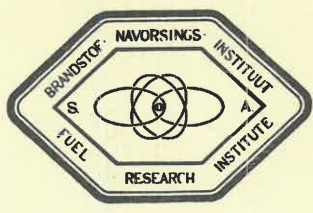


FRI 10/1958

F.R.I. 47.

VERSLAG No. 10 (I)
VAN 1958

REPORT No. 10
OF 1958



U11D/513

BRANDSTOFNAVORSINGSINSTITUUT

VAN SUID-AFRIKA

FUEL RESEARCH INSTITUTE

OF SOUTH AFRICA

ONDERWERP:
SUBJECT: STUDIES ON THE INTERACTION OF OXYGEN

WITH COAL IN THE TEMPERATURE RANGE

0° TO 90°C.

PART I.

AFDELING:
DIVISION: CHEMISTRY

NAAM VAN AMPTENAAR:
NAME OF OFFICER: P.G. SEVENSTER.

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

REPORT NO. 10 OF 1958.

STUDIES ON THE INTERACTION OF OXYGEN
WITH COAL IN THE TEMPERATURE RANGE 0° TO 90°C.

PART I.

When coal is exposed to air, reaction takes place even at low temperatures resulting in changes in the physical and chemical properties of the coal.

At low temperatures the change may occur very slowly but it is continuous over long periods. The rate of oxygen absorption increases considerably with temperature. At higher temperatures the rate of heat evolution may become so great that spontaneous ignition can occur.

In view of its commercial importance and scientific interest, the oxygen absorption process has been the subject of numerous investigations.*)

The experimental conditions in such investigations were usually chosen to simulate those encountered in practice and generally do not lend themselves to the study of the fundamental processes involved in the absorption of gases and vapours at normal atmospheric temperature, especially during the initial stages of the absorption.

*) Coward¹⁾ has made a comprehensive survey of the literature up to 1957.

Some of the conclusions derived from these investigations are:

- (a) Coal consumes large quantities of oxygen.
- (b) The process is activated.
- (c) The rate of absorption is dependent on the pressure.
- (d) Initially, absorption proceeds at a high rate but after some hours this drops off to a slow rate that may, however, be very persistent.

Beyond such general conclusions, very little appears to be known about the fundamental processes and it was the object of conducting this investigation to obtain more detailed information, especially on such aspects as the nature of the absorption and the heat of absorption.

In a fundamental study of the interreaction of oxygen and a coal surface, knowledge of the type of adsorption occurring is important in view of its effect on the rate of gas absorption, the temperature dependence of the amount of gas absorbed at equilibrium and the heat generation.

It was therefore decided to attack the problem by studying various aspects either jointly or separately and this paper deals with some absorption and desorption experiments and a study on the heat of absorption.

Regarding the temperature range of 0°C to 100°C as of the greatest interest in the study of the spontaneous heating of coal, the experimental work was generally confined to this temperature range. Some

experiments/..

experiments were done however, at lower temperatures when it was considered advisable to obtain a more complete picture of trends.

TYPES OF COAL STUDIED:

Although numerous samples of coal were used in some of the studies, most of the experiments were done on the coals listed in Table 1.

TABLE 1.

Sample	% H ₂ O	% Ash	% V.M.	Volume of O ₂ ads. at 30°C in 100 hrs.
A	7.5	24.2	23.9	3.5 c.c.
B	6.2	23.5	23.0	2.2 "
C	4.7	16.9	23.9	2.1 "
D	2.5	12.5	26.5	0.8 "

Fairly large bulk samples of the coals were obtained from fresh faces in collieries and stored under water in lump form. For experimental work the sample was crushed to -60 mesh B.S.S. and stored under water until required. Five to ten gram portions of this finely ground coal were used in experiments. The moisture was usually driven off by heating the coal under vacuum in the apparatus in which the experiment was done.

ABSORPTION EXPERIMENTS:

(a) Absorption Isobars:

Absorption isobars were determined using a constant pressure apparatus. Measurements were made at -183°C (liquid oxygen), -80°C (solid carbon dioxide-alcohol slush bath) -22.9°C (solid carbon tetrachloride slush bath), -6.6°C (solid analine slush bath) 0°C (ice) and at/.....

and at higher temperatures using electrically heated furnaces.

