

CCCLXXX.—*The Heat of Adsorption of Oxygen on Charcoal. Part III.*

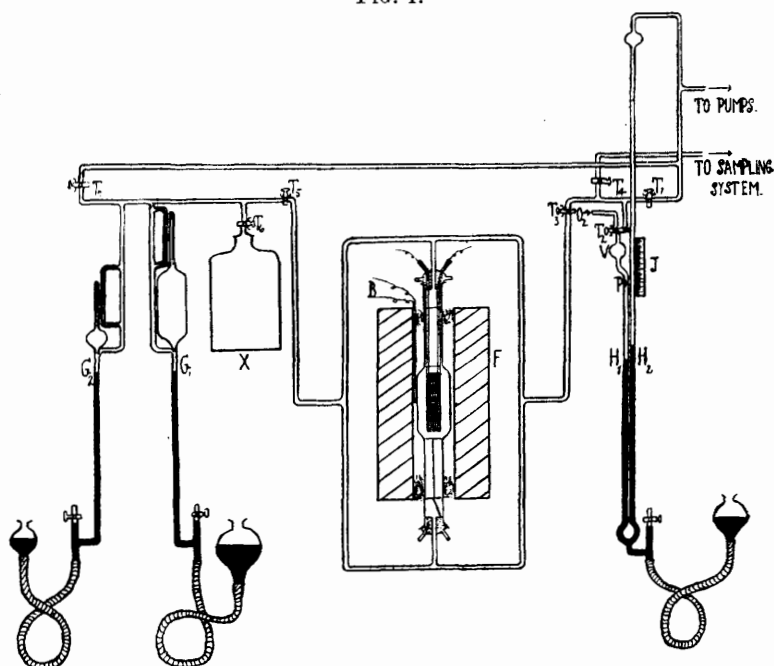
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ATTEMPTS are now described to refine the method of Blench and Garner (Part I; J., 1924, 125, 1288) for determining the heat of adsorption of oxygen on charcoal under various conditions of temperature and pressure, and to extend it to the general case of the measurement of the heat of adsorption of a gas on a solid surface. So far, only one case, *viz.*, that of the adsorption of oxygen on charcoal, has been studied. The results obtained have already been summarised and their theoretical implications discussed in Part II (Garner and McKie, J., 1927, 2451).

Component Parts of Apparatus.—*Reaction vessel.* The reaction vessel is shown on a large scale in Fig. 2; it consisted of a tube of

fused quartz, 40 cm. long and 2 cm. in diameter, open at both ends, the middle section being blown out in the form of a cylindrical bulb, A, 10 cm. long and 4.5 cm. in diameter. Hollow, closed stoppers, S_1 and S_2 , of "Durosil" glass were ground to fit the open ends. A continuous and rapid current of cold water was passed through each stopper *via* the tubes, D D, to prevent undue heating of the rubber grease used to keep the ground joints vacuum-tight. The stoppers were further protected from the heat radiated along the tube of the furnace by means of fused quartz plates, R R,

FIG. 1.

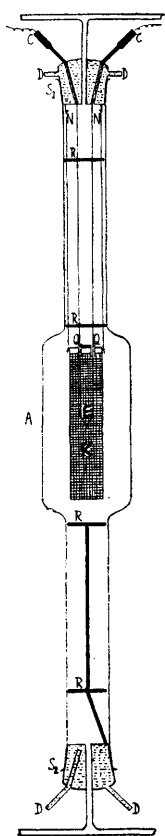


arranged inside the vessel, two being placed on each side of the bulb, one just level with the shoulders of the latter and the other on a level with the end of the furnace. The upper two were attached to the wires carrying the container, K. The lower pair were joined as shown, one being fused to each end of a suitable length of quartz rod, and were supported on the lower stopper by a short limb of quartz, fused obliquely to the lower plate so as to rest clear of the tube passing through the stopper.

