No. 80 samples, 34 and 28 pct, respectively, both hvCb coals, but this was primarily due to the low experimental minimum SHT's, which produce large relative errors for small differences in the predicted versus experimental values. The low-volatile coals had large temperature differences, 10° to 19° C, but low relative errors, 9 to 14 pct, due to their high minimum SHT's. However, at temperatures above 100° C, the allowable margin of error in predicting the minimum SHT is much greater. The best prediction was for the Coal Basin sample, a medium volatility coal. The model worked well for most of the high-volatile A coals, the

TABLE 3. - Experimental and predicted minimum self-heating temperatures of bituminous coals

Seam	SHT, °C	
	Experimental	Predicted[1]
hvCb:		
F	45	38
No. 6	70	72
No. 80-1	35	47
No. 80-2	40	51
hvAb:		
B-1	70	75
B-2	75	77
Clarion	75	82
D-1	90	77
D-2	80	68
E-1	65	68
Lower Kittanning	100	97
Lower Sunnyside-1	85	75
Lower Sunnyside-2	80	78
Pittsburgh	90	93
mvb: Coal Basin-1	120	121
lvb:		
Blue Creek	135	116
Mary Lee	135	123
Pocahontas 3-1	115	125
Pocahontas 3-2	110	123

DAF Dry ash-free.

[1] Based on minimum self-heating temperature 139.74 - 6.57 × [O, pct (DAF)].

largest relative error being for the D-2 sample, 15 pct.

Moisture, which has a significant effect on the self-heating process, as will be shown later, played a surprisingly nonsignificant role in the prediction of the minimum SHT. Forcing the moisture content value of the coal into the model as an independent variable did not adversely affect the correlation coefficient or standard deviation of regression, but the addition of the variable was statistically insignificant based on the F-test. Finally, the addition of squares of the oxygen and moisture contents and their crossproducts in the regression analysis failed to alter the results, producing the same model.

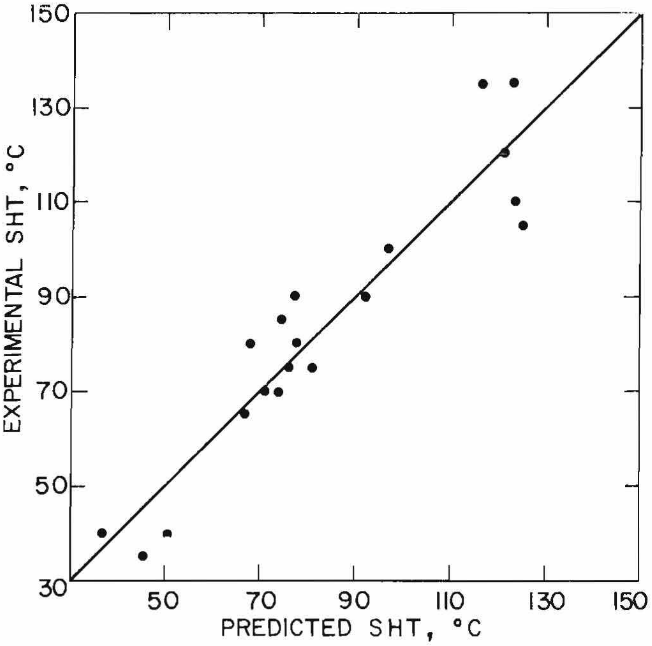

FIGURE 7.—Predicted versus experimental minimum SHT's of bituminous coals evaluated in the adiabatic heating oven.

Kinetics and Mechanisms

The self-heating rate ($\dot{q}$) of a coal mass may be expressed as the sum of the heat release reactions ($\dot{q}_1$), the heat-of-oxidation and the heat-of-wetting, and the heat losses ($\dot{q}_2$), conduction and convection. Under adiabatic conditions, the heat loss term is negligible, and $\dot{q} = \dot{q}_1$. It is generally agreed that the oxidation of coal is a temperature-dependent reaction that obeys an Arrhenius type rate law of the form:

$$\text{rate} = A[\exp](-E/RT),$$

where the rate coefficient A includes the heat of reaction, the specific heat of the coal, and a specific rate constant; E is activation energy; R is the molar gas constant; and T is temperature.

The equation can be written

$$\ln(dT/dt) = -E/RT + \ln(A),$$

and from a plot of the log of the rate versus 1/T, the overall activation energy, E, can be determined from the slope and the preexponential factor, A, from the intercept (6, 13).

The heat-of-wetting is the heat generated by the adsorption of water vapor by the coal surface. The process can be reversed depending on the moisture content of the coal, the relative humidity of the air, and the temperature. The quantity of heat generated by the heat-of-wetting has been measured for various coals, and found, in general, to decrease with increasing rank (14-15), and can be as high as 25 cal/g of dry coal for lignites.

No generally accepted rate equation for the heat-of-wetting is in use. The rate of temperature rise would be expected to decrease with time, under constant humidity conditions, because of the limited amount of surface area available. Eventually the moisture has an inhibiting effect on the self-heating process. As the temperature increases, the decreasing humidity in the air causes a shift in the equilibrium and the subsequent evaporation of the water from the coal, an endothermic process (16-18).

Another factor that plays a role in the rate of self-heating of coals is the synergistic effect of moisture on the oxidation process (19-21). Evidence supporting this concept is presented later in this report.

In summary, assuming adiabatic conditions, the self-heating rate ($\dot{q}$) can be expressed as the sum of the heat release reactions, as follows:

$$\dot{q} = A \exp[-E/RT] + \Delta H_{wet} (T,t,r),$$
$$+ B(T,r),$$

where H_{wet} (T,t,r) represents the heat-of-wetting as a function of temperature, time, and rank, and B (T,r) represents the effects of the interaction of the heat-of-oxidation and the heat-of-wetting, also a function of temperature and rank.

Evidence of these mechanisms are seen in the heating curves of the coals in figure 5, obtained from tests in the adiabatic heating oven using moist air. Initially, the rates of temperature rise were large. The rates decreased as the curves passed through the inflection points before increasing exponentially for the duration of the tests. The following overall mechanism is proposed.

Initially, the heat-of-wetting is the dominant mechanism. In the regions near the inflection points in the curves, many competing processes are occurring. The available sites for moisture adsorption are being used up and with the increasing temperature shifting the water vapor equilibrium, water is starting to be desorbed from the coal. At the same time, the rate of heat being produced by the oxidation reaction is increasing, but neither mechanism is dominating. Past the inflection point, the temperature has been raised enough for the oxidation process to take over as the dominant mechanism.