A fresh representative portion (about 5 grams) of the coal sample under investigation was used for each experiment whether conducted at the same or at different temperatures.

Prior to conducting absorption experiments, the coal was evacuated at 110°C for about 16 hours.

The general trend of the isobars is shown in Fig. 1. It will be noted that the equilibrium amount adsorbed at -183°C is considerably less than that at -80°C . Such an apparently anomalous temperature dependence was first observed by Maggs³⁾ studying the adsorption of nitrogen on British coals. The phenomenon has also been studied by van Krevelen and Zwietering⁴⁾ and Sevenster⁵⁾. It would appear that the decrease in the amount of gas adsorbed at very low temperatures is due to activated diffusion and to some constriction rather than to a change in the nature of the type of adsorption which at low temperatures is generally regarded as a physical process.

From about -80°C the isobar has a negative gradient up to about -10°C where the curve has a minimum.

Such minima in adsorption isobars are usually ascribed to the combined effect of diminishing physical adsorption and the onset of chemisorption with rising temperature. Accepting this explanation one must conclude that, in this case, chemisorption of oxygen becomes appreciable even at -6°C .

One would/.....

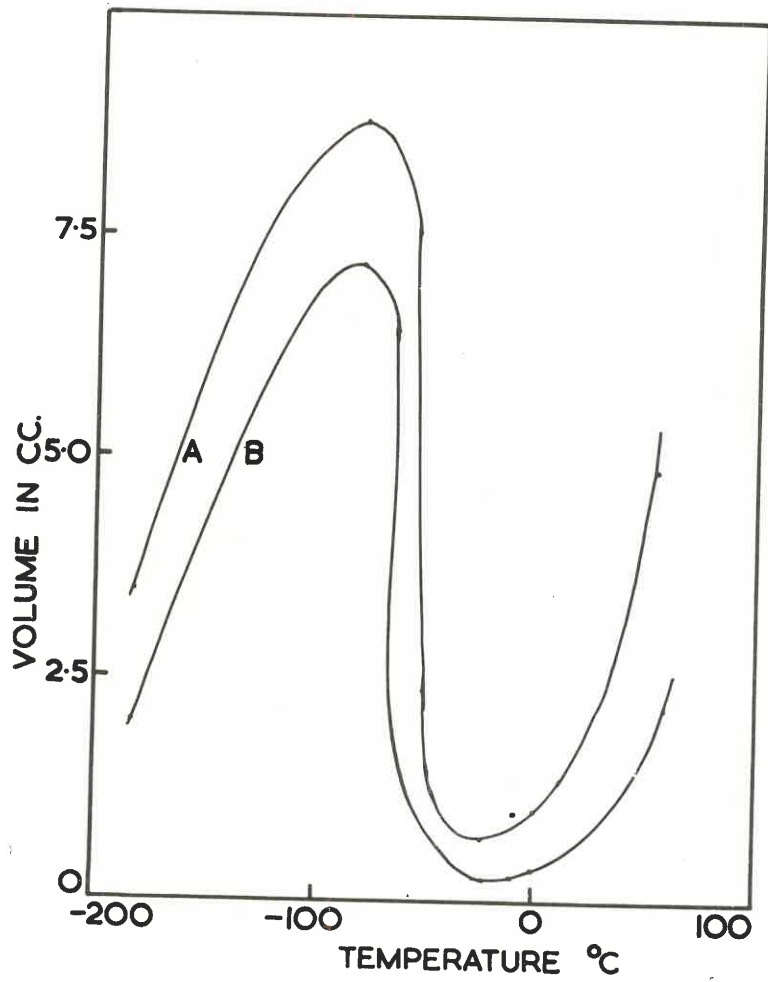


FIGURE 1.

ABSORPTION ISOBARS

OBTAINED AT CONSTANT OXYGEN PRESSURE.

(20 cm. Hg)

One would expect the isobar to rise until chemisorption equilibrium is established. Considering the evidence provided by Fig. 1, one must conclude that such an equilibrium is either not reached at 80°C or an actual chemical reaction between oxygen and carbon superimposed on the chemisorption is responsible for an increasing consumption of oxygen with rising temperature.

