

THE EQUILIBRIUM PRESSURES OF OXYGEN
ON ACTIVATED CHARCOAL

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Introduction.

1

Since the time of Sir James Dewar, much work has been done upon the various phenomena attending the adsorption by activated charcoal, of various gases, such as, oxygen, nitrogen, hydrogen, helium and many others.

Most of the investigators in this field have measured the adsorption at pressures greater than one millimetre of mercury, and there are few published data on the adsorptive powers of activated charcoal at the very low pressures which are of interest to those engaged in high vacuum work.

2

G. Claude has measured the adsorption of hydrogen, helium, neon and nitrogen at low temperatures and down to pressures of .005 millimetres of mercury.

3

Miss. Ida F. Homfray has investigated in some detail the amounts of various gases adsorbed at different temperatures and pressures, but here again we find that the range of pressures investigated did not extend down to the lower limit.

4

More recently, Rowe has measured the equilibrium of oxygen, nitrogen, carbon monoxide and carbon dioxide over a pressure range of 10^{-5} mm. to 10^{-2} mm. at room

temperatures. He arrives at the conclusion that for oxygen the equilibrium pressure, at pressures below 2.5×10^{-3} mm. is a linear function of the quantity of gas adsorbed, while at higher pressures the equilibrium is better represented by an equation of the type

$$\log \frac{\alpha}{p} = A_0 - A_1 \alpha$$

where A_0 and A_1 are constants and α is the quantity adsorbed. This equation is more satisfactory than the familiar Freundlich adsorption isotherm

$$\alpha = kP^{\frac{1}{n}}$$

Turning from pressures to heats of adsorption we find that Keyes and Marshall have shown that the initial heat of adsorption of oxygen on activated charcoal reaches the high value of 72,000 calories per mole, while Marshall and Bramston-Cook have obtained a value of 89,600 calories per mole for the heat of adsorption at zero concentration.

This high value of the heat of adsorption drops off rapidly as the concentration increases, finally reaching a constant value of about 4,000 calories per mole of adsorbed oxygen. Keyes and Marshall have also shown that this high initial heat is much greater in the case of oxygen, other gases not exhibiting such a high initial value.

This suggests that the first oxygen added to a freshly "outgassed" charcoal surface is held in a different manner from that which is subsequently added. In fact, it seems that the reaction may be more a chemical combination

than an adsorption, or it might be that there are certain⁷ "active centers" on the charcoal which hold the adsorbed gas more tenaciously than does the remainder of the surface. These views are supported by the work of Lowry and Hulett⁸ who found that only one half of the adsorbed oxygen could be recovered as such, the remainder coming off as carbon dioxide and carbon monoxide when outgassed at high temperatures.

Object.

The fact that little work has been done upon equilibrium pressures at very low pressures, and that the heats of adsorption of oxygen do not vary linearly at low pressures, suggested that interesting results might possibly be obtained by measuring the equilibrium pressures of oxygen upon activated charcoal at very low pressures. And it was also thought, that by measuring the equilibrium pressures over a range of temperatures, that data would be obtained which would enable the heats of adsorption to be calculated by means of the Clausius Clapeyron equation, which could be applied in this case since any slight change in the pressure would have but little effect on the actual concentration of gas on the charcoal.

