The Reductive Capacity of an Adsorbent Charcoal Surface.

by

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Introduction

Since this thesis is concerned with the treatment of activated charcoal to increase the surface energy available for the chemisorption of carbon dioxide at low pressures, it appeared advisable to include a resumé of the present information concerning the structure and characteristics of activated charcoal. A review of the literature dealing with charcoal activation is given by Findlay.[7] There are several main points of controversy about the characteristics of charcoal. Most authors treat isolated points rather than the problem of how the surface atoms acquire greater free energy than the bulk phase.

The energy available for chemical adsorption, specificity, retentivity and the strictly physical properties vary widely with the sources from which the charcoals are produced. Burrage,[4] dealing with wood charcoals, claims that the active charcoal is derived from the cellulose and the inactive carbon from the lignin. His basis for this theory is the lower carbon content and the relative ease of oxidation of cellulose.

Several investigators have noted a relationship between hydrogen content and adsorptive energy. Barker[2]

showed that the hydrogen content of cocoanut charcoals decreased during the usual commercial steam activation process. From Ray's[23] figures it is seen that on activation the decrease in hydrogen content is proportional to the increased retentivity for carbon tetrachloride of the charcoal. For Birch wood charcoal, Philip and Jarman[21] quote a C:H ratio increasing with higher temperatures and longer periods of heating. There was a steady improvement in adsorptive ability with rise in temperature. Bangham and Stafford,[1] during work on the bombardment of graphite with hydrogen, came to the conclusion that hydrogen broke up the hexagonal arrangement of carbon atoms, thus increasing the adsorptive energy. The high degree of mutual saturation of the atoms in any one plane renders graphite a poor "sorbent". In the above manner the greater hydrogen content of so-called amorphous carbons contributes to the adsorptive ability. Lowry and Hulett[15] analysed the gases removed by outgassing a sample of charcoal after oxygen had been adsorbed on it. Below 1000° C carbon dioxide and carbon monoxide were driven off; above that temperature hydrogen and a small percentage of methane were the effluent gases.

The actual structure of adsorbent charcoals has been studied in several ways. In the hands of different investigators the evidence of X-ray analyses conflicts. But opinions concur that a graphitic crystal structure is present, although the diffraction patterns are overlaid, in some cases,

with scattering.

Debye and Scherrer[6] claim that amorphous carbon is graphite in finely divided particles. Ruff, Schmidt and Olrich[24] state that active carbon is a true modification and does not have exactly the lattice structure of graphite. Jenkins[9] concurs with Debye. Barker[2] shows that primary charcoal gave no diffraction rings. On activation the rings of graphite appear. This evidence would appear to diminish the importance of the adsorbed hydrocarbon theory of activation. Only on long heating did the diffraction patterns become narrow and sharp. Raman and Kristnaturi[22] while studying the diffraction pattern of graphite found scattering which would be due to "free" electrons. It is probably these unpaired electrons which give rise to the surface forces.

Theories of the polymer structure of charcoal have been built upon several bases. An adsorbent carbon can be made from graphite by oxidizing it to graphitic acid and then exploding the product or reducing it with hydroxylamine.[17,23] This suggests that the surface potential is due to lack of orientation of the carbon atoms in charcoal.

Burrage claims that the original macroscopic form of the source is preserved in the particles of charcoal. The activity is due to the unsaturation of carbon atoms, left in the cellulose structure and from which hydrogen has been oxidized away.

Lowry[19] considers that all materials between lignin and graphite can be considered as polymers built of units of six-ring hydrocarbons. The more complex the polymer the less hydrogen it contains. The hydrogen content is a function of the temperature to which the charcoal has been heated and of the length of time that it has been maintained at that temperature. Thus "amorphous" carbon is a complex hydrocarbon of aromatic structure. Briggs[3] also points out that we are not concerned with the ultimate atom but with elaborate polymers. The only structures impervious to gases are crystals and glasses which are made of atomic linkages. Heating simplifies the polymers present in the charcoal and, as some of the carbon is removed as carbon dioxide, recombination does not take place.

In two other papers Lowry[16,18] deals with this theory. If, at a surface, there are C - H bonds whose carbon atoms are so situated with respect to the rest of the solid that when the bonds are broken the carbons cannot orient into a graphite lattice, then the surface carbon atoms have free energy for adsorption. In the formation of amorphous carbon-polymerized residues from the thermal decomposition of hydrocarbons of greater hydrogen content - any treatment which increases the unsaturation must increase the adsorptive capacity. He suggests that with rising temperature (driving off hydrogen) the adsorptive ability increases to a maximum and then decreases as graphitization sets in. King[10] suggests that the hydrogen is in the binding between unsaturated

valences. The removal of this hydrogen leaves these valences with a potential depending on the position of the carbon atoms in the lattice or chain.

King[11] and Kolthoff[12] describe an acid surface resulting from oxidation at temperatures below 450° C and a basic one from treatments at higher temperatures. This condition may be a function of the solutions with which they were working or it may be a feature of the fundamental surface bonding resultant from the heat treatment.

The main result of the Quantum mechanical treatment of surface forces is a realization of the importance of the nuclear distances of the carbon atoms. Sherman and Eyring[25] show that for any given strength of the C - C bond (i.e., single, double, triple) there is a nuclear distance most favourable for adsorption.

It would seem more profitable to work from distance apart of the carbon atoms and known energies of adsorption to the energy of the surface atoms since their energies need not correspond to those of carbon atoms in hydrocarbon molecules.

Lennard-Jones[14] suggests that if the electronic configurations of carbon atom and approaching molecule are such that the resulting electronic state is possible, and if the energy of the pattern, which depends on internuclear distances, is a minimum, then a stable adsorbate results.

The polymer and "structure residual from source" theories to account for the surface energy of charcoals are supported by the two latter mathematical treatments.