(b) The reversibility of the Oxygen Absorption between 0° and 100°C.

Further information on the nature of the absorption process was sought by studying the reversibility of the absorption.

Oxygen physically adsorbed or even in loose chemical combination with the coal should be recoverable by physical means such as evacuation and change of temperature.

Some reports on the reversibility of the oxygen absorption by Winmill⁶⁾, Haldane⁷⁾ and Wheeler⁸⁾ are conflicting and were based on only a few determinations. Olpinski and others⁹⁾ have studied the reversibility of the oxygen absorption process in greater detail and established that the amount of oxygen recoverable decreases with the temperature at which absorption takes place becoming negligible at temperatures above 50°C. These findings were confirmed in the present study.

Appreciating that if oxygen combined chemically with the coal, volatile reaction products could be formed, provision was made in these experiments to analyse the gas recovered from the coal after absorption.

The apparatus/.....

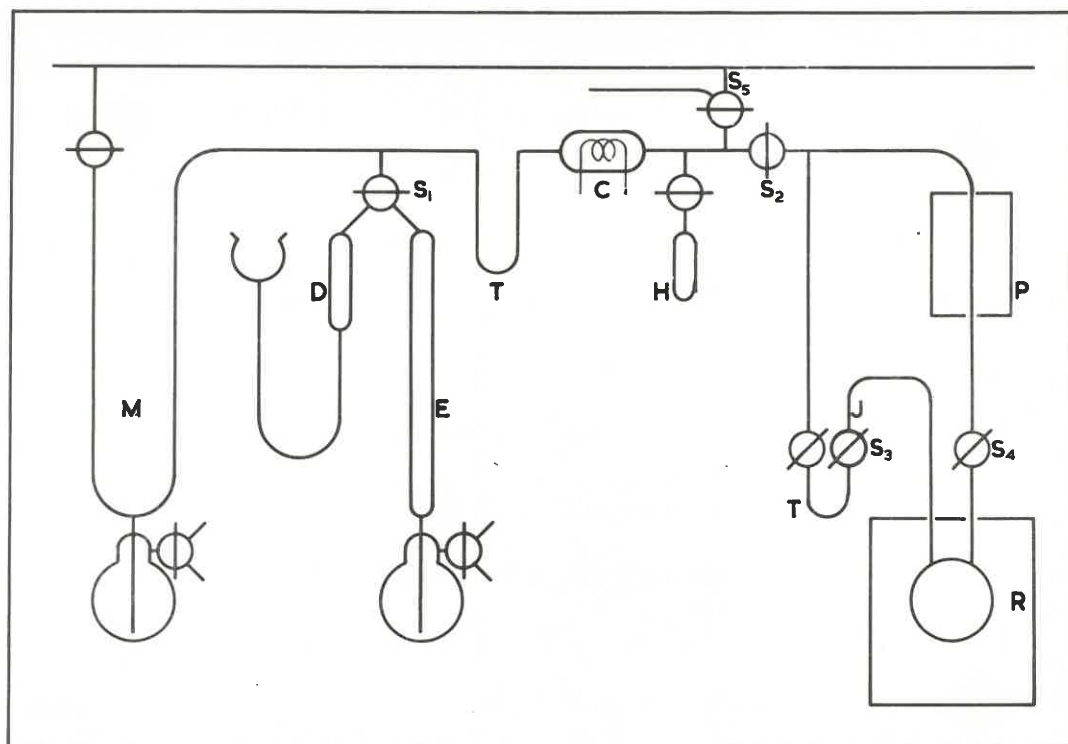


FIGURE 2.

APPARATUS USED FOR OXYGEN ABSORPTION
STUDIES AND ANALYSIS OF GASEOUS RE-
ACTION PRODUCTS.

The apparatus used is shown diagrammatically in Figure 2.

The experimental procedure was as follows:-

About 10 grams of -60 mesh B.S.S. coal were placed in the reaction tube (R). While maintaining this at 110°C , the whole system was evacuated for 16 hours.

The coal was now brought to the desired temperature and maintained there throughout the experiment - including the final evacuation to determine the recoverable oxygen.