A tube was sealed through each stopper for the admission of gas, thus ensuring even distribution to each end of the mass of

charcoal in K. Through the upper stopper there were also sealed two tubes for carrying the wires of the thermocouple, E, each wire being sealed into its tube at a distance of about 3 cm. from the stopper. In the fusion of the glass around the metal, the wires became brittle at this point, where there was always a tendency for them to be bent, and in order to prevent this bending, glass cups, C C, were fused on to the tubes carrying the wires.

FIG. 2.



After the wires had been sealed into the leads just below the cups, the latter were filled with molten wax, which on solidification prevented any movement of the wires near the glass-metal joints.

The charcoal, about 5–6 g., was supported in the container, K, of 200-mesh platinum gauze, suspended by platinum wires from the glass hooks, N N, fused to the base of the stopper, S₁. The top of the container was closed by a platinum lid, bearing an insulating H-tube, Q Q, of fused quartz, carrying the wires of the thermocouple.

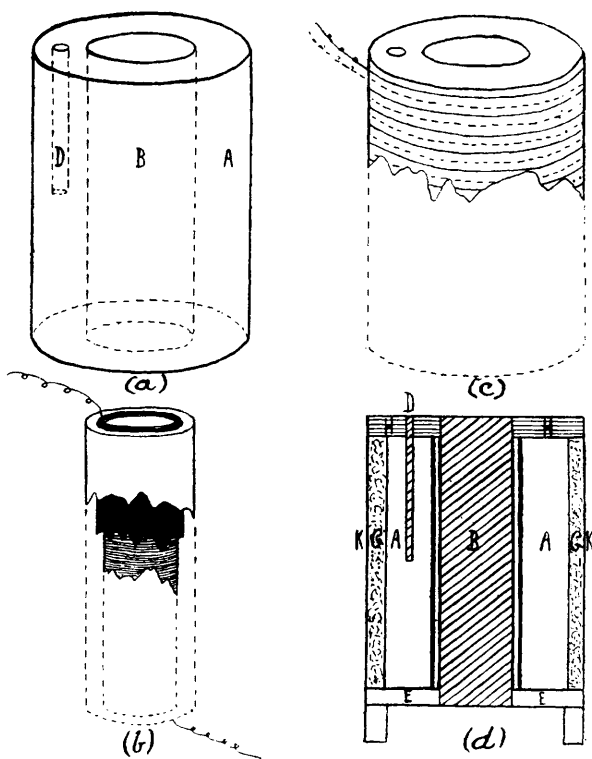
Furnace. The ordinary laboratory pattern of electrical furnace provided sufficient lagging for the reaction vessel to keep it at constant temperature during determinations at room temperature; in the experiments at higher temperatures, however, this furnace was not suitable, as its temperature could not be maintained sufficiently constant owing to variations in the voltage of the mains, and the furnace F was therefore designed. It consisted of a copper cylinder, A (Fig. 3a), about 27 kg. in weight, 25 cm. in length, and 15 cm. in diameter, cast with a central cylindrical bore, B, of 7.5 cm. diameter, which carried two concentric cylindrical quartz tubes of the same length as A. The inner of these had an internal diameter of 5 cm. and walls 0.1 cm. thick. Along its whole length, a coil of nichrome wire (20 S.W.G.) was closely wound and securely fastened at the ends. This tube was placed

inside the outer tube, of external diameter 7.5 cm. and wall thickness 0.7 cm., and cemented into position by packing the annular space with alundum cement. The whole arrangement, shown in Fig. 3(b), was then passed into the bore of the copper cylinder, a thin layer of asbestos paper being placed between the copper and the quartz. The ends of the coil were connected *via* an adjustable series resistance with the 220-volt main. This coil was used to maintain the reaction vessel at 950° during the activation of

the charcoal. The reason for its special construction appears below.