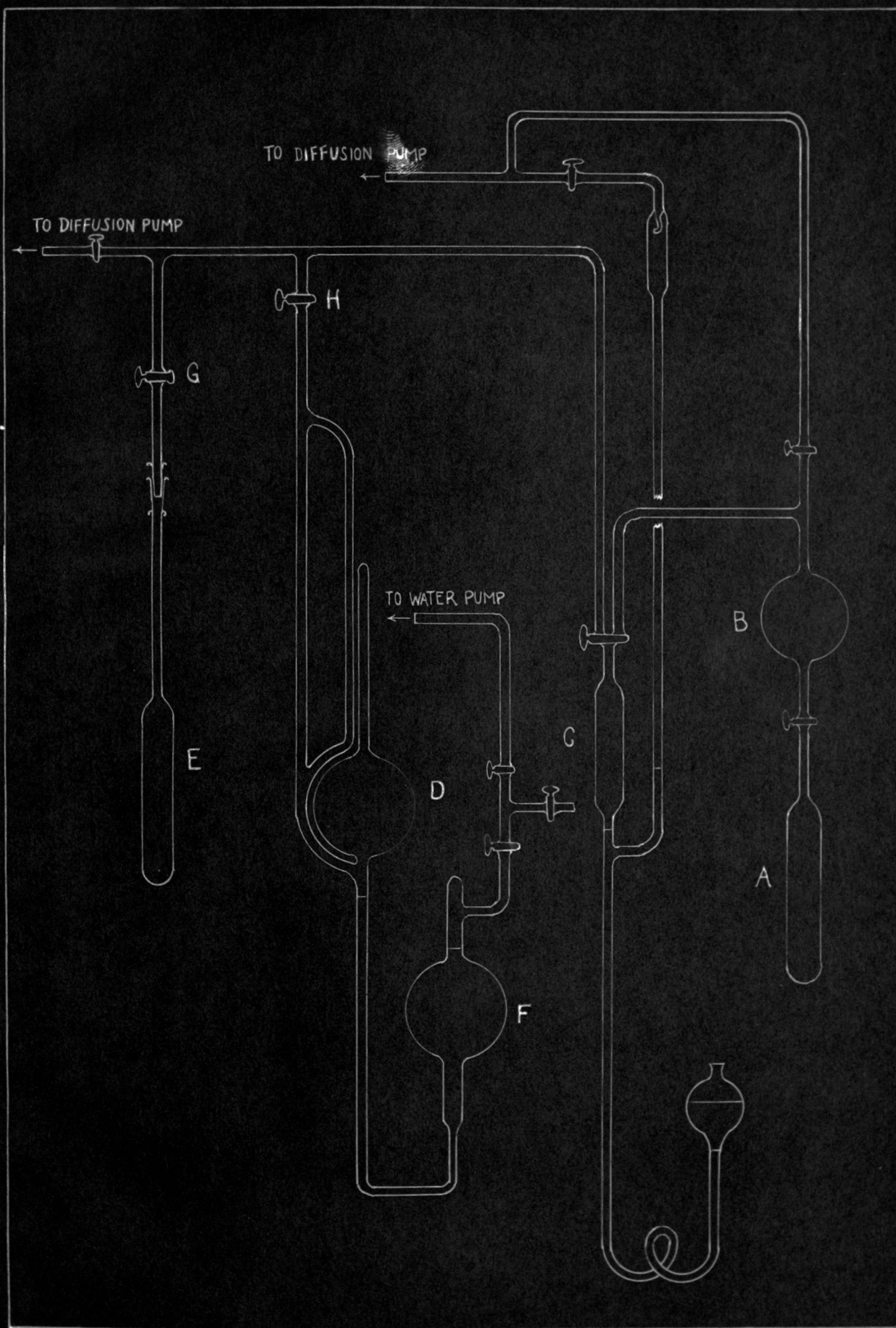
At the low pressures it was proposed to work with, any slight traces of impurity in the oxygen present would invalidate the results. These impurities might be derived from the admitted oxygen, or might possibly be displaced from the charcoal surface by the adsorbed oxygen. A third

possibility presents itself; that carbon monoxide and carbon dioxide are formed as the oxygen adsorbs on the surface. Hence it was proposed to analyse the residual gases over the surface of the charcoal.

To sum up; in this investigation it is proposed to measure the equilibrium pressures of oxygen on activated charcoal over a range of temperatures, and to determine the composition of the residual gases.

Apparatus.

The principle features of the apparatus used are shown in the figure. The tube A contained chemically pure potassium chlorate to which had been added a trace of manganese dioxide. This was carefully melted and exhausted several times in order to remove water vapor and other gases which might possibly be present. The bulb B, of about 250 c.c. capacity, was used to store the oxygen. A 500 c.c. McLeod gauge (D) was used to measure the residual pressures of oxygen over the charcoal. This gauge was carefully standardized and was sensitive down to pressures of 10^{-5} mm. of mercury. The connection between D and the mercury reservoir F was all of glass, the level of the mercury being controlled by means of a water pump and by admitting air through the stop cock as shown. The charcoal was contained in a quartz tube E. The quartz tube was lined with platinum in order to prevent any possible interaction between the charcoal and silica while outgassing.