This is more clearly seen in figure 8, a plot of the log of the rate of temperature rise versus reciprocal temperature for a test of Pittsburgh coal at 90° C. Initially, the heating rate was high, decreasing at an exponential rate approaching the minimum of the curve. This supports the idea that the decrease in the heat produced by the heat-of-wetting is due to the using up of available

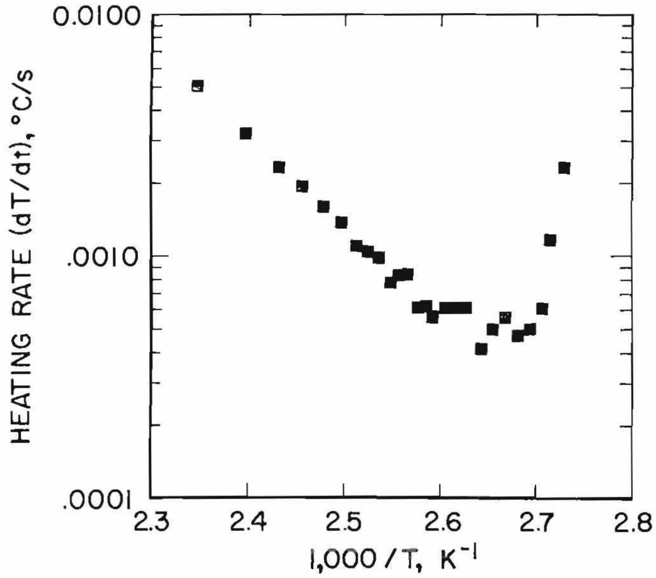

FIGURE 8.—Log of heating rate versus reciprocal temperature for a test of Pittsburgh coal at an initial temperature of 90° C.

surfaces. Past the minimum of the curve, the reaction followed the Arrhenius rate law, agreeing with the idea that the oxidation process has taken over as the dominant mechanism. The flat area near the minimum of the curve is where the mechanisms were competing.

The changes in temperature (Δ temp) from the initial temperature to the temperature at the inflection point in the minimum SHT curves of tests using moist air are shown in table 4 for the 24 coals. The values for the No. 80-1, No. 80-2, and Pittsburgh samples are averages of 2, 5, and 17 runs, respectively. In general, the changes in temperature decreased with rank and increasing minimum SHT. There was no correlation between the time to reach the inflection point and either rank or SHT.

Calculation of the apparent global activation energies and preexponential factors are also shown in table 4 for the coals over the temperature range from the minimum in the semilog plot, or inflection point in the temperature-time curve, to 150° C. These values should be a relative ranking of a coal's reactivity. The Pittsburgh seam values, 21.1 kcal/mol and 4.4×10^8 K/s, represent the geometrical averages of 17 runs and had standard deviations of 3.8 kcal/mol and

TABLE 4. - Summary of kinetic data from tests in the adiabatic heating oven

Seam	Minimum SHT, °C	E, kcal/mol	A, K/s	Δ temp to inflection point, °C
lig:				
Beulah Zap...........	60	16.8	5.1×10^6	52
Lehigh bed...........	35	15.2	4.6×10^8	43
hvCb:				
F....................	45	12.6	3.1×10^5	58
No. 6................	70	14.5	9.2×10^5	27
No. 80-1.............	35	15.9	1.9×10^6	46
No. 80-2.............	40	16.8	6.9×10^6	50
hvAb:				
B-1..................	70	19.6	1.1×10^8	23
B-2..................	75	18.8	5.4×10^7	19
Clarion..............	75	20.4	3.4×10^8	17
D-1..................	90	20.4	2.4×10^8	27
D-2..................	80	17.1	4.8×10^6	12
E-1..................	65	17.6	1.1×10^7	18
E-2..................	65	18.2	1.1×10^7	21
Lower Kittanning.....	100	20.2	7.3×10^7	28
Lower Sunnyside-1....	85	21.1	5.9×10^8	19
Lower Sunnyside-2....	80	24.5	3.0×10^{10}	25
Pittsburgh...........	90	21.1	4.4×10^8	11
mvb:				
Coal Basin-1.........	120	NA	NA	15
Coal Basin-2.........	120	NA	NA	16
lvb:				
Blue Creek...........	135	22.6	4.6×10^8	6
Mary Lee.............	135	20.2	1.4×10^7	4
Pocahontas 3-1.......	115	19.1	1.3×10^7	18
Pocahontas 3-2.......	110	20.8	1.1×10^7	19
an: Anthracite........	>140	NA	NA	NA

A Preexponential factor. NA Not available.
E Activation energy. SHT Self-heating temperature.

9.5×10^1 K/s, respectively. The values for the No. 80-1 and No. 80-2 samples are geometrical averages of two and five runs, respectively. No values were available for the Coal Basin seam samples because of lack of data points beyond the inflection point in the temperature-time curve.

A linear regression analysis of the activation energies available for 21 coals and their minimum SHT's showed a small correlation (0.69). The average activation energy for the 21 coals was 18.7 kcal/mol, with a standard deviation of 2.9 kcal/mol. A similar analysis of the preexponential factors and the minimum SHT's showed little correlation (0.28). The average preexponential factor was 3.7×10^7 K/s with a standard deviation of 1.5×10^1 K/s.

The relative error of the average activation energy and preexponential factor of all the coals was only slightly better than those for Pittsburgh coal, and indicates that a quantitative measurement of the relative reactivities of the coal samples based on their measured activation energies and preexponential factors in the adiabatic heating apparatus is not valid under these test conditions. The activation energies and preexponential factors of the lignite and hvCb coals were, in general, lower than those of the higher ranked coals, but this is only a qualitative evaluation.

In addition to being relative indications of a coal's reactivity, the activation energies and preexponential factors have been used in the development of a mathematical model of the spontaneous combustion process (22).

Factors Affecting Self-Heating

Moisture

In the previous section, it was proposed that the initial portion of the heating curves in the determination of the minimum SHT's were dependent on the heat-of-wetting mechanism and that this dependency decreased with increasing rank and SHT. In this section, the effect of moisture in the airflow on the minimum SHT is examined, along with the heat-of-wetting effect and the synergistic effect of moisture on the oxidation process.

Table 5 shows the effect of moisture on the minimum SHT's of several coal samples. The minimum SHT's of No. 80-2, No. 6, D-1, Pittsburgh, and Pocahontas 3-2 seam samples were determined with flows of moist and dry air under otherwise standard conditions. The largest effect was seen with the No. 80-2 sample, 15° C. The No. 6 coal showed a smaller change, 5° C, while the other three coals showed no change in their minimum SHT's. For these three coals, the time to reach 150° C is shown, and in all cases, this time increased in the tests using dry air.