The copper cylinder was wound on the outside with two subsidiary coils of nichrome ribbon, 0.1588 cm. by 0.0127 cm., each passing along its whole length, as shown in Fig. 3(c), and each having a resistance of about 45 ohms. Insulation between the copper and the coils was provided by a layer of asbestos paper.

FIG. 3.



The copper cylinder, etc., was then mounted on a fire-brick, E, 2.5 cm. high, in which a hole had been drilled of diameter equal to that of the bore of A, and placed in a rectangular tin, K, of cross-section 20 cm. by 20 cm. and height 30 cm., as shown in Fig. 3(d). The hollow portion, G, was packed with asbestos wool; H consists of asbestos boards with circular holes to correspond to the bores at the top of A.

The subsidiary heating coils were used during the determination of heats of adsorption at temperatures above atmospheric. By

means of them, the copper cylinder was heated to the temperature of experiment, both coils carrying current and being separately connected *via* adjustable series resistances with the 220-volt main. The temperature of the cylinder was controlled by means of a mercury-in-glass (hard) regulator, the bulb of which was placed in the hole, D, drilled in the copper, as shown in Fig. 3(a) and (d). This hole was 1.25 cm. in diameter and 12.5 cm. long, and the bulb of the regulator was constructed so as to fill it as exactly as possible. The regulator operated an electromagnetic relay, so arranged as to "break" the current through one of the subsidiary coils, if and when the temperature of the copper exceeded that desired. Thermal contact between the copper and the glass bulb of the regulator was improved by an intermediate film of B.P. paraffin. This system of regulation maintained the temperature constant to within $\pm 0.05^\circ$ at 100° and $\pm 0.10^\circ$ at 200° .

The purpose of the several coils will now be clear. The main coil was designed to carry 10 amps. and thus to provide rapid heating of the reaction vessel to the temperature of activation. The subsidiary coils carried currents of $\frac{1}{2}$ — $1\frac{1}{2}$ amps. Such currents gave small fluctuations of temperature in a furnace of so large a thermal capacity. The smaller current was always less than 1 amp., and was therefore such as to be easily broken by the relay. These subsidiary coils could not be used for activation at high temperature: heating was too slow, and the coils wore out under such drastic usage. Further, if the copper was heated to 950° , considerable oxidation occurred; hence the main coil was introduced for the preliminary activation. The lagging effect produced by the thick, outer, quartz tube was such that the temperature of the copper never rose beyond 600 — 700° during the two hours when the reaction vessel was at 950° , and oxidation was so slight that after months of use scaling was inappreciable. Further, the temperature of the reaction vessel could be raised from 18° to 950° in 10 minutes.

Pumping system. The pumping system consisted of a second-stage mercury-vapour diffusion pump, working under the backing pressure set up by a "Hyvac" rotary oil pump.

Sampling system. The sampling system consisted of a second-stage mercury-vapour diffusion pump in series with a Töpler pump, which allowed of the collection of a sample of gas from the reaction vessel after adsorption had taken place. The sample was collected in a capillary tube, where it was analysed as described below.

Gas burette. The gas burette, V (Fig. I), was the one described in Part I (p. 1291), and the same procedure was followed.

Method of Recording Increments of Temperature.—Changes of temperature produced by adsorption were recorded by means of a

platinum-platinum-rhodium thermocouple, of which the "hot" junction, E, was embedded in the charcoal as shown in Fig. 2, the "cold" junction being maintained at a constant temperature (that of the furnace tube) either by insertion in a Dewar vessel containing water at room temperature in the experiments at that temperature, or by being placed inside the tube of the furnace close to the bulb of the reaction vessel in the experiments at higher temperatures. The thermocouple system was connected in series with a rigidly mounted Moll galvanometer, the mirror of which was illuminated by a 100 c.p. "Pointolite" lamp, enclosed in a light-tight box, and so arranged that an image of a slit as a fine vertical line of light was reflected from the mirror on to the cylindrical lens of a clock-work camera. This lens focussed the line to a point image, the movements of which were recorded on bromide paper, wound on a moving drum.