Aim.

This was a continuation of an investigation started in conjunction with F. Cook[5] in order to understand the anomalous behaviour, at low pressures, of two samples of activated cocoanut from the same source (National Carbon Co. 1929). One was used by R. A. Findlay[8] and found by H. O. McMahon[20] to reduce CO_2 to CO at room temperature during studies on the mechanism of gas adsorption. The second sample, in use in the heat measurement apparatus, did not reduce CO_2, even at the lowest concentrations (2 micro-mols per gram). The treatment of the two samples had differed very little but an investigation was initiated to decide which of the differences had caused the surface variation.

The reductive active surface had been more extensively oxidized and had been subjected to heating, gas readsorption and subsequent cooling; it had also been widely oxidized by saturating the surface with oxygen added at 90°A and allowed to chemisorb at room temperature. Both samples had on occasion been outgassed at higher temperatures than the usual 1000°C. Each of these differences was investigated in turn.

Part I.

Experimental.

The charcoal studied was that removed from the heat measurement apparatus by Cook and Wright in March, 1937. It was very inactive in reducing carbon dioxide. On adding 1.83 micro-mols per gram of carbon dioxide the equilibrium pressure was 224 x 10^{-4} mm. and only 5% of it was due to carbon monoxide. The apparatus used was that described by McMahon in his thesis. The saturated weight of the charcoal was 24.4635 grams. Carbon dioxide was prepared from commercial "dry ice". It was purefied by freezing in a liquid air trap, pumping off any residual gas and resubliming the CO_2. This procedure was repeated several times.

After an outgassing at 1100° C for 20 hours McMahon found an increase in activity. On adding 2.05 M-M/gm. of gas the pressure fell slowly to 36 x 10^{-4} mm; the residual gas was 47% CO. After 20 hours the pressure was 25 x 10^{-5} mm. and the gas was 80% CO.

A standard run was made by which to gauge the results of methods of activation. The charcoal was outgassed for 12.5 hours, the temperature never rising above 1074° C. In each outgassing the temperature was raised slowly to drive off gases at as low a temperature as possible. At the end of the outgassing the charcoal was cooled quickly with the pumps running.

A surface concentration of 2.56 micro-mols per gram of CO_2 was added. The change of pressure and CO_2 content of the residual gas with time were noted. The results are given in table I. The first column gives the temperature, the second the time after addition, third, gives the total pressure, fourth the pressure of gas uncondensable in liquid air and the fifth the CO_2 content of the gas as a percentage.

TABLE I.

Temp. (°C)	Time in Hours	Pressure in MM.x10^5 Total	Liq. Air. On.	% CO_2 in Residual Gas
20°C	.12	4000	-	-
"	1.87	1300	185	86%
"	2.33	850	115	88%
"	4.87	600	77	87%
"	6.33	430	56	87%
"	19	57	11.8	79%
64°	0	297	-	-
72	1.12	550	65	88
126	3.5	1270	-	-
"	4.0	780	-	-
"	4.5	560	40	93
128°	6.0	370	32	91
171	7.5	1920	42	96
180	21.0	500	260	48%
238	1.5	8000 Approx.		
"	2.5	8000 "	4500 Approx.	44
"	7.25	"	-	-

During the first six runs the time (1/2 hr.) that the gas in the McLéod gauge was cut off from the charcoal during analyses, was deducted. But it was observed that when the cut-off was lowered the pressure very quickly reached a new value which fitted the time pressure curve in which the 1/2 hour was not deducted. In the results the 1/2 hr. periods have been added to the times of the first six runs as given in the laboratory notes. The residual gas quickly adsorbs on the spaces left vacant by the rearrangement of the adsorbed molecules in the intervening time.

Since previous work had shown no activation resultant from desorption and readsorption of added oxides of carbon through temperature variation, it was decided to observe the effect of outgassing of longer duration and at higher temperatures than was customarily employed.

In the succeeding six runs the same procedure as in Run I was followed. Approximately 15 cms of CO_2 on the pipette scale were added after outgassing for a given time at a carefully noted temperature.

Run II outgassing was for 15 hrs at 1015° C
and for 6 hrs at 1100°C.
CO_2 added - 2.22 micro-mols per gram.

Run III outgassing at 1020° for 6 1/2 hrs.
at 1100° for 12 hrs.
the pressure build-up in 5 mins. was 100×10^{-5}mm.
CO_2 added - 2.5. M-M/gm.

Run IV outgassing at 1100°C for 22 hrs.

Pressure build-up 17 hrs. - 113×10^{-5}mm.

20 hrs. - 62×10^{-5}mm.

21 1/2 hrs. - 56×10^{-5}mm.

CO_2 added - 2.39 M-M/gm.

Run V outgassing at 1100°C for 20 hrs.

Pressure build-up above 63×10^{-5}mm. during run.

CO_2 added - 2.275 M-M/gm.

Run VI outgassing for another 20 hrs. at 1100°C.

Pressure build-up fell to 37×10^{-5}mm.

CO_2 added - 2.37 M-M/gm.

Run VII Charcoal was outgassed for 15 1/2 hrs. at 1100°C.

then the temperature was raised to 1150°C.

for 4 1/2 hrs.

CO_2 added - 2.56 M-M/gm.

Results:

For ease in reading the graphs, Table II is a description of every run made during the investigation. Column (1) is the run number, Columns (2) and (3) are the length of time and temperature of outgassing and Column (4) is the concentration of CO_2 added.

TABLE II.