These results indicate that the effects of moisture on the minimum SHT's are most important at low temperatures and/or for

TABLE 5. - Effect of moisture on minimum self-heating temperatures

Seam	Moist air		Dry air	
	SHT, °C	Time to reach 150° C, h	SHT, °C	Time to reach 150° C, h
hvCb:				
No. 80-2..........	40	NAp	55	NAp
No. 6.............	70	NAP	75	NAp
hvAb:				
D-1...............	90	16.2	90	25.2
Pittsburgh........	90	16.7	90	36.3
lvb: Pocahontas 3-2	110	17.7	110	40.5

NAp Not applicable.
SHT Minimum self-heating temperature.

low rank coals, although the distinction cannot be made from this data. This is in agreement with the results from the previous section on the change in temperature from the start of a test to the inflection point in the heating curves, shown in table 4, in which changes in temperature decreased with rank and increasing minimum SHT.

The heating rates and temperature rises attributed to the heat-of-wetting were measured using dried samples of Pittsburgh, E-1, and No. 80-1 coal exposed to flows of humidified N_2 under standard conditions at several initial temperatures, to study the effect of rank and temperature on the heat-of-wetting. The results are shown in table 6. From initial temperatures of 30° or 35° C, the three coals had equal temperature rises, 13° C, before the samples begin to cool, with the No. 80-1 coal having a higher heating rate, 3.1° C/h, compared to the others, 2.3° and 2.2° C/h. The heating rates and temperature rises were also measured for the Pittsburgh and E-1 seam coals at higher initial temperatures. The Pittsburgh coal, starting at 90° C, and the E-1 coal, at 70° C, both produced initial heating rates of 1.4° C/h and temperature rises of 4° C.

These results indicate that the heat-of-wetting has a strong dependence on temperature, due to the smaller change in temperature (Δ temp), for the E-1 and Pittsburgh seam coals at the higher temperatures. The rank dependence is still evident in the comparison of the heating rates of the three coals at the lower temperatures, since the lower rank No. 80-1 coal has a higher heating rate than the E-1 and Pittsburgh coals. A calculation of the heat-of-wetting in calories per gram of dry coal for these coals at the lower temperatures yielded a value of 3.3 cal/g, assuming that the heat capacities of the dry coals are 0.25 cal/(g-K) at 25° C. This value falls in the range given for dry bituminous coals in references 14, 15, and 23.

The last effect of moisture examined was a possible synergistic effect of moisture on the oxidation process in the self-heating of coal. Figure 9 shows the individual contributions of the heat-of-wetting, using moist N_2 as the test gas, and the heat of-oxidation, using dry air as the test gas, as well as the combined effect of O_2 and moisture using moist air as the test gas, on the No. 80-2 seam coal from an initial

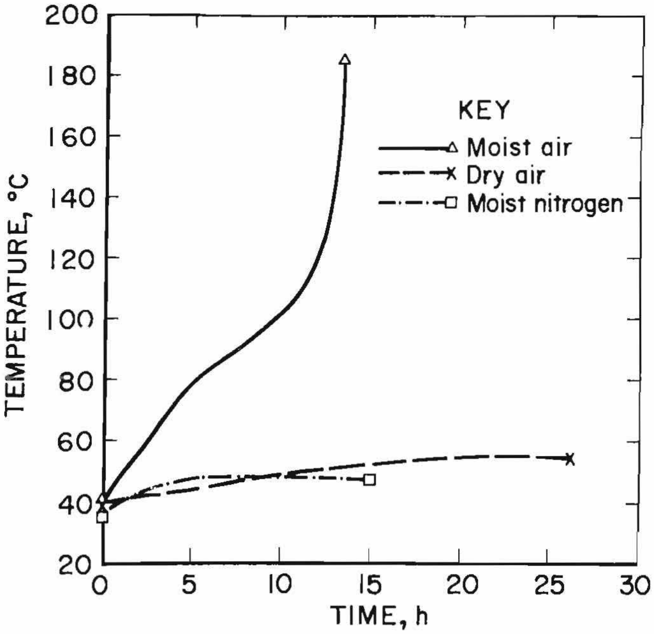

FIGURE 9.—Synergistic effect of moisture on the self-heating of No. 80-2 coal.

TABLE 6. - Effect of temperature on the heat-of-wetting

Seam	Apparent rank[1]	Initial temp., °C	Initial heating rate, °C/h	Temp rise, °C
No. 80-1....	hvCb	35	3.1	13
E-1.........	hvAb	30	2.3	13
Pittsburgh..	hvAb	35	2.2	13
E-1.........	hvAb	70	1.4	4
Pittsburgh..	hvAb	90	1.4	4

[1] See table 1.

temperature of 40° C. In the test with dry air, the sample reached a maximum temperature of 55° C, with an initial heating rate over the first 3 h of 1.8° C/h. In the test with moist N_2, a maximum temperature of 48° C was reached, with an initial heating rate of 2.9° C/h. The coal self-heated in the test with moist air, with an initial temperature rise of 8.3° C/h. The synergistic effect was seen in comparing the heating rate and temperature histories in the test with moist air with those in the tests with moist N_2 and dry air. The heating rate using moist air was almost twice that of the sum of the rates of the heat-of-oxidation and the heat-of-wetting and was more than four times greater than with dry air alone. So the synergistic effect moisture has on the oxidation process may be the most important role that moisture can play in the self-heating process.

It is generally agreed, and is supported by this study, that the heat-of-wetting can cause greater temperature increases in a coal mass than the heat-of-oxidation at low temperatures (24-25). But without the oxidation process taking over at some point in the self-heating process as the dominating mechanism, the heating cannot be sustained because of the limited pore surface area available for water vapor absorption. Oxidation, on the other hand, can sustain self-heating in the absence of moisture, but either higher initial temperatures are required for low rank coals or longer heating times are required for high rank coals. The lowest SHT's and therefore the highest self-heating tendencies were found in the adiabatic heating oven using moist air as a test gas, evidence of the importance of the synergistic effect of moisture on the oxidation of coal.

Particle Size

The effect of increasing the particle size on the self-heating of coal was examined in the adiabatic heating oven by determining the minimum SHT of four samples of Pittsburgh coal of increasing particle dameter, under otherwise standard conditions. The results are shown in table 7.

The minimum SHT of Pittsburgh coal under standard test conditions, in which the particle diameters are between 74 and 150 µm (minus 100 plus 200 mesh), was 95° C. Doubling the particle diameters to include particles from 150 to 297 µm (minus 50 plus 100 mesh) increased the minimum SHT of the coal to 100° C. Doubling the particle diameter again, to 297 to 597 µm (minus 30 plus 50 mesh) increased the minimum SHT to 105° C. Decreasing the particle size to less than 74 µm (minus 200 mesh) resulted in no change in the minimum SHT.

Also shown in table 7 are the results of tests on samples of No. 80-2 coal, with particle diameters of 74 by 150 µm (minus 100 plus 200 mesh) and less than 40 µm (minus 400 mesh), tested from an initial temperature of 45° C. The 74- by 150-µm sample self-heated while the less than 40-µm sample did not, reaching a maximum temperature of 75° C in 5 h before cooling.