Calibration of Thermocouple.—The thermocouple was calibrated at 0° by means of two Dewar vessels, one containing crushed ice and water, and the other water at 3–4°. Calibration at 15° was carried out in the same manner by means of two samples of water at different temperatures near 15°. Similar calibrations were made at 60°, 100°, and 190° by means of a pair of baths at constant neighbouring temperatures. All temperatures were read on standard thermometers. The differential deflexions per degree were then plotted against the corresponding temperatures, and a smooth curve was drawn through the points obtained. From this the deflexion per degree difference of temperature could be read at any desired temperature.

Correction for the "Gas Effect."—The temperature-time curves obtained on the photographs were corrected for loss of heat by radiation as described later, but a further correction was necessary in the case of determinations at temperatures above atmospheric. This was due to the "gas effect," which has already been described in detail (Part I, pp. 1291–1292)—briefly, it is that rise of temperature which occurs on admission of any gas, whether adsorbed or inert, to the hot, evacuated reaction vessel. The phenomenon is largely due to the gradient of temperature inside the vessel between the walls of the latter and the thermocouple, this gradient being caused by convection currents in the reaction vessel. At very low pressures, heat is conducted away to the ends of the vessel by convection more rapidly than it is conducted inwards to E from the walls of A (Fig. 2).

This effect was allowed for as follows. Argon, purified as described later, was admitted to the reaction vessel from the gas burette in such amount that it gave in that vessel a pressure approximately

equal to that which obtained there after the adsorption of oxygen in the experiment to which the correction was to be applied. The rise of temperature occurring on admission of argon, *i.e.*, the "gas effect," was measured photographically as in the method previously described. The experiments showed that the temperature rose slowly, taking several minutes to attain its maximum, and then remained at a steady level, say, x units higher than the original temperature. It could be restored to that value only if and when the argon was removed by evacuation. The actual increment of temperature due to adsorption of oxygen was therefore taken to be the difference between x and the rise of temperature occurring when adsorption of oxygen took place. Similar experiments with argon were made at the various pressures and temperatures at which experiments with oxygen took place, and the corrections thus determined were applied to their respective experiments.

Complete Apparatus.—The assembled apparatus is shown in Fig. 1. On one side the reaction vessel was connected *via* tap T_5 with the bottle X (see below), and thence with the McLeod gauges, G_1 and G_2 , which in turn were connected with the pumping system by means of the tap T_7 ; and on the other side it was connected with the pumping system *via* tap T_1 . A further tap, T_3 , was inserted between tap T_1 and the reaction vessel. Tap T_2 connected the reaction vessel with the gas burette. At a suitable point the sampling system was connected to the main apparatus by way of tap T_4 . Save for the stoppers S_1 and S_2 , the glass parts of the apparatus were of soft glass. Junction between the soft- and hard-glass parts of the apparatus was effected through ground joints, not shown in the diagrams.

Volume of the Apparatus.—The volume of the apparatus was determined by admitting a measured amount of oxygen from the gas burette to that part of the evacuated apparatus between taps T_1 , T_4 , and T_7 , measuring the resulting pressure on the McLeod gauges, and then applying Boyle's law. The value obtained applied only to determinations at room temperature, because in the other experiments the reaction vessel was at a higher temperature, and the consequent thermal expansion of the gas led to an apparent decrease in the volume of the apparatus. To allow for this, the "apparent" or "equivalent" volume of the apparatus (see Part I, pp. 1291—1292) was determined by the method just described with the reaction vessel at various temperatures, carbon being absent.

Materials.—Oxygen was obtained by heating pure potassium permanganate and was dried by passage through phosphoric oxide.

The charcoal consisted of those particles of the vegetable charcoal, "Norit," which were sieved by the 100- and screened by the

150-mesh sieve. This portion was repeatedly boiled with hydrochloric and hydrofluoric acids to remove lime and silica, the ash content being thereby reduced from 7% to 0.3% and all traces of lime removed.

