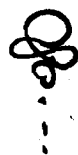# The Heat of Adsorption of Oxygen on Charcoal.

## by

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THE HEAT OF ADSORPTION OF OXYGEN ON CHARCOAL

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# THE HEAT OF ADSORPTION OF OXYGEN ON CHARCOAL.

## Introduction

The first quantitative work on the adsorption of gases on charcoal was carried out by de Saussure[1]. Since that time many investigations have been prosecuted to determine the quantitative relationships existing between quantity of gas adsorbed, temperature and pressure. In a few cases (Favre[2], Chappins[3], Titoff[4], Lamb and Coolidge[5], Blench and Gainer[6],) the heat of adsorption has been measured at different temperatures and pressures. Dr. M.J. Marshall[7], while working on the heats of adsorption of gases and vapours on charcoal, obtained very striking results in the case of low concentration of oxygen. He found:

1. that the initial heat values were very high - 70000 cal./ mole/ gm. of charcoal, and the final values very low - 4000 cal./ mole/ gm.
2. the first adsorption was characterized by the satisfaction of primary valences, further adsorption resulting from a modification of existing molecular fields.
3. the active surface of the charcoal was very small, approximately 0.5 sq. metres per gm. He used only a a small quantity of charcoal- 2 to 3 gms., and his ice calorimeter could only be relied upon for five hours. Further, the charcoal used was French war charcoal, very likely not the most active available. The present research was instituted in order that the previous conclusions might be checked with a different type of charcoal, using a larger quantity to enable a closer study of the initial heats to be made, and working under calorimetric conditions permitting a more leisurely study of the heat evolution.

## GENERAL EXPERIMENTAL PROCEDURE.

1. **Preparation of Charcoal**

The charcoal used was a standard sample of activated cocoanut charcoal obtained from the National Carbon Co. Before use it was extracted repeatedly with hydrochloric acid to remove any soluble salts, and then with hydrofluoric acid to remove the silica. This reduced the ash content to 0.2668%. Finally it was graded to pass a mesh of cross-sectional area 2.725 sq. mm. and be retained on one 0.689 sq. mm. Prior to the first run the charcoal was exhausted at $1000°$ C. for sixty hours. The final pressure was $1 \times 10^{-4}$ cm. at this temperature. The pumps were kept going until the mass had cooled to room temperature. The exhaustion preparatory to the second run required only ten hours pumping at $1000°$ C.