With stopcock S_2 closed, oxygen was admitted through S_5 to the burette (B) to a pressure of 20 cm.Hg. (noted on manometer M). The initial volume of oxygen was calculated from this pressure and the burette setting.

Liquid oxygen was placed around trap T_1 to freeze out any water vapour and carbon dioxide formed during the reaction. The oxygen was then admitted to the coal through stopcock S_2 and the glass circulating pump (P) was started. The rate of oxygen circulation was about 5 litres per hour.

The pressure in the system was held constant automatically, by raising the mercury in the burette by means of a device described by Taylor and Strother¹⁰⁾.

Adsorption was allowed to proceed for about 6 hours and then stopcock S_4 was closed to ensure that all the gas from the reaction tube should pass through trap T_1 on evacuation, thus ensuring that all the water vapour and carbon dioxide present would be trapped.

The gas was/.....

The gas was then pumped into vessel D using a Töpler pump. The pumping was continued until the heights of the mercury columns in M were equal, as observed by a cathetometer capable of reading to 0.001 cm. This usually required one hour of continuous pumping.

Analysis of the Gas:

With stopcock S_2 closed, the gas was transferred from D to the burette and its pressure was noted. This gas could contain carbon monoxide in addition to the excess oxygen.

The carbon monoxide was burned on the platinum coil C. The carbon dioxide formed was trapped in T_2 which was immersed in liquid oxygen. To ensure that all the carbon monoxide would be burned, the gas in the system was moved to and fro by raising and lowering the mercury in the burette.

After combustion, the oxygen was pumped out of the system through stopcock S_5 .

The liquid oxygen was now removed from T_2 . After T_2 had attained room temperature the pressure due to carbon dioxide was noted and the gas was then pumped out of the system.

Trap T_2 was again cooled in liquid oxygen, while the liquid oxygen bath around T_1 was replaced by one containing dry ice and stopcock S_2 was opened. Thus carbon dioxide was transferred to T_2 while water was retained in T_1 . After closing S_2 the liquid oxygen trap was again removed from T_2 and the pressure due to carbon dioxide was noted as before.

Depending on the/....

Depending on the quantity formed during the experiment, the water was either weighed by detaching trap T₁ at the ground glass joint (J) or, in the case of small quantities, the carbon dioxide in the system was first removed and then the water was allowed to react with calcium hydride contained in a small tube (H) and the hydrogen formed was determined volumetrically.

Discussion of Results:

The results of experiments conducted on four coal samples at various temperatures are summarised in Table 2.

TABLE 2.

Amount of Oxygen absorbed by Coals and Analysis of the desorbed gas.

(The values are in ml. at N.T.P. calculated for 10gm. of coal)

Temp. °C	Vol. Oxygen absorbed.	Analysis of desorbed Gas				Eqv. O ₂
		O ₂	H ₂ O	CO	CO ₂	
<u>Coal A.</u>						
0	8.5	3.3	-	-	-	3.3
32	15.4	1.0	-	-	-	1.0
42	18.8	0.6	-	-	-	0.6
55	24.2	0.7	-	0.8	0.5	1.6
72	32.2	0.0	1.5	0.8	0.9	2.0
92	-	0.2	12.0	0.6	2.0	8.5
<u>Coal B.</u>						
0	6.1	2.4	-	-	-	2.4
32	13.2	1.6	-	-	-	1.6
42	13.8	0.6	0.5	1.0	0.5	1.8
55	16.0	0.5	0.5	1.2	0.6	1.7
72	23.2	0.1	2.0	0.8	0.9	2.4
92	-	0.0	10.4	-	2.4	7.6
<u>Coal C.</u>						
32	7.0	1.0	-	-	-	1.0
42	9.0	0.0	-	-	-	0.0
55	12.0	1.7	0.3	-	-	1.8
72	15.7	0.4	1.0	-	-	.9
92	-	0.0	5.6	0.0	1.6	4.4
<u>Coal D.</u>						
32	6.5	0.0	-	-	-	0.0
42	7.3	0.3	-	-	-	0.3
55	10.0	1.7	0.3	-	-	1.8
72	16.2	0.0	1.0	-	0.6	1.1
92	-	0.0	6.0	0.5	1.4	4.6

The volume/.....