The argon was obtained from a sample containing about 5% of nitrogen and traces of oxygen and of the rare gases. For our purposes, this last impurity could be ignored. Nitrogen was removed by a modified form of the method of Rayleigh and Ramsay (*Phil. Trans.*, 1895, A, **186**, 197), the confining liquid being mercury instead of weak alkali. The author's thanks are due to Dr. M. W. Travers, F.R.S., who very kindly constructed the necessary apparatus, directed him in the technique of the process, and purified a large sample of the argon used. The nitrous gases formed were absorbed by a layer of aqueous caustic soda solution floating on the mercury. Excess of oxygen was subsequently removed by ignited phosphorus. Possible traces of phosphorus vapour were then condensed by cooling with solid carbon dioxide and alcohol. As a test of its purity, 1 c.c. (N.T.P.) of the argon was admitted at room temperature to 5 g. of charcoal previously activated at 950° in the usual manner. No measurable rise of temperature occurred, and the residual pressure indicated that only a negligible trace, if any, of the argon could have been adsorbed.

Method of Experiment.

This can best be followed by reference to Fig. 1. About 5–6 g. of the purified charcoal were heated in the reaction vessel by means of the furnace, F, for 2 hours at 950° under the high vacuum set up by the pumping system. During this time, the vacuum progressively improved to a steady value of 0.002 cm., below which it could not be reduced while the high temperature was maintained. The temperature of the furnace during this activation was recorded by means of a platinum–platinum–rhodium thermocouple, B, operating a sensitive millivoltmeter, giving direct readings of temperature. At the end of the 2 hours, the current through the furnace was cut off, but pumping was continued. As the temperature fell, the vacuum improved, and at 650° it was 1×10^{-4} mm. All taps, except T₆, were then closed.

When the furnace had cooled to the temperature of the experiment, suitable currents were passed through the subsidiary heating coils, and the thermoregulator was adjusted to give the temperature desired. When constancy of temperature had been obtained, or, if the experiment was at room temperature, when the furnace had cooled to that temperature, a measured amount of oxygen was admitted from the burette through tap T₂ to that section of the

leading tubes between taps T_1 , T_3 , and T_4 , and confined there by closing tap T_2 . The shutter of the camera was then opened, and one minute later the gas was admitted to the reaction vessel by opening tap T_3 . After the lapse of another minute (test experiments having shown the maximum temperature to be reached within this time), tap T_5 was opened for 10 seconds for removal of a sample of the residual gas to that part of the apparatus between taps T_5 and T_7 . The pressure of this gas was then read on the McLeod gauges. As indicated above, tap T_6 was open during this sampling; this tap connected the apparatus with the large bottle, X (of about $2\frac{1}{2}$ litres capacity), which was incorporated in the apparatus to remove from the reaction vessel as much as possible of the gas remaining after adsorption, preliminary experiments having shown that the initial rapid process of adsorption was followed by a much slower one, in which the oxygen was gradually taken up over a period of several days. This immediate removal of the bulk of the residual gas greatly reduced the pressure in the reaction vessel, and therefore either arrested further adsorption after the maximum temperature had been reached or reduced it to negligible proportions, thereby giving the true cooling curve and so permitting accurate correction for loss of heat by radiation.

When the temperature of the charcoal had fallen to its original value, the shutter of the camera was closed and the photographic record developed. At the same time taps T_4 and T_5 were opened, and the residual gas was removed by means of the Töpler pump for analysis. The apparatus was then evacuated to a pressure of 1×10^{-4} mm. without raising the temperature, after which a second admission of oxygen was made, and sometimes a third. After the last admission the charcoal was reactivated at 950° as before.