Run No.	Outgassing Time in Hours	Outgassing Temperature (°C)	Conc. of Added CO_2(M-M/gm)
I	12.5	1074	2.56
II	15 6	1015 1100	2.22
III	6.5 12	1020 1100	2.51
IV	22	1100	2.31
V	20	1100	2.275
VI	20	1100	2.37
VII	15.5 4.5	1100 1150	2.56
VIII	23 5	1100 1150	4.09
IX	11 5	1100 1150	4.05
X	8 5	1100 1150	4.57
XI	4 11	1100 1200	8.39
XII	4 10	1100 1200	11.315
XIII	10	1100	11.44
XIV	15	1100	11.67
XV	16	1100	11.68
XVI	14	1100	11.70
XVII	19	1150	14.56
XVIII	16	1150	16.38
XIX	17	1150	18.29

After the first outgassing at 1100°C. the pressure over the charcoal was considerably lower; in Run I, 290 minutes after addition of CO_2 the pressure was 85×10^{-4} mm., in Run II the pressure after 220 minutes was 140×10^{-5} mm. The CO_2 and CO pressures fell correspondingly, for the CO_2 content, 80 minutes after zero time, was 80%. In 6 3/4 hrs. the CO_2 content of the residual gas fell to 64%.

In Run III after a total outgassing at 1100°C. of 18 hrs. the pressures over the charcoal were of the same order as in Run II. The gas phase was still over 60% CO_2.

In Run IV after a total of 40 hrs. outgassing at 1100°C. there was a marked reduction in both pressure and CO_2 content of the residual gas. The results of the run are shown in Table III.

TABLE III.

Temp. (°C.)	Time (hrs.)	Pressure in mm.x10^5 Total	Liq.Air On	% CO_2 in Residual Gas
21	.42	830	--	--
21	2.42	79	35	55
21	4.75	27	24	11
21	7.25	16	14	12
21	20.00	6	5	12
62	1.5	47	25	47
62	3.0	22	14	37
62	5.0	15	8 ?	45
120	1.25	115	24	79
120	3.0	55	--	--
160	1.0	255	92	64
166	2.5	360	130	64
166	4.0	245	118	50
166	15.0	102	64	36
210	16.0	2100	1380	34
210	18.5	1070	790	26

The 5th run after 60 hrs. outgassing at 1100°C. showed slightly greater activity in that the pressure decreased more quickly and no CO_2 could be detected in the residual gas after 20 hours.

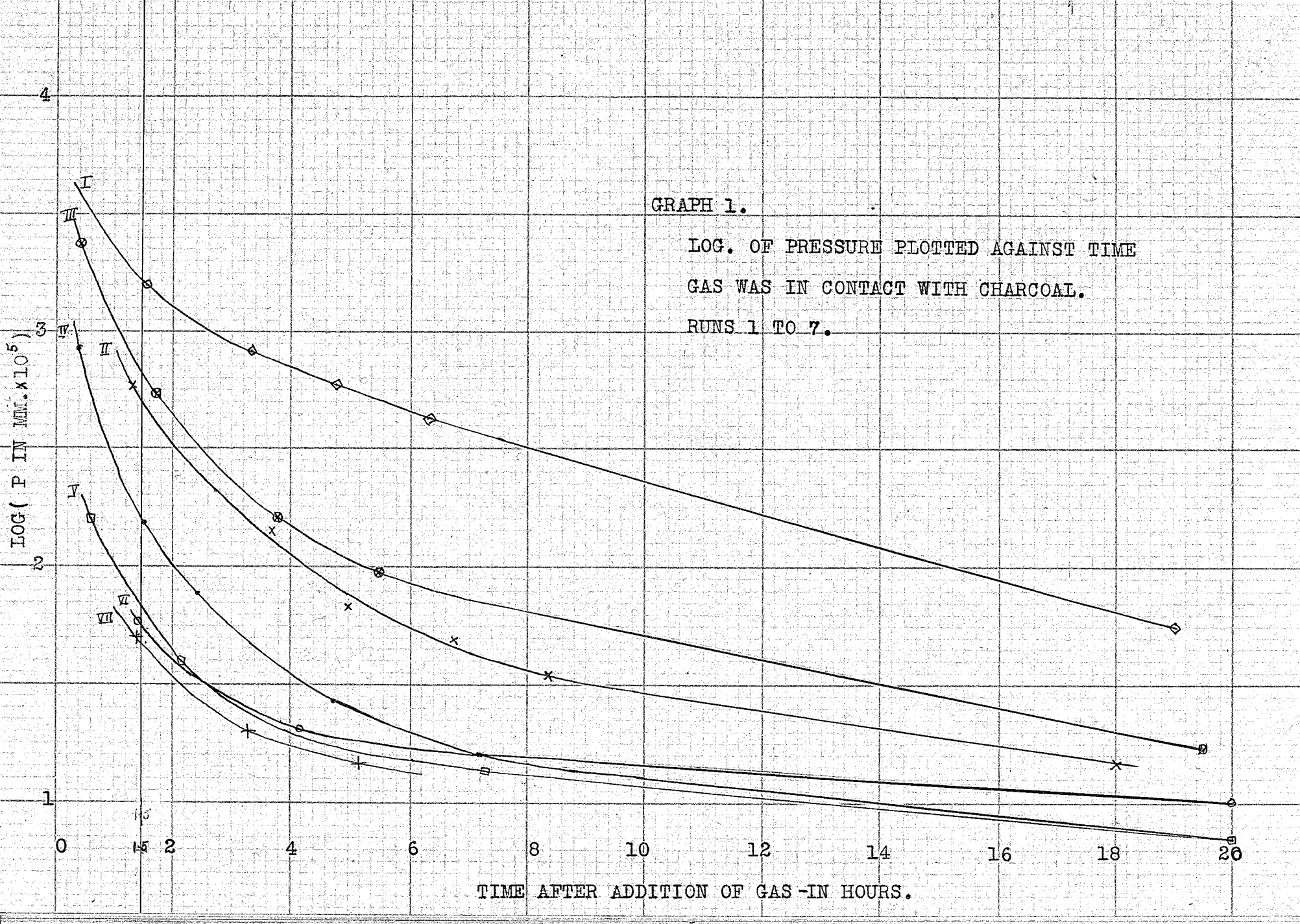
Run VI was similar to Run V. The pressure decrease was more rapid than previously.