TABLE 7. - Effect of particle size on minimum self-heating temperature

Particle size, mesh	Particle diam, µm	Minimum SHT, °C	Comments
Pittsburgh seam:			
Minus 200...........	Minus 74	95	None.
Minus 100 plus 200..	Minus 150 plus 74.	95	Standard test conditions.
Minus 50 plus 100...	Minus 297 plus 150	100	None.
Minus 30 plus 50....	Minus 597 plus 297	105	Do.
No. 80-2 seam:			
Minus 100 plus 200..	Minus 150 plus 74.	45	Standard test conditions.
Minus 400...........	Minus 40..........	45	Reached 75° C in 5 h.

These results indicate a dependence of the minimum SHT on particle size, down to a particle diameter of 74 by 150 µm (minus 100 plus 200 mesh), in the adiabatic heating oven. The results were in good agreement with Elder (3) and Carpenter (26), who determined that the oxidation rate of coal increases with a decrease in particle size, to a critical diameter, beyond which the dependence ceases. Carpenter also determined that the total surface area is independent of particle size in the range of 36-to 2,000-µm average diameter and that the main effect of decreasing particle size on reactivity is due to the increased accessibility of oxygen to the internal surfaces with decreasing particle size (27). The inverse dependence found for the ultrafine No. 80-2 sample was unexpected and may have been due to agglomeration, causing the particles to behave as larger particles.

Oxygen Concentration

In tests to investigate the effect of the O_2 availability on the self-heating of coal, Pittsburgh coal samples were exposed to flows containing 21, 16, and 14 vol pct O_2 and No. 80-2 coal samples were exposed to flows of 21, 18, and 14 vol pct under standard conditions, and the minimum SHT's determined. The results are shown in table 8.

In the tests with Pittsburgh coal, which had a minimum SHT of 95° C under standard conditions, reducing the O_2 concentration to 16 pct increased the minimum SHT to 100° C. At an O_2 concentration of 14 pct, the coal self-heated at 100° C, but the time to reach thermal runaway, 186° C, was increased by 30 pct compared with the test at 16 pct (from 13.5 to 17.3 h).

In the tests with the No. 80-2 coal, which had a minimum SHT of 40° C using standard conditions, reducing the O_2 concentration to 18 pct increased the minimun SHT to 45° C, and reducing the O_2 concentration to 14 pct increased the minimum SHT to 50° C. In both cases, the results showed a decrease in reactivity due to O_2 deficiency, the decrease being slightly larger for the No. 80-2 coal. This is in qualitative agreement with Elder (3), who found that the rate of oxidation was proportional to the O_2 concentration in contact with the coal raised to the 0.66 power. Recently, Wiemann showed that the tendency of a low rank coal to self-ignite decreased with reduced O_2 concentration, but that considerable self-heating occurred at O_2 concentrations as low as 5 pct (28).

Prior Oxidation

The effect of low-temperature surface oxidation because of the exposure of the coal surfaces to air during sample preparation was also examined in the adiabatic heating oven. Samples of No. 80-2 coal were first pulverized and sieved in a glovebox under an Ar atmosphere. The minus 100- plus 200-mesh fraction was then dried under a flow of Ar and tested at initial temperatures of 40° and 45° C. The results of this test were compared with the results of tests on this coal prepared in air in the normal manner. The temperature-time traces are shown in figure 10.

In the tests at an initial temperature of 40° C, neither sample attained thermal

TABLE 8. - Effect of O_2 concentration on minimum self-heating temperature

Seam	O_2 conc, vol pct	Minimum SHT, °C	Comments
Pittsburgh....	21	95	Standard test conditions.
	16	100	Reached 186° C in 13.5 h.
	14	100	Reached 186° C in 17.3 h.
No. 80-2......	21	40	Standard test conditions.
	18	45	None.
	14	50	Do.

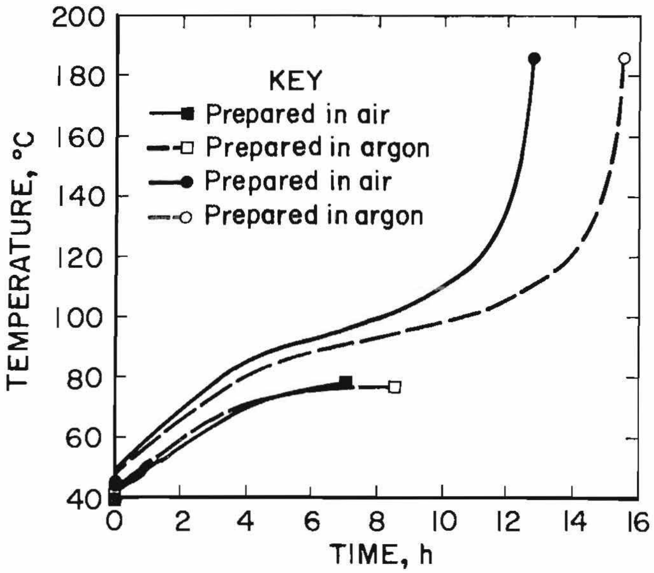

FIGURE 10.—Effect of low-temperature surface exposure of coal to air during sample preparation.

runaway, with the sample prepared in Ar reaching 76° C in 8.5 h, and the sample prepared in air reaching 78° C in 7.0 h. In the tests at an initial temperature of 45° C, both samples underwent thermal runaway, with the sample prepared in Ar reaching 186° C in 15.5 h and the sample prepared in air reaching 186° C in 12.7 h.

In both sets of tests, the samples prepared in air were slightly more reactive than those prepared in Ar based on their times to reach maximum temperature. Therefore, there was no apparent effect of the exposure of the coal surfaces to air during sample preparation. There was no clear reason for the decreased reactivity seen in the samples prepared in Ar. Possibly, the Ar filled the internal pores of the coal during the preparation and drying of the sample causing the rate of oxidation in the tests with the Ar, which is dependent on the diffusion of O_2 into the pores, to slow.