The charcoal used was a sample of cocoanut charcoal obtained from the National Carbon Co. It was washed in a Soxhlet extractor with hydrochloric acid and afterwards treated with hydrofluoric acid, the final ash content being .267%. Before use it was outgassed for 20 hours at 950°C. After outgassing it weighed 25.792 grams.

A platinum wound resistance furnace was used for heating. An electrical pyrometer was used to check the resistance furnace. Plotting amperes against temperature we obtain a straight line over the range 900° to 1,000°C. The electrical pyrometer had previously been checked against a constant boiling point sulphur bath and had been found accurate to within one degree, hence the outgassing temperature was known with considerable accuracy. The apparatus was exhausted with a mercury diffusion pump backed by a Cenco-Hyvac oil pump. With this arrangement it was possible to obtain a vacuum which would register no pressure whatever on the sensitive McLeod gauge employed, certainly below 10^{-6} mm.

Experimental.

After the apparatus had been set up, all accessible parts were baked and exhausted simultaneously in order to eliminate, as far as possible, gas adsorbed on the walls. This process was repeated until no appreciable pressure developed in the apparatus after standing for 24 hours. It was found that much gas could be removed from the walls by means of a high frequency discharge, this method being particularly applicable where a flame could not be used.

The charcoal was outgassed at 950° C until the pressure fell to approximately 6×10^{-4} mm. of mercury. This usually required from 6 to 8 hours. Prolonged heating failed to decrease the pressure further. In order to be sure that all undesirable gases were removed from the charcoal surface, it was saturated with oxygen several times, outgassing after each addition of oxygen.

The first attempt to measure the equilibrium pressure was performed as follows. Oxygen was admitted, sufficient to produce a concentration of about $.6 \times 10^{-6}$ moles of oxygen per gram of charcoal. This was given about 5 minutes to attain equilibrium and the pressure was read off on the guage. This value was apparently steady and showed but little drop with time. The stop-cock G was then closed and the system evacuated completely. G was then opened and after 5 minutes the pressure was read off. This value increased slightly with time but never reached the pressure value ob-

tained immediately after admitting the oxygen. It is assumed that the true equilibrium lies between these two pressures. A series of readings were made in this fashion from concentrations of $.6 \times 10^{-6}$ to 8×10^{-6} moles per g. of charcoal. Above this concentration equilibrium took longer to occur and even with the concentrations used, it is believed that the values are not strictly accurate, owing to the fact that not sufficient time was given for a true equilibrium to occur.

At the higher concentrations used it was thought worth while to make a series of measurements on the rates of adsorption. This was done merely by taking pressure measurements at regular time intervals until the pressure showed some signs of reaching a constant value.

A further careful attempt was made to obtain an equilibrium pressure in the following manner. As before, a small amount of oxygen was added and the pressure observed, G was closed, the system evacuated, G was opened again and the system allowed to come to equilibrium, the pressure being taken again. Next G was closed again, the system evacuated and then oxygen was admitted to the system at a pressure somewhat greater than the approximate equilibrium pressure. The stop-cock G was then opened, and the pressure read after 5 minutes. In this fashion fairly consistent and reproducible results were obtained. The last small addition of oxygen would have a negligible effect on the concentration of oxygen

already on the charcoal. These readings were repeated at 0° C. and at room temperature which was 22° C.

Results.

The first series of equilibrium pressures obtained are given in Table 1 and are plotted on Graph 1. Concentrations are expressed in moles of oxygen per gram of charcoal. P is the pressure after the oxygen has stood over the charcoal for 5 minutes, and P is the pressure obtained after closing G, evacuating the system, then opening G and reading the pressure after equilibrium has been reached. As was stated before, the true equilibrium probably lies between these two values.

Table 1.