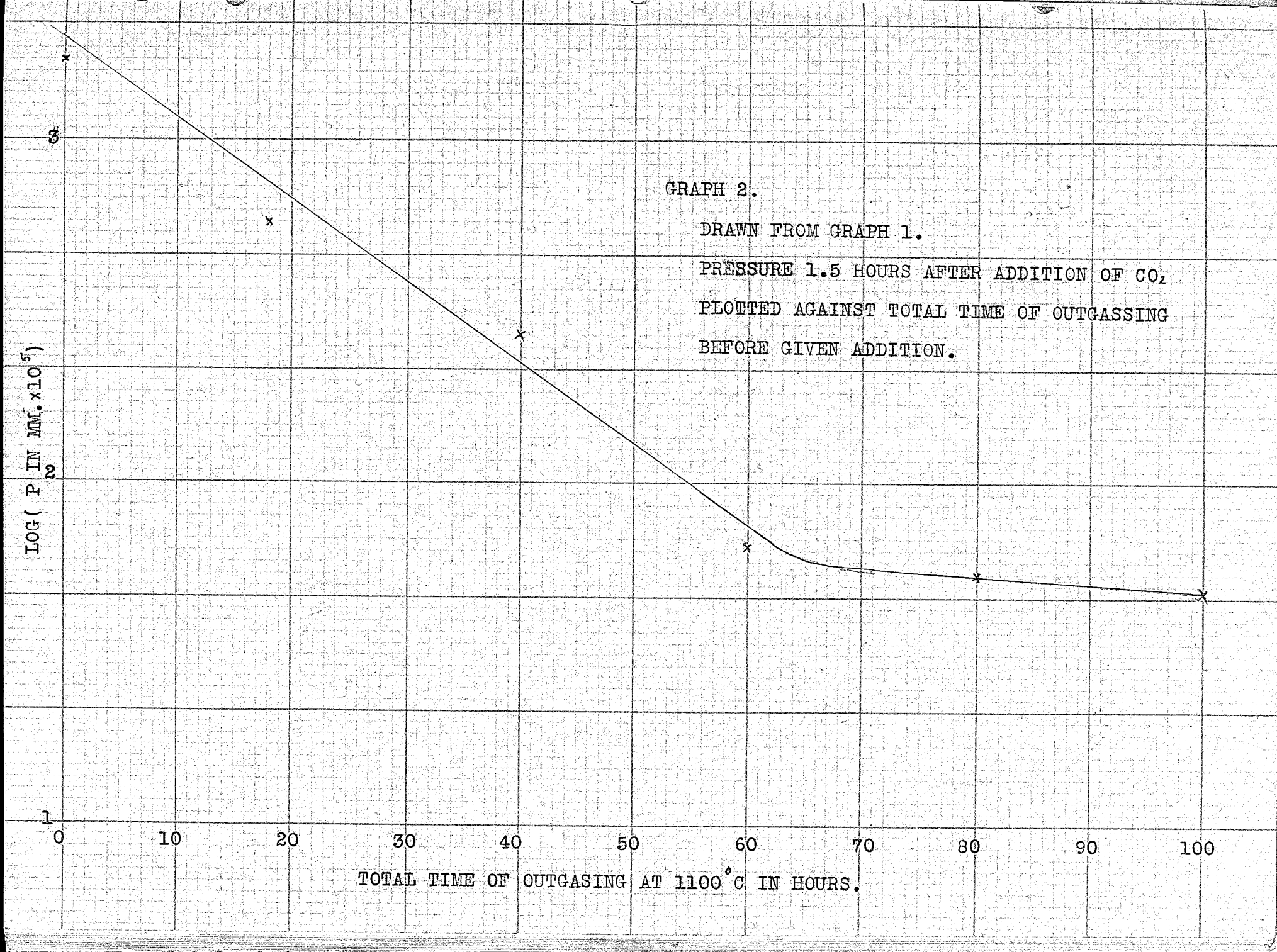
Run VII was the first in which the temperature was raised to 1150°C. The pressure fell at approximately the same rate as in Run VI. The CO_2 content fell very much more rapidly. It was the first run in which the CO_2 content of the gas did not rise above 50% in the temperature range from 110°C. to 180°C.