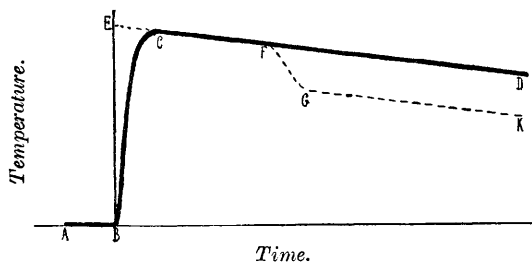
The sample of residual gas, collected *via* the Töpler pump in a capillary tube, was tested for carbon dioxide with an aqueous solution of caustic soda, for oxygen with alkaline pyrogallol, and for carbon monoxide with ammoniacal cuprous chloride. The various contractions were measured in the usual manner and the composition of the gas was calculated therefrom.

In the removal of the bulk of the residual gas to the bottle X and the McLeod gauges, the tap T_5 was opened for 10 seconds only. This interval of time was insufficient for the attainment of equal pressure throughout the apparatus, and therefore calibrations were made to find what equilibrium pressure corresponded to the pressure recorded by the gauges. The charcoal was removed from the apparatus, which was then evacuated to a pressure of 1×10^{-4} mm., after which taps T_1 , T_4 , T_5 , and T_7 were closed. A measured sample of oxygen was admitted from the gas burette, and the same

procedure followed as in an actual experiment. After the pressure of the sample had been measured on the McLeod gauges, tap T_5 was opened. When equilibrium had been attained throughout the apparatus, the pressure was again read on the McLeod gauges. Varying amounts of oxygen were admitted in this manner so as to obtain figures covering the range of pressure of the experiments carried out. Values of the equilibrium pressure were then plotted against corresponding values of the observed pressure, and a smooth curve was drawn through the points obtained. From this curve the pressure corresponding to any observed pressure could be read, and from this value and the known volume of the apparatus the volume of gas unadsorbed was then calculated.

The volume of oxygen adsorbed by the charcoal was obtained by taking the difference between the volume admitted and that unadsorbed. Reduction of this volume to standard temperature

FIG. 4.



was made in the final calculation. The correction in the volume necessary in determinations of the heat of adsorption at temperatures higher than atmospheric has already been described.

The photographic curves obtained in these experiments were of the form shown in Fig. 4, in which ordinates represent intervals of temperature, and abscissæ intervals of time. The complete curve is represented by the thickened line, ABCD. During the interval of time from B to C, *i.e.*, the time taken to attain the maximum temperature, heat was being lost by the system through radiation, and to correct for this loss the line CD was produced backwards to cut the axis of temperature in the point E. The interval of temperature represented by BE was then taken to be the increment due to adsorption.

In the calculation of the heat evolved, this increment was multiplied by the thermal capacity of the materials undergoing that increment, *viz.*, the charcoal and the platinum container. The specific heats of platinum from 0° to 200° have been given by Mills (*J. Physical Chem.*, 1917, 21, 345), who has also given similar data

for graphite. As Weber (*Pogg. Ann.*, 1875, **154**, 557) has shown that the specific heat of wood charcoal over the range 0—225° exceeds that of graphite by the constant amount 0.003, the following values were used in calculating thermal capacities :

Temp.	Specific heat (g.-cals.).		
	Platinum.	Graphite.	Wood-charcoal.
0°	0.0310	0.156	0.159
50	0.0318	0.195	0.198
100	0.0323	0.233	0.236
200	0.0332	0.298	0.301

The heat due to the adsorption of oxygen, *i.e.*, the difference between the total heat liberated and that due to the production of oxides of carbon (determined from the analyses of gaseous products), was expressed as kg.-cals. per g.-mol. of oxygen adsorbed, the oxygen being corrected to standard temperature. No correction was necessary for deviations from Boyle's law.

In the experiments at temperatures above that of the room, correction was made for the "gas effect" by the method already described.

Results.