MODERATE-SCALE APPARATUS

Minimum Self-Heating Temperatures

In this section, the results of tests to determine the minimum SHT's of the Pittsburgh and No. 80-2 seam coals in the moderate-scale spontaneous combustion apparatus are described. In the determination of the minimum SHT of the No. 80-2 sample, tests were made at initial temperatures of 30°, 40°, and 50° C. Figure 11 shows the temperatures of the coal bed at the 5.1-, 15.2-, and 25.4-cm depths of

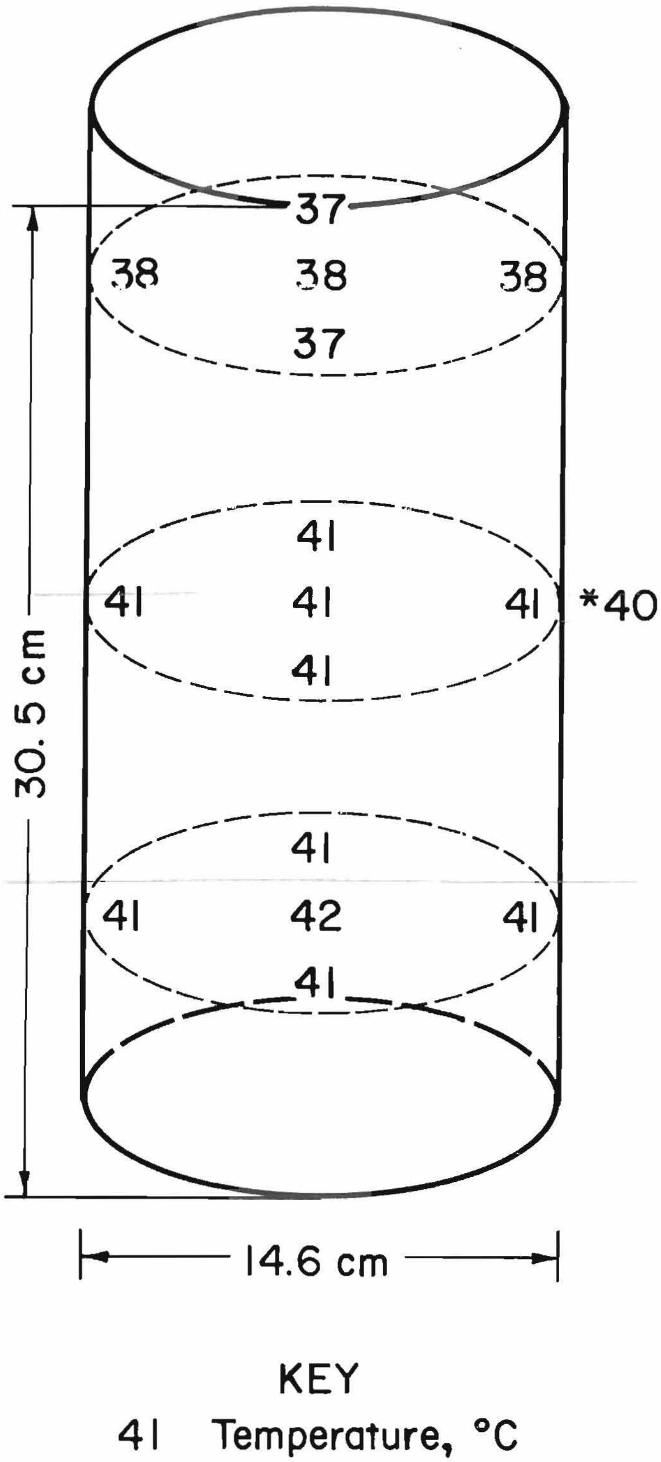

FIGURE 11.—Temperature profile of coalbed at start of test with No. 80-2 coal at 40° C.

the 30.5-cm-deep, 14.6-cm-diam sample bed at the start of the test at 40° C, the temperature of the wall at the center of the sample bed, denoted by the asterisk. The temperatures were uniform throughout the bottom and center regions, while being 3° to 4° C lower in the top region, probably because of heat losses out the top of the sample container.

The temperature-time traces of the thermocouples located along the center axis of the coal bed at depths of 5.1 cm (top), 15.2 cm (middle) and 25.4 cm (bottom) for the tests at 40° C are shown in figure 12*A*. The radial thermocouples at the three depths generally followed the center axis thermocouples but were at lower temperatures because of heat losses through the walls. When moist air was introduced to the sample, signaling the start of the test, the temperature rose rapidly in the bottom region, reaching 55° C in 9 h. The temperature in this region then remained fairly constant until 25 h, when it began to rise at a rate of about 2° C/h for the duration of the test, reaching 104° C at 53 h, when the test was terminated. The temperatures in the middle and top regions lagged behind the bottom temperature by several hours, increasing slowly until about 20 h into the test, when the temperatures in these regions increased sharply, reaching 140° C in the middle region, and 126° C in the top region of the coal bed in 53 h. There was a decrease in the heating rates in the middle and top regions at about 100° C, probably because of the evaporation of moisture from the coal surfaces, an endothermic process, which competes with the heat being generated by the oxidation processes.

Similar results were found in the test at an initial temperature of 50° C. The temperature-time traces of this test are shown in figure 12*B*. Initially, there was a rapid rise in the temperature in the lower region of the coalbed, lasting about 3 h. The temperature in that region then leveled off before rising at a steady rate for the duration of the test. The temperatures in the middle and top