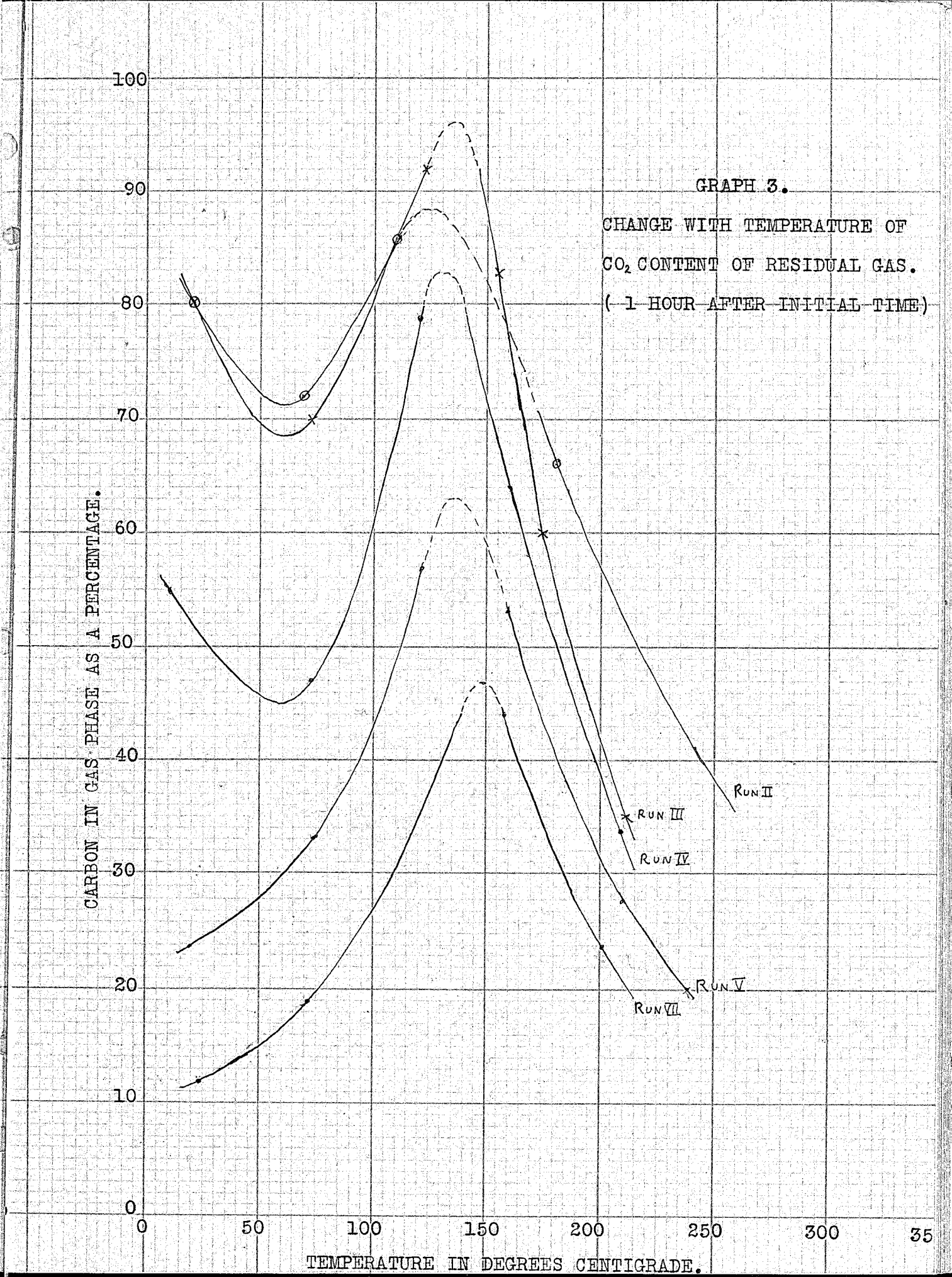
The figures for this run are given in Table IV.

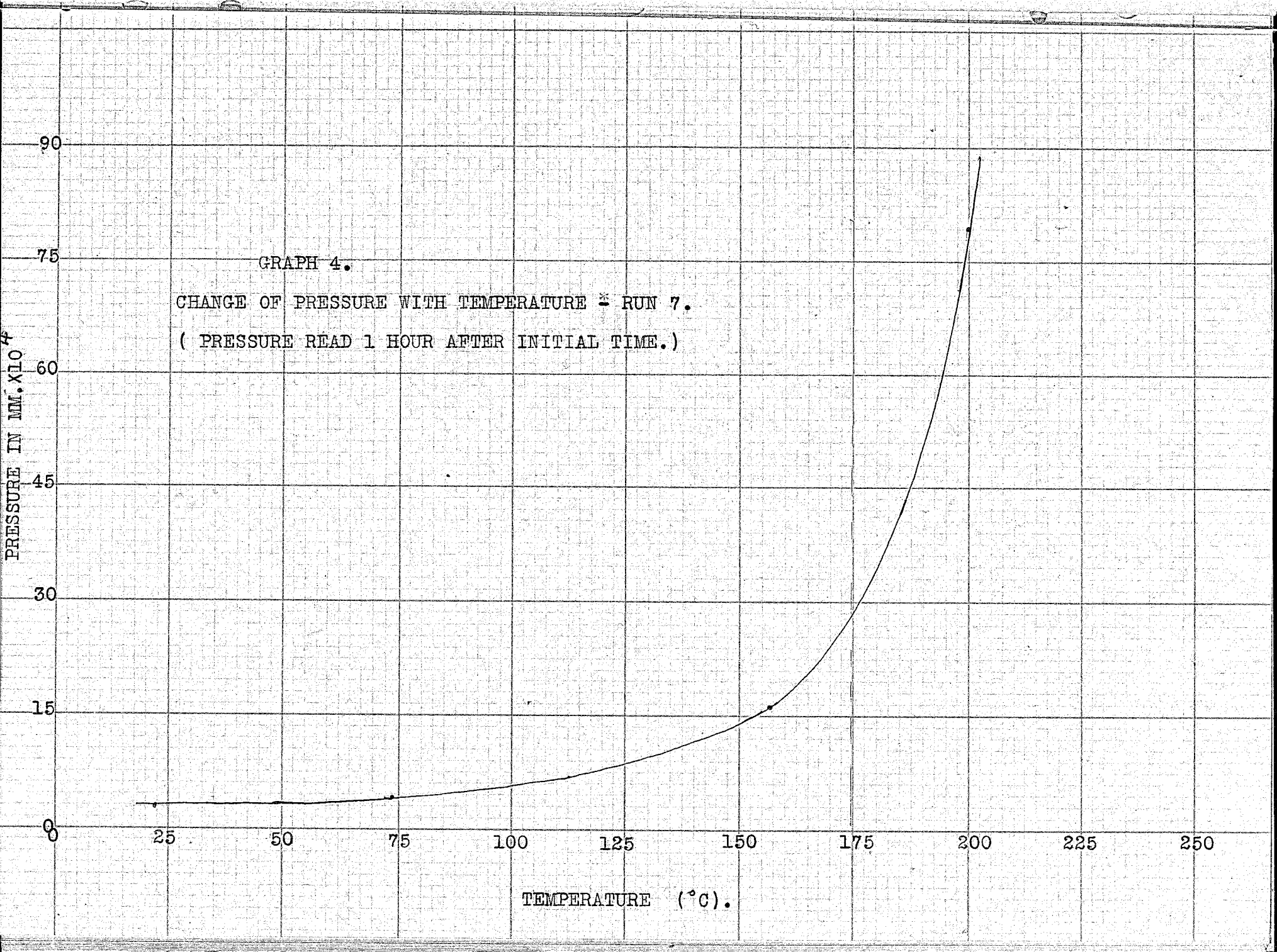
TABLE IV.