The volume of oxygen absorbed refers to the amount consumed during the experimental period of 6 hours and not to the equilibrium amount that can be absorbed at the stated temperature.

In calculating the volume of oxygen absorbed, it was borne in mind that any carbon monoxide formed during the experiment would remain in the circulating oxygen, and a suitable correction was made.

The amount of free oxygen desorbed from the coal was calculated from the known volume of the system, the volume of gas (oxygen plus carbon monoxide) recovered after the experiment and pumped into vessel D, and the determined amount of carbon monoxide in this gas.

The other reaction products were determined as already described.

Referring to Table 2, it will be observed that the amount of oxygen absorbed increases steadily as the temperature of absorption is raised.

On the other hand the amount of free oxygen recoverable generally shows a steady decrease, especially if considered as a proportion of the amount absorbed under the experimental conditions.

The total amount of recoverable gas increases from about 42⁰, but this is due to the higher rate of conversion of oxygen into carbon dioxide, carbon monoxide and water at higher temperatures. These products being only physically adsorbed by the coal are desorbed readily.

The results/.....

The results suggest that the physical adsorption of oxygen plays only a minor rôle in the temperature range from 30°- 40° upwards. On the other hand, chemical reaction leading to the evolution of carbon monoxide, carbon dioxide and water sets in between 40°C and 55°C.

However, even at 72°C the amount of oxygen absorbed greatly exceeds that recoverable either as free oxygen or as gaseous reaction products.

This unbalance, observed by many investigators, has led to hypotheses of the formation of intermediate coal-oxygen complexes.

While Yohe and Harman¹¹⁾ and Jones and Townend¹²⁾ have reported that at least part of this oxygen forms reactive oxygen groups, giving an oxidising power to the coal, Russel¹³⁾ and Haslam¹⁴⁾ were able to show that oxidised coal was capable of affecting a photographic plate even if this is not in contact with the coal. The latter author ascribed this to the formation of formaldehyde, the formation of which he could demonstrate.

No effort was made in the present investigation to determine the nature of coal-oxygen complexes.

Heat of Absorption Studies.

The evidence of the absorption studies suggests that a change from physical adsorption to chemisorption may occur at about -6°C and that at higher temperatures (40°C upwards) the latter may merge into, or be superimposed by chemical reaction.

If this is/.....

If this is the case, one might expect differences in the heat of absorption at temperature levels where the process is (1) purely physical adsorption (2) mainly chemisorption (3) wholly chemisorption with possibly superimposed chemical reaction.

The determination of the heat of absorption of oxygen on coal is rendered difficult by some characteristics of the process. One of these is that the rate of absorption and the rate of heat generation fall off quite rapidly with time until a low level is reached. This may, however, be continuous over long periods.

A consequence is that, in the temperature range studied, absorption equilibrium may not be reached for days, so that it becomes very difficult to obtain reliable absorption isotherms. The Clausius-Clapeyron equation can, therefore, hardly be used to determine the heat of absorption.

The persistent low rate of heat generation in the later stages of an experiment also practically rules out the use of adiabatic calorimeters for determining the heat of absorption.

Attention was therefore given to the use of isothermal calorimeters to determine the heat of absorption at different temperatures.

Isothermal Calorimeters.

The construction and calibration of the calorimeters have been described elsewhere.¹⁵⁾

Since they are operated at the melting point of the calorimetric substance, these substances must be very pure.

Ice (M.P. 0°C)/....

Ice (M.P. 0°C), phenol (M.P. 41°C) and naphthalene (M.P. 80°C) have been used. Chemical reagent quality phenol and naphthalene were used and were further refined using a zone melting technique.

The calorimeter was brought to the desired conditions, (i.e. part of the calorimetric substance solid and part molten) before the coal sample was introduced. This procedure ensured that the required solid mantle was formed round the reaction tube.

Due to the difficulty of maintaining exact equilibrium between the solid and liquid phases of the calorimetric substance, the temperature of the bath was adjusted to such a value that a very slight drift of the mercury in the measuring capillary was observed. This drift was measured at one hour intervals at a fixed bath temperature over long periods.