2. **Preparation of Oxygen**

The oxygen was prepared by gently heating anhydrous potassium chlorate containing a trace of manganese dioxide. In a previous run no manganese dioxide was used and a severe explosion occurred.
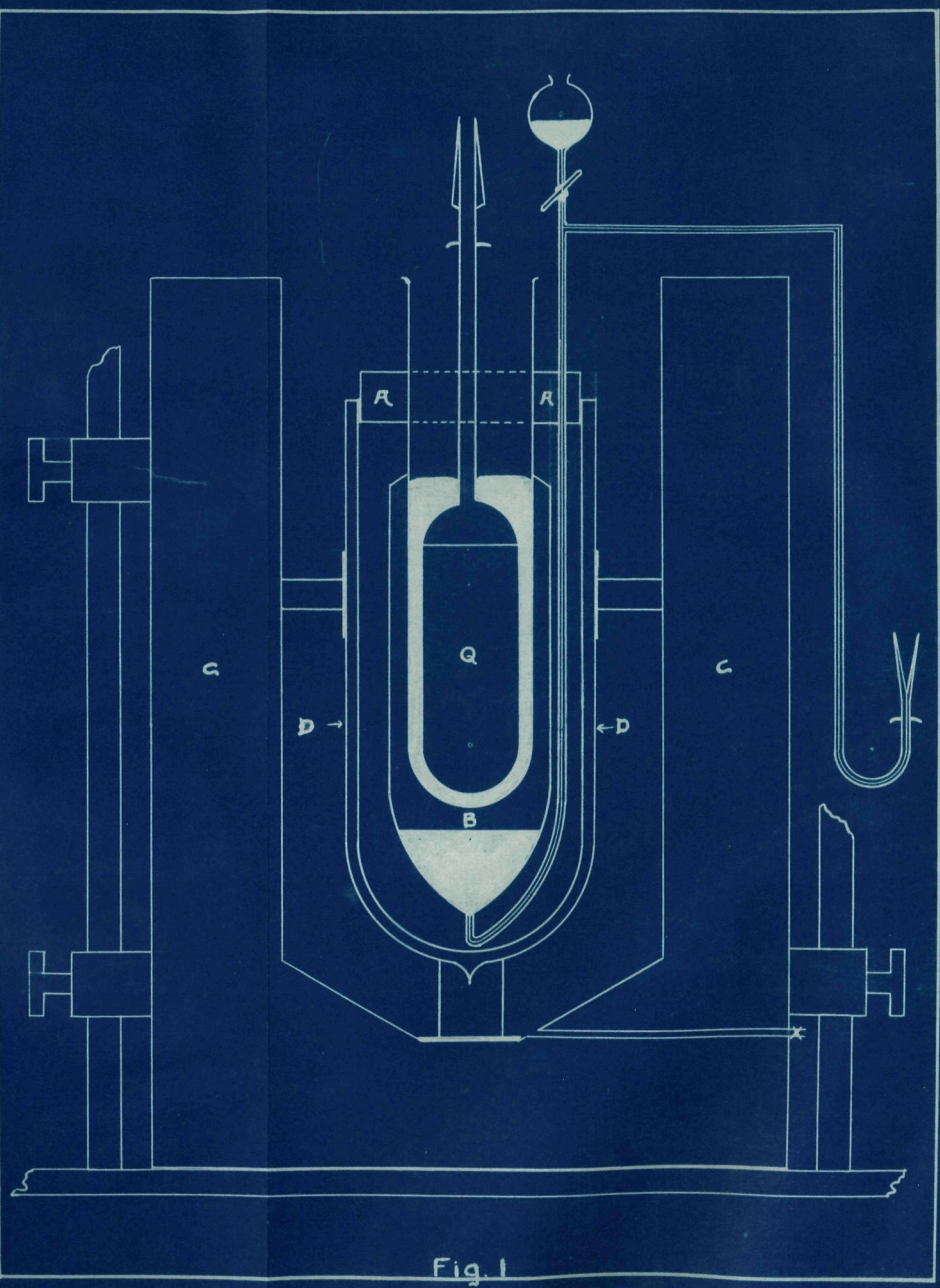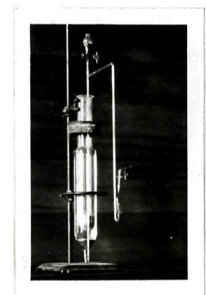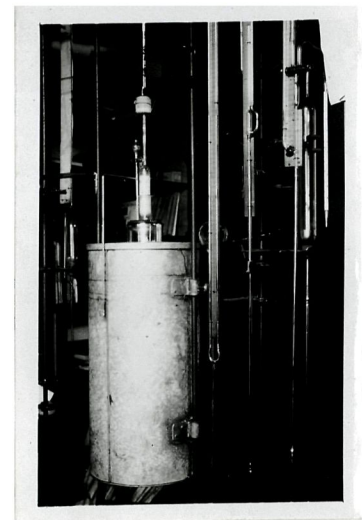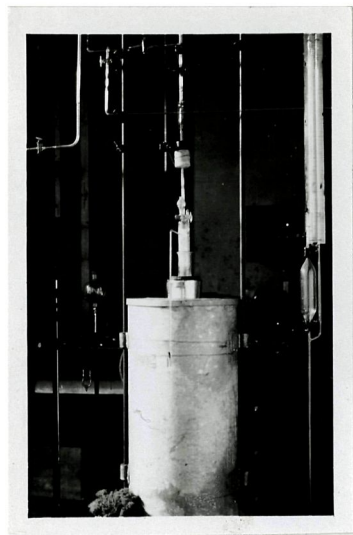
Fig.1

3. Apparatus

The apparatus used is shown in the accompanying diagram and photographs. The feature of the apparatus is the calorimeter, a modification of that designed by Griffiths[8]. It consisted of the galvanized iron container C, the jacket of which was packed with felt; the Dewar flask D, and the Bunsen ice calorimeter B. The cork A provided a water-tight seal when the ice calorimeter was lowered into the Dewar flask and this permitted crushed ice to be packed in C up to the top of B. A plug of felt was packed around the quartz tube where it entered the neck of B. Distilled water was added up to the ice level. Using this arrangement an ice mantle was maintained in B continuously for twenty days.