Temp. (°C.)	Time (hrs.)	Pressure in MMx10^5 Total	Liquid Air On	% CO_2 in Residual Gas
23	1.25	52	46	12
23	3.33	21	20	5
23	5.0	15	14	6
23	22.0	7.7	74	4
72	1.0	43	35	19
72	3.0	10	9	10
158	1.0	167	92	45
158	3.0	86	57	34
165	18.0	78	64	18
200	1.0	800	610	24
200	3.0	670	560	16
200	6.0	670	600	10
223	22.0	920	860	6.5


GRAPH 1.
LOG. OF PRESSURE PLOTTED AGAINST TIME
GAS WAS IN CONTACT WITH CHARCOAL.
RUNS 1 TO 7.
LOG (P IN MM. x 10^5)
TIME AFTER ADDITION OF GAS -IN HOURS.
I
II
III
IV
V
VI
VII
0
2
4
6
8
10
12
14
16
18
20
1
2
3
4


GRAPH 2.
DRAWN FROM GRAPH 1.
PRESSURE 1.5 HOURS AFTER ADDITION OF CO_2
PLOTTED AGAINST TOTAL TIME OF OUTGASSING
BEFORE GIVEN ADDITION.
LOG (P IN MM. x10^5)
3
2
1
0
10
20
30
40
50
60
70
80
90
100
TOTAL TIME OF OUTGASING AT 1100°C IN HOURS.


GRAPH 3.
CHANGE WITH TEMPERATURE OF
CO_2 CONTENT OF RESIDUAL GAS.
(1 HOUR AFTER INITIAL TIME)
CARBON IN GAS PHASE AS A PERCENTAGE.
TEMPERATURE IN DEGREES CENTIGRADE.
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
RUN II
RUN III
RUN IV
RUN V
RUN VI


GRAPH 4.
CHANGE OF PRESSURE WITH TEMPERATURE - RUN 7.
(PRESSURE READ 1 HOUR AFTER INITIAL TIME.)
PRESSURE IN MM. X10 4
90
75
60
45
30
15
0
0
25
50
75
100
125
150
175
200
225
250
TEMPERATURE (°C).

In Graph 1. pressure-time curves are plotted for Runs I to VII. The logarithms of the pressures are plotted for facility in handling a wide range of values. From these curves corresponding pressures for each run can be obtained. In Graph 2 the pressure 1.5 hrs. after addition of CO_2 is plotted against the total time of outgassing previous to the addition. For the first 60 hrs. the pressure decreased rapidly with time of outgassing. On further outgassing the pressure decrease was not so rapid.

It was noticed in these runs that as the temperature was raised the carbon dioxide content of the gas phase first decreased then rose again in the interval 100° to 160°. Above 180° the CO_2 content decreased rapidly. This effect is shown graphically in Graph 3. This phenomenon suggests that below 160° CO_2 desorbs more rapidly than CO as the temperature is raised and at the new temperature re-adsorbs more slowly. Above 180° reduction takes place independent of the reducing energy of the surface at 20°C.

In every run the pressure increased sharply above 175°. This is shown in Graph 4 plotted from the figures of Run VII. The pressure one hour after the temperature is reached is plotted against temperature. It is noticeable that this change in the order of the pressure and the change in the CO content of the gas occur at the same temperature. This is also the temperature range in which McMahon found a

hump in the distribution curve for the desorption of CO from a reductive charcoal surface.

Part II.