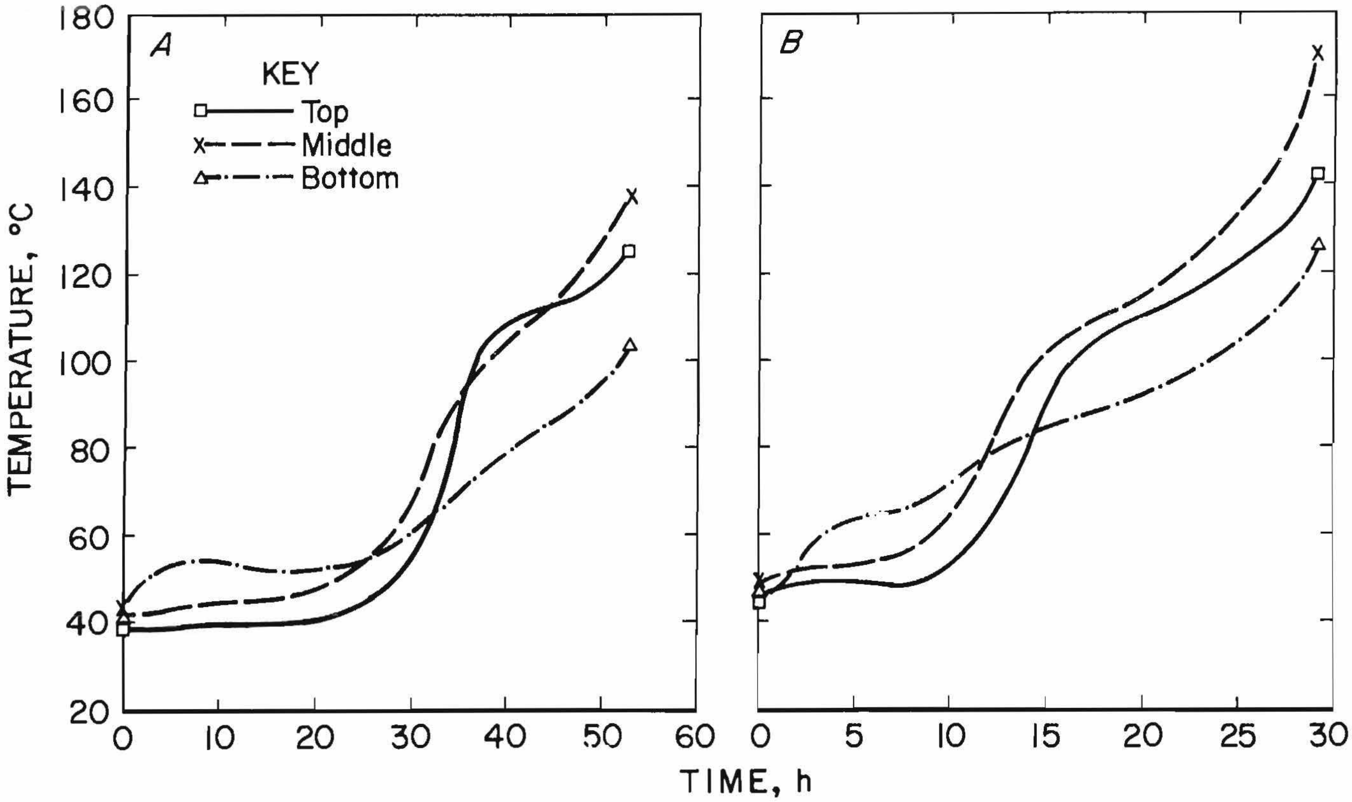

FIGURE 12.—Temperature histories of thermocouples located along center axis of coalbed in test with No. 80-2 coal. *A*, initial temperature, 40° C; *B*, initial temperature, 50° C.

regions lagged behind, showing little activity in those regions for the first 8 h of the test. The temperature in the middle region then rose rapidly, overcoming the bottom region temperature at 12 h, followed by the top region, which overcame the bottom region in temperature at 15 h. The rate of temperature rise slowed in the top and middle regions as the temperatures neared 100° C in those regions, before rising rapidly again. The test was terminated at 29.5 h, when the temperature was 127° C in the bottom region, 171° C in the middle region, and 142° C in the top region.

In the test at 30° C, the sample reached a maximum temperature of 35° C in 16 h in the bottom region of the coal bed. The temperature-time traces are not shown.

The heating rates in degrees per hour are plotted as a function of time in figure 13, for the test from an initial temperature of 50° C to better illustrate the movement of the reaction through the coalbed. Initially, the highest rates were found in the bottom region at 2.6 h, the middle region at 12 h, and the top region at 14 h. The rates in the middle and top regions had minimums at 18 and 21 h, respectively, when the temperatures in those regions were near 100° C, again, probably because of moisture evaporation from the coal surfaces. The rates in all three regions then increased at an exponential rate until the test was terminated.

The minimum SHT of the Pittsburgh sample in the moderate-scale apparatus was 110° C. The temperature profile of the the coal bed at the start of the test at 110° C is seen in figure 14. The 110° C figure used as the initial temperature in this test was the temperature of the wall at the center of the sample bed, denoted

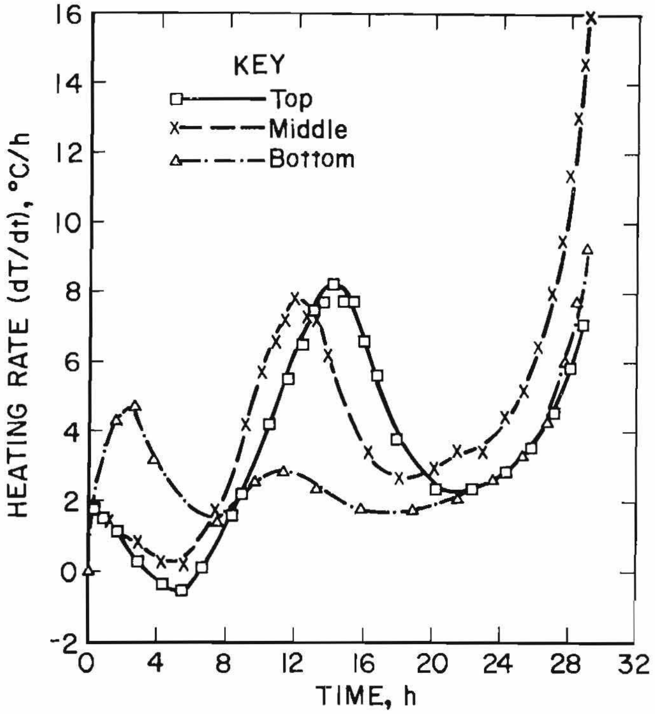

FIGURE 13.—Heating rates at thermocouples located along center axis of coalbed in test with No. 80-2 coal at initial temperature of 50° C.

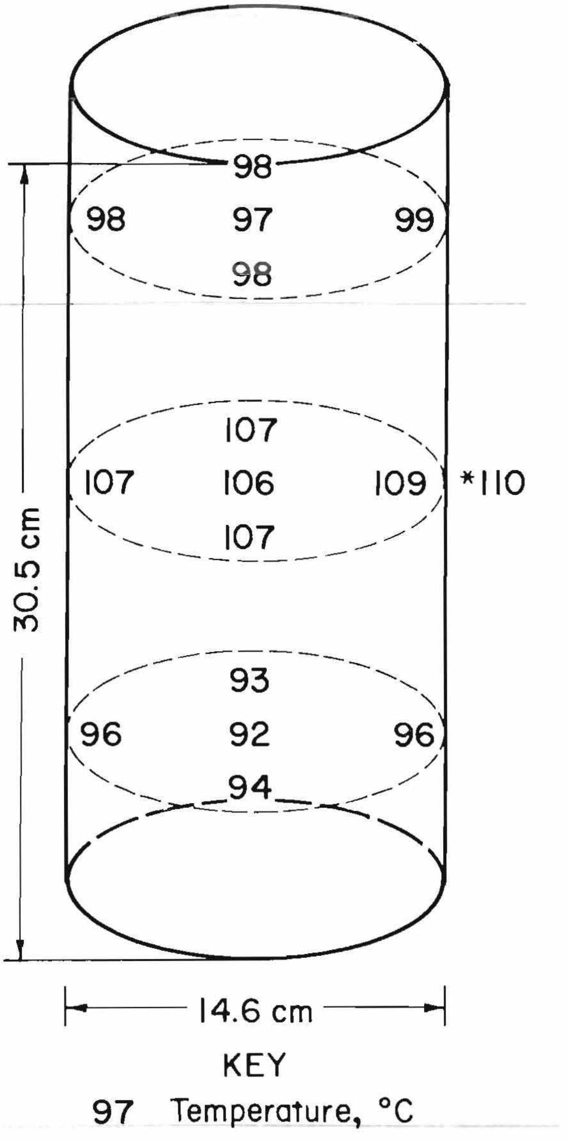

FIGURE 14.—Temperature profile of coalbed at start of test with Pittsburgh coal at 110° C.

by the asterisk. The lower temperatures at the thermocouples at the top and bottom of the bed were indications of the heat losses at the top and bottom of the apparatus that were not as evident in the tests at the lower temperatures with the No. 80-2 samples.