The charcoal was contained in the quartz bulb Q . This bulb was lined with platinum in order to prevent the reduction of the quartz by the carbon at the high temperatures of evacuation.

Contact between the walls of the ice calorimeter and the bulb Q was made by means of a film of mercury.

A very even ice mantle inside the Bunsen calorimeter was obtained by immersing a long tube containing an ether-solid carbon dioxide mixture in the mercury. This tube was slightly larger than Q . By adjusting the level of the mercury a mantle of uniform thickness was obtained.

The performance of the calorimeter was studied for
eight days. As a result it was found possible to maintain
a constant leak for periods of sixteen - eighteen hours.
The absolute value of the leak could be varied by adjusting
the room temperature. As a result of studies made during
the first run it was determined that the value of the leak
increased with additions of gas, the increment from run
to run being very small. Values of the leak varying
from zero to .03 cm. per five minutes were obtained. The
crushed ice had to be renewed every twenty-four hours
when the room was kept at $20^{\circ}$ C.


4. Method

The quartz bulb Q was charged with about 25 gms. of
charcoal, exhausted at $1000^{\circ}$ C. for several hours, filled
with hydrogen, sealed and weighed. The charcoal was again
exhausted as described above. When this was complete the
ice calorimeter was prepared and the apparatus assembled
for a run. The whole was given two days to stabilize in
before a run was commenced. At first small quantities,
less than 1 c.c., of oxygen were admitted to the charcoal.
These were increased until about 70 c.c. quantities were
admitted. The heat evolved was measured by means of the
drop in mercury in the capillary tube. This tube was
carefully calibrated on the basis of one mean calorie
equal to 0.01549 grams of mercury[8]. A single charge was

studied for a period of from nine to twenty hours.

## RESULTS.

Two runs were made. The data are shewn in Tables I and II. The total calories per gram of charcoal, q, was plotted against total moles $\times 10^4$ of oxygen adsorbed per gram of charcoal, n, on a very large scale. This curve is reproduced in Fig. 2. The tangents to this curve, $\frac{dq}{dn}$, will give the values of the heat of adsorption at constant volume per gram molecule of gas per gram of charcoal, $Q_V$ , at the concentration n. These values are given in Table III and plotted in Figure 3.

After completion of run B the apparatus was maintained at $0^\circ$ C. while the gas was pumped off by means of a Topler pump. The gas was passed through baryta water. Only a very slight precipitate was formed.

While conducting the preliminary exhaustion to run A, it was noticed that after prolonged exhaustion at $1000^\circ$ C the charcoal and quartz bulb were charged electrostatically with charges of opposite sign. If a piece of charcoal came in contact with the quartz it would adhere. By sharply tapping the bulb the charcoal could lie detached and it would then pass in a curved orbit to a new point on the quartz, maintaining the same general level. After being detached several times it would fall back into the mass of charcoal.

## DISCUSSION OF RESULTS.

Examination of Figure 3 shows that the initial heat of adsorption is very high, 84,400 calories per mole per gram. This value is higher than any previous value the highest recorded being 70,000 calories per mole per gram due to Marshall. The final values are the same in each case - approximately 4000 calories per mole per gram.

In view of the high initial values it would seem that the first quantities adsorbed were held by primary valences, later layers being held by modification of the existing molecular fields. The curve in Figure 3 is also periodic in nature, tending to have steps occur at increasing concentration intervals. This periodicy gives an explanation of the phenomenon observed:

During the preparation of charcoal the carbon chains existing in the fibres are denuded of their hydrogen but are not much modified, if at all, in form. The result is that a certain few atoms will be thrust clear of the aggregate and present a point of intense attraction for the oxygen. Also, although the charcoal has a general porosity, it also contains some pores of molecular dimensions in the carbon chains. These pores will also represent regions of intense attraction. Since the attractive forces at these points will of necessity be very variable no constant heat value could be expected until they are all