For the naphthalene calorimeter the value of the drift expressed as cal/hour varied between 0.1 and 1.1 and an average of 0.6 cal/hour was used for the correction. With the phenol calorimeter the drift varied between 0.1 and 0.3 cal/hour and the average was 0.2 cal/hour.

With the ice calorimeter the temperature of the surrounding ice bath was maintained as close as possible to 0°C and the drift measured over a period of 24 hours. A positive drift, the average of which was equivalent to 0.3 cal/hour was observed.

The coal sample was dried and evacuated for 16 hours at 110°C in a special container designed to permit the transfer of the sample to the calorimeter under vacuum.

After charging/..

After charging the calorimeter, it was connected to a constant volume absorption system. The calorimeter was allowed to reach thermal equilibrium, which required about 2 hours and the oxygen was then admitted to the reaction tube of the calorimeter.

Three coal samples with different oxygen absorption characteristics were used in these experiments. The oxygen pressure was maintained constant at 42 cm.Hg. The measurements were made for about 3 to 4 hours at the three temperatures.

Results of these experiments are summarised in Table 3.

TABLE 3.

Heat of Oxygen Absorption by different Coals and at different Temperatures. (Average values of duplicate measurements).

Time in Hours.	Heat of absorption (in kilo.cal/mole at:								
	0°			41°			80°		
	A	C	D	A	C	D	A	C	D
0.25	67	-	-	70	68	62	70	69	68
0.5	60	-	-	67	67	64	70	70	70
1.0	70	-	-	67	70	65	68	68	66
1.5	68	-	-	69	64	67	69	67	65
2.5	-	-	-	65	67	65	67	65	65
2.5									
3.0									
3.5	-	-	-	66	68	67	66	67	65
4.5	-	-	-	65	68	67	66	65	65

The magnitude of the heat of absorption indicates that the absorption process is of a chemical nature, and that chemisorption overshadows any physical adsorption even at 0°C.

It would also/.....

It would also appear that the surfaces of the different coals studied are of the same nature as far as the absorption of oxygen molecules is concerned. Differences in the rate of absorption from one coal to another (and consequently differences in the rate of heat release) must be ascribed to greater or lesser accessibility of surface capable of bonding oxygen.

TABLE 4.

Heat of Oxygen Absorption by Coal
at different temperatures over
long periods.

(Average value of duplicate experiments)

Time in Hours.	Heat of Absorption in kilo.cal/mole at:		
	0°	41°	80°
1	68	70	67
2	67	69	69
3	67	69	68
4	-	68	70
5	-	69	70
6	-	69	64
8	-	67	68
10	-	69	67
12	-	-	66
14	-	-	66
16	-	-	66
18	-	-	67
20	-	-	68

Another interesting fact borne out by these results is that no decrease in the heat of absorption per mole of oxygen is observed, although the rate of absorption decreased considerably with time. This suggests that the surfaces covered during this period are homogeneous in respect of their oxygen bonding properties.

It was, therefore, attempted to gain further information regarding the dependence of the heat of absorption on the quantity absorbed by measuring the heat release over longer periods.

Long/.....

Long Period Experiments.

Owing to the variation in the drift, measurements at the different temperatures were continued only until the rate of heat release dropped to about five times the average drift. A maximum error of about 10% will then be involved due to the uncertainty of the correct value of the drift.

To obtain a higher heat release in the region where the rate of absorption is small, bigger samples were used and the measurements were confined to the most reactive coal available. Increasing the oxygen pressure had little effect on the rate in the later stages of the absorption.

However, since the amount of oxygen absorbed increases with pressure, a larger fraction of the surface was covered at higher pressures. The experiments were, therefore, conducted at 65 cm. Hg. oxygen pressure.

Even when using reactive coals, accurate measurements at 0°C were only possible for about three hours due to the very rapid decrease in the rate of heat release at this temperature.

The results reported in Table 4 indicate that the heat of absorption per mole of oxygen remains practically constant during the entire period of the experiments.

Bearing in mind that at 40°C and a pressure of 65 cm.Hg. the oxygen absorbed by this coal represents about 30% of the total amount absorbable under these conditions (as determined in absorption experiments) it would appear that a large percentage of the total surface
capable of/.....

capable of bonding oxygen molecules is highly homogeneous towards oxygen. The change in the rate of absorption with time is probably governed by transport phenomena and not by differences in the nature of the surfaces still available.