Heat of Adsorption of Oxygen on Charcoal at Room Temperature.—

In Table I are the values obtained for the heat of adsorption of oxygen on charcoal at room temperature after activation at various temperatures from 750° to 950°, approximately the same amount of oxygen, about 1.5 c.c. (N.T.P.), being admitted in every case.

TABLE I.

Heats of Adsorption of Oxygen on Charcoal at Room Temperature after Activation at Different Temperatures.

Expt.	Temp. of activation.	Temp. of expt.	Oxygen admitted, c.c.	Pressure of sample (mm.),		Oxygen adsorbed, c.c.	Rise of temp.	Heat evolved, g.-cals.	Heat of adsorption, Cals./mol.
				obs.	corr.				
1	950°	20°	1.545	0.026	0.051	1.303	2.89°	3.61	67
2	950	20	1.620	0.035	0.062	1.325	2.93	3.66	66
3	900	19.5	1.556	0.053	0.086	1.147	2.59	3.24	68
4	950	20	1.556	0.040	0.069	1.228	2.89	3.61	71
5	950	20.5	1.549	0.047	0.079	1.174	2.78	3.50	72
6	850	20	1.542	0.094	0.134	0.905	2.11	2.64	70
7	800	21.5	1.535	0.130	0.174	0.709	1.59	2.00	68
8	800	22	1.478	0.077	0.117	0.922	2.19	2.76	72
9	750	21	1.556	0.142	0.186	0.672	1.59	2.00	72
10	950	21	1.474	0.047	0.079	1.099	2.52	3.18	70
11	800	20.5	1.492	0.110	0.153	0.765	1.78	2.24	70

Mean molar heat of adsorption = 70 Cals.

Note.—The experiments were carried out in the order shown, *i.e.*, with intermediate activations at 950° to ascertain whether any decay in the activity of the charcoal had occurred. Mass of charcoal = 5.96 g. Mass of platinum = 6.665 g. All volumes are referred to normal pressure and room temperature.

TABLE II.

Heats of Adsorption of Oxygen on Charcoal at Room Temperature after Activation at 950°.