covered with at least a monomolecular layer. Even then prominent points would have greater attractive properties than the general surface and hence would still tend to attract the oxygen preferentially. A constant heat value would not be obtained until they were saturated, or rather their attractive force reduced to a value represented by the attractive force of the general surface. Then a general covering would occur, after which the heat value would be a more or less constant low value. The point representing a monomolecular layer would be the concentration at which the heat values drop off to approximately a constant value. Hence, assuming that the first layer corresponds to $1 \times 10^{-4}$ grams molecules of oxygen, that $N = 6.06 \times 10^{23}$, and that the distance apart of the centres of the oxygen atoms is $1.25 \times 10^{-8}$ cms. as shown by Bragg[9], we can calculate the minimum surface per gram of charcoal as follows:

$$S = 2 \times 1 \times 10^{-4} \times 6.06 \times 10^{23} \, (1.25 \times 10^{-8})^{2}$$

$$= 1.8937 \times 10^{4} \text{ sq. cm. per gm.}$$

$$= 18.937 \text{ sq. metres per gm.}$$

## SUMMARY

1.  The heat of adsorption of oxygen on charcoal
    at  $0^{\circ}$ C. has been carefully measured over a
    large range of concentrations, using 25 grams
    of cocoanut charcoal.

2.  The initial concentrations used are smaller,
    and the initial heats larger than those obtained
    by any previous investigator.

3.  The mechanism of adsorption has been discussed.

4.  The active surface of cocoanut charcoal has
    been calculated to be 18.937 sq. metres per gm.

5.  Charcoal has been heated for sixty hours at
    $1000^{\circ}$ C. without apparent loss of activity,
    although previous investigators claimed great
    loss of activity from continued heating above
    $800^{\circ}$ - $900^{\circ}$ C.

6.  The activity of charcoal depends more upon
    the temperature of evacuation than upon
    the time.

7.  No appreciable quantity of carbon dioxide
    is formed when oxygen is adsorbed at $0^{\circ}$ C.

8.  Interesting electrical phenomena have been
    observed after long heating and continued
    evacuation.

    Further work is being done in connection with
the oxygen results. It is hoped to measure the
heat of adsorption of acetylene.

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# TABLE I.

## Wt. of Charcoal = 25.7920 gr.

| | Run | gas Admitted | Final Pressure mm. | Total gas not adsorbed | Gas adsorbed | Total c.c. adsorbed | Heat in Cal... | Total Heat | q = cal 1 gm. | $R \times 10^4$ = Moles 1 gm. |
|---|---|---|---|---|---|---|---|---|---|---|
| A | 1 | 0.8728 | 0.0 | 0 | 0.8728 | 0.8728 | 3.203 | 3.203 | .1242 | .015115 |
| | 2 | 1.2120 | 0.0 | 0 | 1.2120 | 2.0848 | 3.828 | 7.031 | .2715 | .036103 |
| | 3 | 2.4951 | 0.0 | 0 | 2.4951 | 4.5799 | 7.371 | 14.402 | .5584 | .079307 |
| | 4 | 0.8466 | 0.0 | 0 | 0.8466 | 5.4265 | 2.350 | 16.752 | .6495 | .096694 |
| | 5 | 1.1904 | 0.0 | 0 | 1.1904 | 6.6169 | 3.008 | 19.760 | .7661 | .114580 |
| | 6 | 2.0984 | 0.0 | 0 | 2.0984 | 8.7153 | 6.253 | 26.013 | 1.0087 | .150940 |
| | 7 | 2.4501 | 0.0 | 0 | 2.4501 | 11.1654 | 7.162 | 33.175 | 1.2862 | .193340 |
| | 8 | 2.2044 | 0.0 | 0 | 2.2044 | 13.3698 | 6.602 | 39.777 | 1.5422 | .231540 |
| | 9 | 3.2036 | 0.0 | 0 | 3.2036 | 16.5734 | 9.344 | 49.121 | 1.9046 | .287000 |
| | 10 | 2.2572 | 0.20 | .0237 | 2.2335 | 18.8069 | 7.637 | 56.758 | 2.2006 | .325700 |
| | 11 | 3.5713 | 0.34 | .0403 | 3.5547 | 22.3616 | 6.910 | 63.668 | 2.4684 | .404270 |
| | 12 | 6.8989 | 3.25 | .3860 | 6.5532 | 28.9148 | 11.453 | 75.121 | 2.9127 | .500720 |
| | 13 | 6.8562 | 7.40 | .8832 | 6.3590 | 35.2738 | 8.631 | 83.752 | 3.2472 | .610800 |
| | 14 | 10.5830 | 14.73 | 1.7741 | 9.6921 | 44.9659 | 8.253 | 92.005 | 3.5672 | .778700 |
| | 15 | 22.3205 | 35.60 | 4.2861 | 19.8085 | 64.7744 | 6.854 | 98.859 | 3.8330 | 1.121730 |
| | 16 | 29.4030 | 83.40 | 9.5605 | 24.1286 | 88.9030 | 7.036 | 105.895 | 4.0954 | 1.532400 |
| | 17 | 45.7284 | 140.00 | 16.7946 | 38.4943 | 127.3973 | 8.127 | 114.022 | 4.4207 | 2.206300 |
| | 18 | 27.9632 | 179.20 | 21.6260 | 23.1318 | 150.5291 | 4.476 | 118.498 | 4.5945 | 2.605550 |
| | 19 | 62.3590 | 271.50 | 33.1900 | 50.7950 | 201.3241 | 10.434 | 128.932 | 4.9990 | 3.48780 |
| | 20 | 77.0983 | 382.20 | 46.4470 | 63.8413 | 265.1654 | 11.260 | 140.192 | 5.4356 | 4.59920 |