The equilibrium amount of oxygen absorbed at 80°C was not determined. However, at this temperature the absorption process is complicated by the fact that a fraction of the oxygen absorbed reacts with the coal surface to form gaseous reaction products.

It is, therefore, doubtful whether the constant heat release at this temperature is due to homogeneity of surface or to a definite chemical reaction.

DISCUSSION AND CONCLUSIONS:

The study of adsorption isobars of a range of South African coals provides evidence of an apparently anomalous behaviour at temperatures below about -80°C. This has not been studied in detail as interest in this investigation was centered around the temperature range 0° to 100°C. Considering the isobars from -80° to 100°C one is inclined, in analogy with the conventional interpretation of minima etc., to postulate physical adsorption to predominate at about -80°C. One would expect the amount thus adsorbed to decrease with rising temperature and the negative gradient of the isobar appears logical.

However, from somewhere in the region of -20 to -10°C this downward trend appears to be checked by the onset of chemisorption which increases rapidly with rising temperature. There is no sign of saturation at

the maximum/.....

the maximum temperature where measurements were made.

The study of the reversibility of the absorption and the analysis of gaseous reaction products proved that even at 0°C a considerable portion of the oxygen absorbed was bound irreversibly, suggesting that it was chemisorbed. The amount of oxygen thus retained, increased with the reaction temperature up to about 42°C . The observed increase in the amount of gas desorbed at higher temperatures can be ascribed to the formation of easily desorbable carbon monoxide, carbon dioxide and water. These reaction products incidentally suggest that at about 50°C actual chemical reaction becomes significant.

The measurement of the heat evolution during absorption revealed that the heat of absorption per mole of oxygen absorbed is virtually constant over the entire temperature range 0°C to 80°C . This suggests that even at 0°C physical adsorption has only a negligible effect.

One may therefore conclude that, for all practical purposes, oxygen is chemisorbed or reacts chemically with the coal at temperatures from at least 0°C upwards. At -80°C physical adsorption may predominate, but this decreases rapidly as the temperature is raised to -10°C . Even before this temperature is reached, chemisorption sets in so that the absorption isobar shows a minimum in the region of -10°C .

REFERENCES:

- 1) Coward, H.F., Research on Spontaneous Combustion of Coal in Mines. A Review. Research Report No. 142. Safety in Mines Research Establishment.
- 2) Sevenster, P.G. The Oxygen Absorption Characteristics of South African Coals. J. Chem. Met. Soc. of S.A., 6 (1952) 163.
- 3) Maggs F.A.P., Nature, 169 (1952) 793.
- 4) Zwietering, P., and van Krevelen, D.W., Fuel 33 (1954) 331.
- 5) Sevenster, P.G., Studies on Some Physical Properties of Coal. J. S.A. Chem.Inst. 49 (1954) 163.
- 6) Winmill, T.F., The Absorption of Oxygen by Coal., Trans. Inst. Min. Eng., 48 (1914-1915) 508.
- 7) Haldane, J.S., Spontaneous Firing of Coal., Trans.Inst. Min. Eng., 53 (1916-1917) 194.
- 8) Wheeler, R.V., Oxidation and Ignition of Coal., J. Chem.Soc., 113 (1918) 945.
- 9) Olpinski, W., Reference given in (1).
- 10) Taylor, H.S., and Strother, C.O., J. Am. Chem. Soc., 56 (1934) 586.
- 11) Yohe, G.R., and Harman, C.A., Oxidizing power of Illinois Coal., J. Am. Chem.Soc., 63 (1941) 555.
- 12) Jones, R.E., and Townend, D.T.A., Mechanism of the Oxidation of Coal. Nature, 155 (1945) 424.
- 13) Russel, W.J., Proc. Roy. Soc., 63 (1898) 102.
- 14) Haslam, G.S., A study of the Action of Coal on a Photographic Plate in the Dark., Fuel 7 (1928) 253.
- 15) Sevenster, P.G., The S.A. Ind. Chem., 11 (1957) 97.