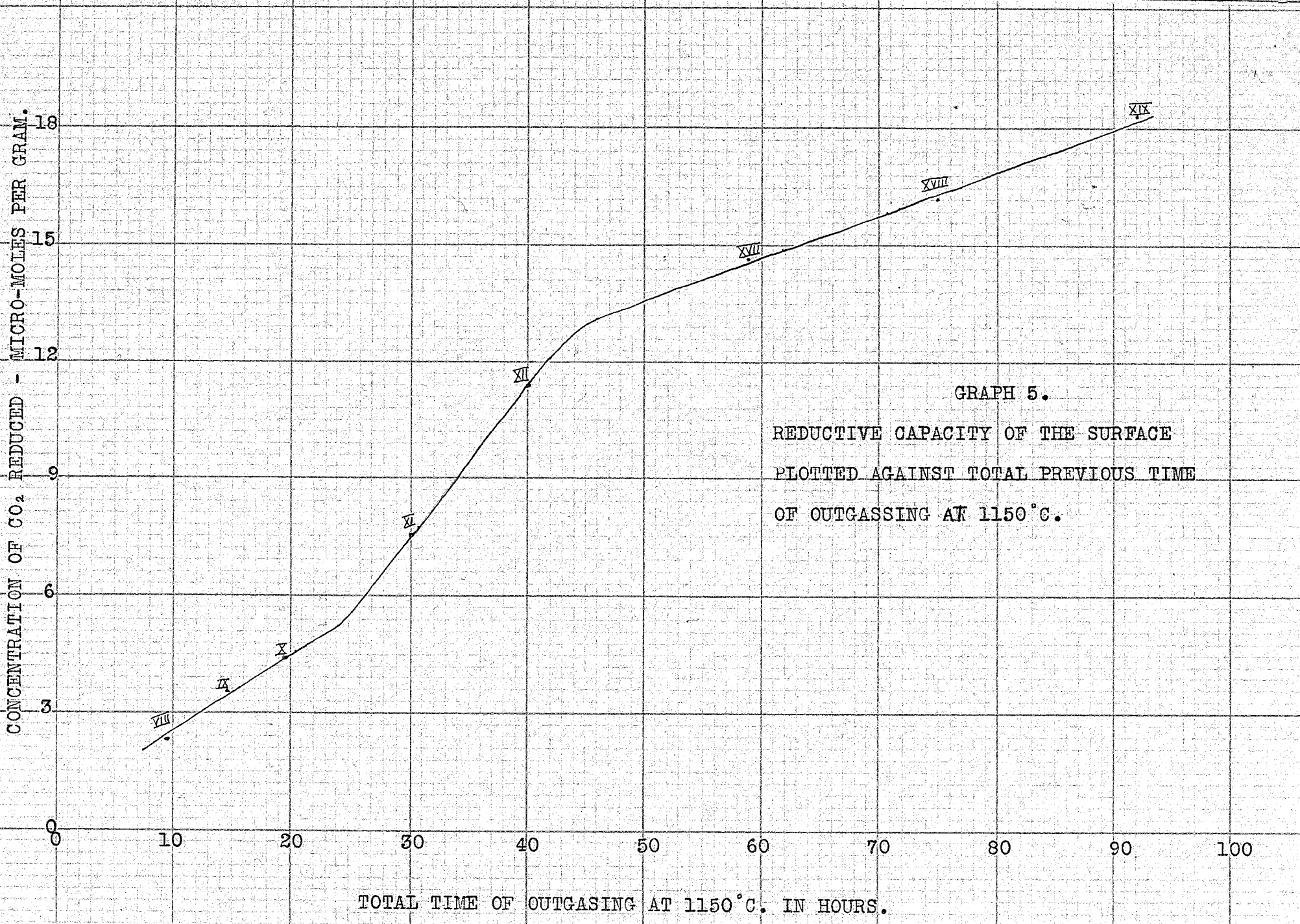
Experimental.

In Run VIII the CO_2 content of the residual gas fell to zero in less than 3 1/2 hours after the addition of 2.29 M-M/gm. Accordingly a new procedure was adopted. In succeeding runs carbon dioxide was added in concentrations of 4 micro-mols per gram or less, the pressure decrease followed until it became slow, then another addition made, and so on until an addition was not totally reduced in 30 minutes. The total concentration of gas added indicated the reductive capacity of the charcoal.

Runs VIII to XII and XVII to XIX inclusive are discussed in this section since the treatment of each was similar. In each run the outgassing was at 1150°C. for times varying from 5 to 20 hours. Runs XI and XII were outgassed at a higher temperature (as the bulb collapsed slightly it was probably 1200°C or more) due to a fault in the thermocouple wire used for temperature measurement.

Results.

The reductive capacity increased steadily with the total time of outgassing at 1150°C.



GRAPH 5.

REDUCTIVE CAPACITY OF THE SURFACE PLOTTED AGAINST TOTAL PREVIOUS TIME OF OUTGASSING AT 1150°C.

The pressure over the charcoal for corresponding concentrations of CO_2 decreased with increased outgassing at 1150°C. except for Run XI the first outgassing at 1200°C. In Run IX, 1.5 hrs. after adding 2.44 M-M/gm the pressure was 61×10^{-5}mm. In Run XI, 2 hrs. after adding 2.31 M-M/gm the pressure was 77×10^{-5}mm. But in Run XII, although the outgassing temperature was as high as in Run XI, the pressure 2 hrs. after adding 2.34 M-M/gm was 61×10^{-5}mm. On continued outgassing the velocity of adsorption increased. This is shown for Runs XVII, XVIII, XIX in Table V below.

TABLE V.

Run	Total Time of Outgassing at 1150°C. (hrs.)	Surface Conc. of CO_2 $\left(\frac{M-M}{gm}\right)$	Pressure after 1/2 hr. in mm.x10^5
XVII	64	4.045	125
XVIII	80	3.96	62
XIX	97	4.68	50

The increase in reductive capacity with time of outgassing is shown graphically in Graph 5, in which the surface concentration at which CO_2 was first detected in the residual gas is plotted against total time of outgassing at 1150°C. That the rate of change of reductive capacity could be increased by higher temperatures is indicated by the hump

in the curve for Runs XI and XII. The pressure build-up during these two outgassings was greater than 100×10^{-5}mm. in 5 minutes.