The temperature-time traces of the center thermocouples located at the 5.1-, 15.2-, and 25.4-m depth of the sample bed are shown in figure 15. The test ran for 21 h and reached a temperature of 195° C in the center of the sample before being terminated. The heating rates throughout the test were essentially the same at all three levels, with the difference in temperatures being due to the differences at the start of the test.

There was little evidence of the movement of the higher heating rates, or reaction, through the coalbed as in the tests on No. 80-2 samples. There was an increased heating rate initially in the bottom region during the first hours of the test, and a slight increase in rate in the center region at about 4 h. For the duration of the test in these regions, and for the entire test in the top region, the rate increased at an exponential rate.

Table 9 shows a comparison of the experimental parameters used in the moderate-scale tests with those used in the adiabatic heating oven. Both tests used predried samples and humidified air. The moderate-scale tests used larger particles, 6,350 µm by 0 mesh compared to 74 by 150 µm in the adiabatic heating oven tests, as well as a larger sample, 3,000 g versus 100 g, and a higher flow rate, 900 cm³/min versus 200 cm³/min. The results, shown in the table, were that the minimum SHT of the No. 80-2 coal was 40° C in both the moderate-scale apparatus and adiabatic oven, whereas the Pittsburgh coal self-heated from a minimum initial SHT of 110° C in the moderate-scale apparatus compared with an SHT of 95° C in the adiabatic oven. Since the moderate-scale apparatus behaves adiabatically only in the region near the differential thermocouples, the large heat losses in the other regions of the coal sample bed at the high initial temperatures required for the self-heating of Pittsburgh coal account for the discrepancies in the results for that coal.

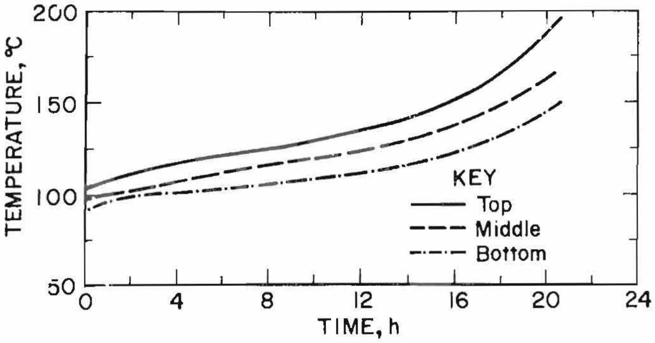

FIGURE 15.—Temperature histories of thermocouples located along center axis of coalbed in test with Pittsburgh coal at initial temperature of 110° C.

Moisture Effects

The lack of significant changes in the heating rates through the coal sample bed in the test with Pittsburgh coal, along with the demonstrated dependence of the heat-of-wetting effect on temperature and rank in the adiabatic oven, indicates

TABLE 9. - Experimental parameters[1] used in the adiabatic heating oven and moderate-scale spontaneous combustion apparatus

	Moderate-scale apparatus	Adiabatic oven
Flow rate.....cm³/min..	900	200
Particle size......µm..	Minus 6,350	Minus 150, plus 74
Sample size.........g..	3,000	100
SHT, °C:		
Pittsburgh seam......	110	95
No. 80-2 seam........	40	40

[1] Both tests used predried samples and humidified air.

that moisture is playing a large role in the self-heating of the No. 80-2 coal in the moderate-scale apparatus, while having little effect in the self-heating of the Pittsburgh coal.

Another test was conducted with No. 80-2 at an initial temperature of 40° C to investigate the role of moisture. In this test a humidity-temperature probe was used to measure the temperature rise in the sample as a function of moisture content of the air. The probe was inserted slightly off the center axis at a depth of 15.2-cm into the sample. Figure 16 shows the temperature histories of the three center axis thermocouples. The test ran for 23 h, at which time the temperatures reached 78°, 99°, and 97° C in the bottom, middle, and top regions, respectively. The sample temperatures were still rising, but the test was terminated since the relative humidity being measured by the probe was 100 pct and the objective of the test was accomplished.

The movement of the maximum heating rates through the sample occurred much the same as the earlier test at 40° C on this coal, with the highest heating rates being 4.1° C/h at 4 h in the bottom region, 5.5° C/h at 16 h in the middle region, and 6.7° C/h in the top region at 19.h.

Table 10 shows the relative humidity measured at the probe tip and heating rate measured at the center thermocouple in the middle region from 10 to 18 h from the start of the test. Figure 17 is a plot of the heating rate and relative humidity at the center thermocouple throughout the test. The heating rate increased as the relative humidity increased, reaching a maximum rate of 5.5° C/h at 16 h and 76.4° C and a relative humidity of 50 pct. The heating rate decreased to 4.2° C/h as the relative humidity reached 100 pct at 18 h in the test.

Based on these results it appears that the reaction wave moving through the coal sample bed corresponded to the movement

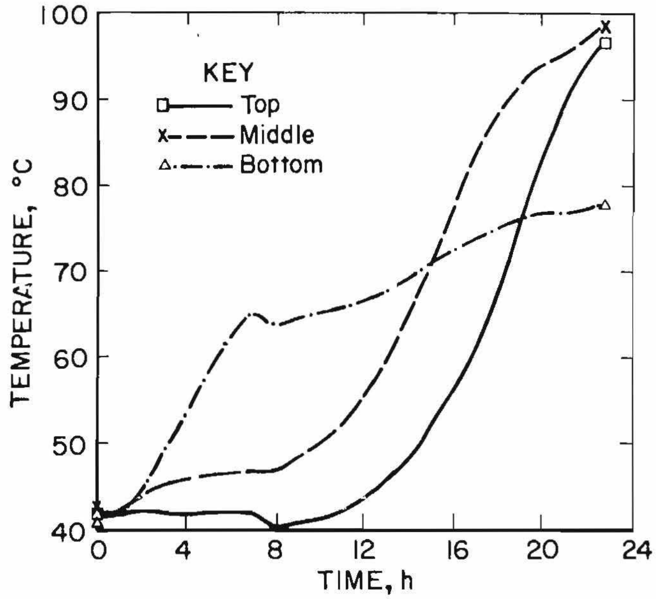

FIGURE 16.—Temperature histories of thermocouples located along center axis of coalbed in test with No. 80-2 coal at initial temperature at 40° C.