## TABLE II.

### Wt. of Charcoal = 24.8428 gms.

| | Run | Gas Admitted | Final Pressure (mm) | Total gas not adsorbed | Gas adsorbed | Total c.c. gas adsorbed | Heat in Cal. | Total Heat in Cal. | q = Cal/gm. | $R \times 10^4$ Moles/gm. |
|---|---|---|---|---|---|---|---|---|---|---|
| B | 1 | .7572 | 0 | 0 | .7572 | .7572 | 2.966 | 2.966 | 0.1194 | .013614 |
| | 2 | 1.4952 | 0 | 0 | 1.4952 | 2.2524 | 5.091 | 8.057 | 0.3243 | .040493 |
| | 3 | 2.4695 | 0 | 0 | 2.4695 | 4.7229 | 8.015 | 16.072 | 0.6469 | .084910 |
| | 4 | 3.7552 | 0 | 0 | 3.7552 | 8.4781 | 11.274 | 27.346 | 1.0951 | .152420 |
| | 5 | 3.8696 | .05 | .0060 | 3.8636 | 12.3417 | 11.792 | 39.138 | 1.5754 | .221905 |
| | 6 | 7.4069 | .40 | .0479 | 7.3650 | 19.7067 | 20.702 | 59.840 | 2.4091 | .354300 |
| | 7 | 11.3680 | 6.85 | .8202 | 10.5957 | 30.3024 | 14.910 | 74.750 | 3.0091 | .544775 |
| | 8 | 15.5690 | 20.25 | 2.4242 | 13.9650 | 44.2674 | 11.246 | 93.102 | 3.6091 | .795772 |
| | 9 | 20.4246 | 43.50 | 5.2123 | 17.6365 | 61.9039 | 5.945 | 99.047 | 3.8402 | 1.113000 |
| | 10 | 67.9940 | 128.20 | 15.3671 | 57.8382 | 119.7421 | 15.290 | 115.337 | 4.4715 | 2.153000 |
| | 11 | 87.5640 | 259.0 | 31.0660 | 72.8651 | 192.6072 | 15.848 | 130.820 | 5.0715 | 3.462600 |
| | 12 | 73.2420 | 374.0 | 44.9310 | 59.3770 | 251.9842 | 11.583 | 142.403 | 5.5211 | 4.530000 |
| | 13 | 75.2550 | 513.9 | 61.4760 | 58.7100 | 310.6942 | 11.400 | 153.803 | 5.9631 | 5.58580 |

## TABLE III.

| $N \times 10^4$ | $\dfrac{dq}{dn}$ |
|---|---|
| 0 | 85,200 |
| 0.01 | 84,400 |
| .02 | 81,100 |
| .05 | 73,970 |
| .10 | 69,800 |
| .15 | 68,263 |
| .20 | 63,165 |
| .30 | 59,000 |
| .40 | 42,667 |
| .50 | 32,500 |
| .60 | 28,400 |
| .70 | 19,467 |
| .80 | 12,217 |
| 1.00 | 7,266 |
| 1.50 | 5,900 |
| 2.00 | 5,166 |
| 2.50 | 4,633 |
| 3.5 - 6.0 | 4,250 |

Fig. 2