Moles per gram.	P x 10 ⁵ mm.	P x 10 ⁵ mm.
.613 x 10 ⁻⁶	2.19	1.5
1.31 x 10 ⁻⁶	3.21	1.94
1.95 x 10 ⁻⁶	3.76	2.23
2.57 x 10 ⁻⁶	3.89	2.45
3.19 x 10 ⁻⁶	3.85	2.26
4.95 x 10 ⁻⁶	8.57	4.02
5.87 x 10 ⁻⁶	22.1	10
6.48 x 10 ⁻⁶	21.3	13.1
7.9 x 10 ⁻⁶	32.3	15.5
8.03 x 10 ⁻⁶	38.4	17.5

The results of the study of rates of adsorption are given in Table II and are plotted on Graph II. The

concentration of oxygen on the charcoal before measurements were commenced was 37.42×10^{-6} moles per gram while the fraction admitted was 4.94×10^{-6} mole. The range of the McLeod gauge was such that measurements could only be commenced after 40 minutes.

Table II.

Time in mins.	$P \times 10^{-4}$ mm.	Time in mins.	$P \times 10^{-4}$ mm.
40	242	100	34
45	185	110	28
50	146	120	24.5
55	116	130	23
60	95	140	20
65	83.5	150	18.3
70	70.5	160	17.3
75	63	170	15.8
80	53	180	14.1
85	46.5	190	13.1
90	42.5	200	12.1
95	39.5	∞	9.95

The following are the results obtained from an attempt to find the equilibrium pressure at two temperatures. The concentration of oxygen on the charcoal was 2.04×10^{-6} moles per gram. It was allowed to stand for 24 hours, which at that concentration would be ample time for equilibrium to be attained. The stop-cock G was closed and the system exhausted, G was then opened, a pressure of 1.88×10^{-5} mm.

was observed. The system was exhausted again and then oxygen at a pressure of 2.5×10^{-5} cm. was added, the pressure observed was 2×10^{-5} mm. Further addition of two small quantities of oxygen both gave pressures of 2.04×10^{-5} mm. The mean pressure of the four measurements being 2.04×10^{-5} mm. at 22° C. The same procedure was repeated at 0° C, a mean pressure of 1.178×10^{-5} mm. being obtained. Applying these results to the integrated form of the Clausius Clapeyron equation

$$\log \frac{P_1}{P_2} = - \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

we obtain for the heat of adsorption 3,990 calories per mole.

Discussion of Results.

From Graph I we see that at very low concentrations the equilibrium pressure is a linear function of the amount of gas adsorbed, while at higher concentrations it departs from this linear relationship. It is possible that if more time had been allowed for the gases to come to equilibrium, that a linear relationship would have been observed even at the higher concentrations.

It was observed that only at concentrations below 2.5×10^{-6} moles of oxygen, per gram of charcoal, was equilibrium attained almost instantaneously. At low concentrations however, activated charcoal appears to a very efficient means of creating high vacuum. In one particular

case the pressure was decreased from .478 mm. to .0000219mm. in one minute, i.e. the fraction of oxygen not adsorbed amounted to only .0000458 of the whole.

At higher concentrations of oxygen such as is shown in Table II, although the greater part of the gas goes on very quickly there is always a certain fraction which adds on slowly in a regular manner. The rate of decrease is not a linear function of pressure but will very likely be a function both of pressure and of the condition of the charcoal surface. These observations suggest that the rapid adsorption is due to condensation taking place on the more active carbon centers first, this being followed by a surface rearrangement of the molecules or by a diffusion into the interior of the charcoal particles.

Another interesting observation made was that, when the concentration of oxygen on the charcoal was small, there was a rapid drop to the equilibrium value, this being followed by a slow increase in pressure which occurred invariably when the sample was allowed to stand for any length of time. For example, after standing for 12 hours the pressure increased from 2.67×10^{-5} mm. to 5×10^{-5} mm. It seems probable that this is caused by the formation of carbon monoxide or carbon dioxide, although this can not be stated definitely until an analysis of the gases has been carried out.

The heat of adsorption determined by means of the

Clausius Clapeyron equation does not agree with the high initial heat found by Keyes and Marshall⁵ and by Marshall and Bramston-Cook,⁶ but does agree quite closely with the final heat of 4,000 calories per mole found by these investigators.

Summary.

1. At concentrations below 2.5×10^{-6} moles of oxygen per gram of charcoal, adsorption is almost instantaneous.
2. At higher concentrations a large fraction of the oxygen goes on quickly, the remainder being adsorbed slowly.
3. At small concentrations, after attaining equilibrium, a slow but regular increase in pressure occurs.
4. A value of the heat of adsorption was obtained of 3,990 calories per mole.

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