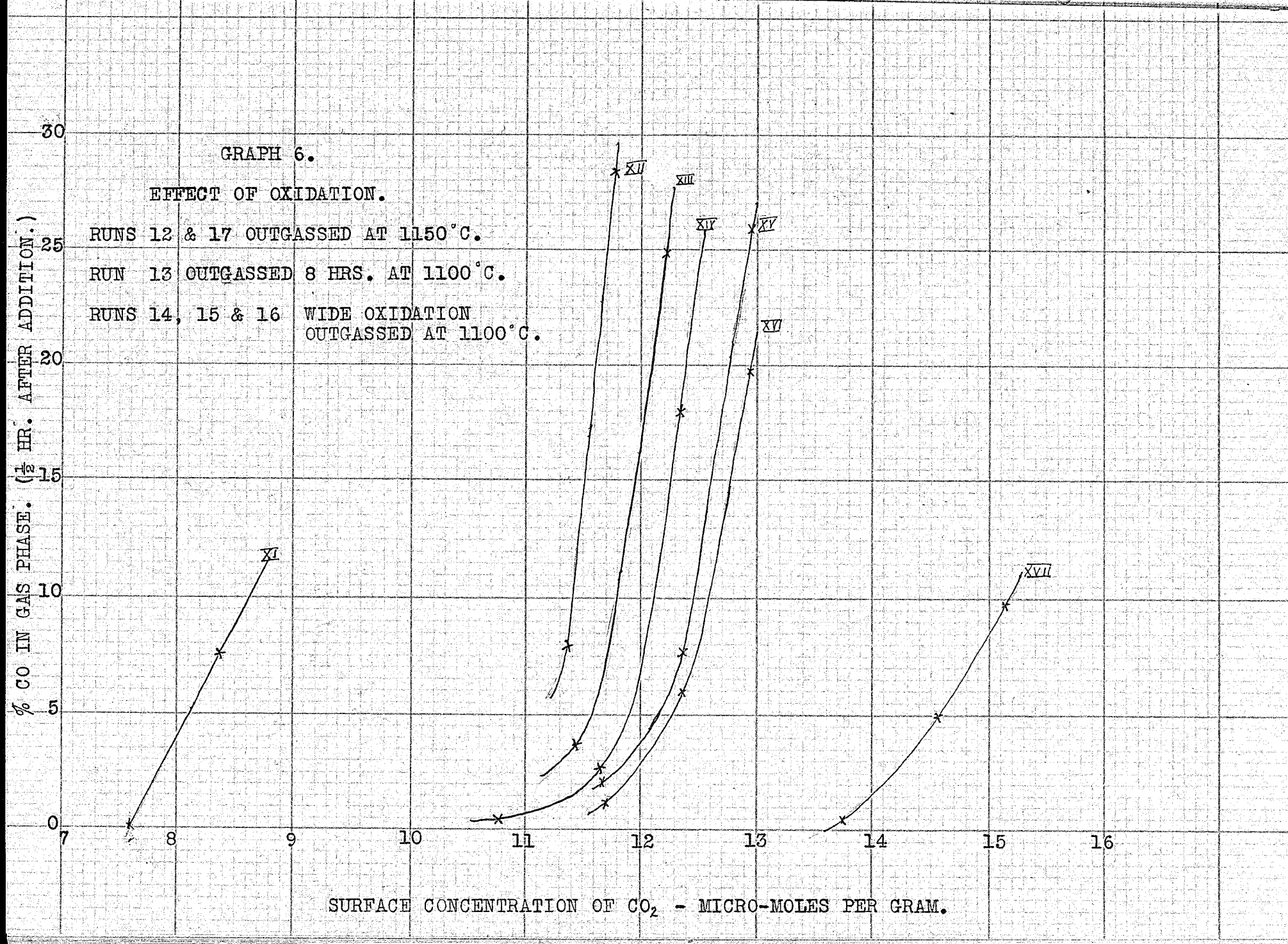
Part III.

Experimental.

Deep oxidation was tested as a method of activation. Run XIII was made as a comparison. The outgassing was at 1100°C. for 10 hours. CO_2 was added at room temperature until the residual gas was 25% CO_2.

The added gas was pumped off during 6 hrs. outgassing at 1100°C. The charcoal bulb was immersed in a Dewar flask containing liquid air. Oxygen, which was generated from potassium chlorate, was added from the storage flask in quantity to saturate the charcoal surface chemically at room temperature. After 5 hours, when the pressure was scarcely measureable, the Dewar flask was removed. The pressure rose to more than one centimetre then dropped slowly as the oxygen readsorbed. 17 hours later the pressure was 17×10^{-5} mm. The charcoal was then outgassed at 1100°C. for 8 hours.

CO_2 was then added according to the procedure used in Part II. The addition of oxygen and subsequent heating were repeated three times.


GRAPH 6.
EFFECT OF OXIDATION.
RUNS 12 & 17 OUTGASSED AT 1150°C.
RUN 13 OUTGASSED 8 HRS. AT 1100°C.
RUNS 14, 15 & 16 WIDE OXIDATION
OUTGASSED AT 1100°C.
% CO IN GAS PHASE. (½ HR. AFTER ADDITION.)
SURFACE CONCENTRATION OF CO_2 - MICRO-MOLES PER GRAM.
XI
XII
XIII
XIV
XV
XVI
XVII
0
5
10
15
20
25
30
7
8
9
10
11
12
13
14
15
16

Results.

The treatment gave only a slight increase in activity as can be seen in Graph 6 in which the percentage of carbon dioxide in the residual gas is plotted against the surface concentration of carbon dioxide. The displacement towards greater reductive capacity is no larger than that caused by the outgassing treatment alone in Run XIII. The fact that it is less suggests a possible deactivation due to the oxidation.

Conclusions.

1. The reductive capacity of the charcoal for carbon dioxide is increased by vapourizing constituents of the charcoal at 1100°C. and higher. This suggests that the reductive ability is a function of the bond energy of the surface carbon atoms.

2. Oxidation of the surface has no activating effect on the reductive capacity of the surface.

3. On first outgassing at a higher temperature, the pressure over the charcoal was higher for a given concentration of carbon dioxide than after previous lower temperature outgassing. On further outgassing at the same temperature the pressure decreased to a new lower value. This suggests an explanation of the "deactivation" found by Lemon[13] and Lowry[15] on high temperature outgassing. They

did not outgas long enough to remove the freed gases from the charcoal.

4. The pressure rose sharply over the inactive charcoal in the same temperature range in which McMahon found a hump in the distribution curve on desorbing gas from a saturated reductive surface. The energies of the two surfaces are therefore not greatly different.

5. There is a temperature range in which the residual gas over the inactive surface has a high carbon dioxide content.

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