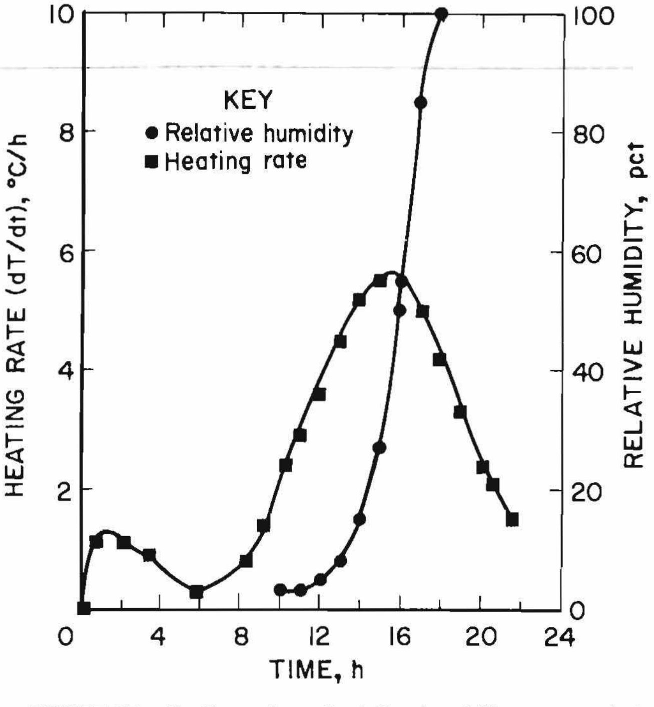

FIGURE 17.—Heating rate and relative humidity measured at center thermocouple in the coalbed during test with No. 80-2 coal at initial temperature of 40° C.

TABLE 10. - Heating rate and relative humidity (RH) in the middle region of the sample in test of No. 80-2 coal from an initial temperature of 40° C

Time from start of test, h	Temperature, °C	Heating rate, °C/h	RH, pct
10.............	50.2	2.3	3
11.............	52.1	2.9	3
12.............	55.3	3.6	5
13.............	59.5	4.4	8
14.............	64.6	5.2	15
15.............	70.2	5.5	27
16.............	76.4	5.5	50
17.............	82.9	5.0	85
18.............	87.5	4.2	100

of moisture through the coal sample bed, and showed the large effect moisture has on the self-heating process for a low rank coal. The absence of this so-called reaction or moisture wave in the tests on Pittsburgh coal, a high rank coal, shows that the effect of moisture has a dependence on temperature and/or rank in the moderate-scale apparatus, just as it had in the adiabatic oven.

CONCLUSIONS

Laboratory experiments were conducted to evaluate the relative self-heating tendencies of coals. In addition, several of the factors that can affect the self-heating process were evaluated. The main conclusions from the experiments are summarized as follows:

1. The relative self-heating tendencies of coals, as measured by their minimum self-heating temperatures (SHT's) in an adiabatic oven, increased with decreasing rank. The minimum SHT's ranged from 35° C for a lignite and high-volatile C bituminous coal to 135° C for low-volatile bituminous coals. Anthracite showed virtually no reactivity at temperatures up to 140° C, the limit of the apparatus.

2. A multiple linear regression analysis of the results from the adiabatic heating oven showed that the minimum SHT of a bituminous coal was strongly dependent on the dry ash-free (DAF) oxygen concentration of the coal, and could be predicted by the following empirical expression:

$$\mathrm{SHT}_{min},\ ^{\circ}\mathrm{C} = 139.74 - 6.57 \times [\mathrm{O,\ pct\ (DAF)}].$$

The relationship had a correlation coefficient of 0.934, with an average relative error of 10.6 pct.

3. The heating curves from the self-heating of coal in the adiabatic heating oven, using moist air as the test gas, can be divided into three regimes. Initially, the rate of temperature rise depends on the heat-of-wetting. The curves pass through an inflection point, in which no mechanism dominates. In the final phase of the test, the oxidation mechanism dominates.

4. Computation of activation energies in the region in which the oxidation mechanism dominates showed that the activation energy, in general, decreased with coal rank, but a quantitative ranking of reactivity based on these values was not possible. The average activation energy for bituminous coals in this study was 18.7 kcal/mol.

5. The heat-of-wetting was dependent on coal rank and temperature. The temperature range in which the heat-of-wetting dominates decreased with increasing rank and the corresponding increase in temperature. Results of tests measuring the heat-of-wetting of different rank coals using humidified N_2

showed a strong dependence of the heat-of-wetting on temperature, with a smaller dependence on rank.

6. The lowest SHT's and corresponding highest self-heating risks were found using humidified air instead of dry air, as the test gas. In tests on the No. 80-2 coal, heating rates in tests using humidified air (8.3° C/h) were almost twice the sum of the heating rates of tests with dry air (1.8° C/h) and moist N_2 (2.9° C/h), demonstrating the synergistic effect of moisture on the oxidation process in the self-heating of coal.

7. Decreasing the particle size of the coal sample in the adiabatic heating oven resulted in a decrease in the minimum SHT, to a critical size of 74 by 150 µm. Below 74 µm, the SHT was not affected, probably because of particle agglomeration.

8. Decreasing the O_2 concentration from 21 to 14 pct increased the minimum SHT's of Pittsburgh coal by 5° C and No. 80-2 coal by 10° C, showing that the tendency of a coal to self-heat decreases with reduced O_2 concentration, and is slightly dependent on rank.

9. The results of self-heating tests in the moderate-scale apparatus (3 kg) on Pittsburgh and No. 80 seam coal showed good agreement with results from the adiabatic heating oven. The minimum SHT of Pittsburgh coal was 95° C in the adiabatic oven and 110° C in the moderate-scale apparatus, while the No. 80 coal had a minimum SHT of 40° C in both. The difference in the minimum SHT of the Pittsburgh coal in the moderate-scale apparatus is attributed to the large heat losses from the apparatus at high temperatures.

10. The rate of temperature rise through the coal sample bed in the moderate-scale apparatus showed a strong dependence of the self-heating process on the moisture content of the air for the No. 80-2 coal. The absence of this dependence in tests on Pittsburgh coal indicated a strong dependence of the heat-of-wetting effect on rank and temperature.

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Btu	British thermal unit
Btu/lb	British thermal unit per pound
cal	calorie
cal/g	calorie per gram
cal/(g-K)	calorie per gram-Kelvin
cm	centimeter
cm^3	cubic centimeter
cm^3/min	cubic centimeter per minute
°C	degree Celsius
°C/h	degree Celsius per hour
°C/s	degree Celsius per second
g	gram
g/kJ	gram per kilojoule
h	hour
kcal/mol	kilocalorie per mol
kg	kilogram
kJ/g	kilojoule per gram
K/s	degree Kelvin per second
lb	pound
µm	micrometer
min	minute
mL	milliliter
pct	percent
vol pct	volume percent
W	Watt
wt pct	weight percent

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