Expt.	Temp. of expt.	Adm. i, ii, or iii.	Oxygen admitted, c.c.	Pressure of sample (mm.),		Oxygen adsorbed, c.c.	Rise of temp.	Heat evolved, g.-cals.	Heat of adsorption, Cals./mol.
				obs.	corr.				
Volume of oxygen admitted = 0.5 c.c. (approx.).									
12	20.5°	i	0.639	0.006	0.016	0.563	1.17°	1.39	59
13	21	ii	0.604	0.010	0.024	0.490	0.93	1.11	55
14	20.5	i	0.586	0.001	0.004	0.567	1.21	1.44	61
15	15	i	0.519	0.003	0.008	0.481	1.07	1.24	61
16	15	ii	0.533	0.033	0.059	0.253	0.50	0.58	54
17	15	iii	0.526	0.047	0.078	0.155	0.18	0.21	32
Volume of oxygen admitted = 1.0 c.c. (approx.).									
18	21	i	1.172	0.032	0.059	0.892	1.90	2.26	61
19	21.5	ii	1.137	0.051	0.083	0.743	1.45	1.73	56
20	22.5	iii	1.119	0.114	0.157	0.373	0.52	0.62	40
21	18	i	1.098	0.005	0.013	1.036	2.24	2.64	61
22	18	i	1.119	0.007	0.017	1.038	2.31	2.73	63
23	18.5	ii	1.084	0.077	0.117	0.528	0.93	1.10	50
24	17	i	1.006	0.008	0.019	0.916	2.11	2.47	64
25	21	i	1.119	0.004	0.013	1.057	2.21	2.63	60
Volume of oxygen admitted = 1.5 c.c. (approx.).									
26	18	i	1.563	0.014	0.033	1.406	3.45	4.07	69
27	18	i	1.510	0.024	0.048	1.282	3.17	3.74	70
28	19	ii	1.545	0.118	0.161	0.780	1.72	2.03	62
29	19	i	1.517	0.027	0.051	1.275	3.07	3.62	68
30	19	ii	1.482	0.086	0.126	0.892	1.90	2.24	60
31	19	iii	1.492	0.179	0.224	0.428	0.62	0.73	41
32	19	i	1.553	0.027	0.052	1.306	3.31	3.91	72
33	19.5	ii	1.545	0.147	0.191	0.638	1.41	1.66	62
34	20	i	1.531	0.020	0.042	1.331	3.34	3.94	71
35	20.5	ii	1.563	0.150	0.194	0.641	1.38	1.64	62
36	19.5	i	1.538	0.020	0.042	1.338	3.21	3.79	68
37	18.5	i	1.492	0.017	0.038	1.311	3.17	3.74	68
38	18	i	1.538	0.030	0.056	1.272	3.28	3.87	73
39	18.5	ii	1.482	0.108	0.152	0.760	1.66	1.96	62
40	18	i	1.545	0.028	0.053	1.293	3.34	3.94	73
41	18	ii	1.560	0.156	0.200	0.610	1.28	1.51	59
42	20	i	1.486	0.028	0.053	1.234	3.10	3.66	71
43	19	i	1.496	0.035	0.062	1.201	2.93	3.46	70
44	15	i	1.510	0.049	0.081	1.125	2.93	3.40	71
45	17	i	1.492	0.047	0.078	1.121	2.89	3.38	72
46	21.5	i	1.439	0.048	0.079	1.064	2.59	3.08	70
47	20.5	i	1.538	0.041	0.070	1.205	2.90	3.45	69
48	21.5	i	1.439	0.043	0.073	1.092	2.69	3.19	71
Volume of oxygen admitted = 2.0 c.c. (approx.).									
49	20.5	i	1.990	0.058	0.092	1.553	3.86	4.59	71
50	21	ii	1.986	0.267	0.311	0.508	0.83	0.99	47
51	21.5	i	1.979	0.069	0.106	1.475	3.59	4.27	70
52	22	ii	1.990	0.255	0.299	0.570	0.83	0.99	42
Volume of oxygen admitted = 2.5 c.c. (approx.).									
53	20	i	2.441	0.090	0.130	1.823	4.55	5.37	71
54	20	ii	2.398	0.348	0.392	0.536	0.83	0.98	44

Note.—The results tabulated here were obtained in two series of experiments, in one of which 5.58 g. of charcoal were used, and in the other 5.575 g. Mass of platinum = 6.665 g. All volumes are referred to normal pressure and room temperature.

In Table II are the values for the heat of adsorption of amounts of oxygen varying from 0.5 to 2.5 c.c. (N.T.P.), the temperature of activation throughout this series being 950°, this temperature having been shown by Rhead and Wheeler (J., 1913, **103**, 467) to be necessary for the removal of the oxygen adsorbed at lower temperatures. The results of Table II are summarised in Table III. In the column headed "Adm.," the figures i, ii, and iii indicate whether the admission of gas was a first, second, or third, respectively. In view of a result subsequently to be described, no correction was necessary for the heat developed by the formation of oxides of carbon at the temperature of these experiments.

A separate sample of charcoal was used for each series, and in the second series the charcoal was once replaced by a fresh sample : no difference was observed in the results obtained. The experiments of Table II were not performed in the order shown. The first experiments were made by admitting 1.5 c.c. of gas ; after this, 2.0 c.c. and 2.5 c.c. were admitted, followed by several admissions each of 1.0, 0.5, 1.0, and 1.5 c.c. ; then admissions of 1.5 c.c. alternated with 1.0 c.c., and, finally, the series closed with an admission of 0.5 c.c.

TABLE III.

Mean Values of the Heat of Adsorption at Room Temperature after Activation at 950°.

Approx. volume of oxygen admitted, c.c. at N.T.P.	Mean heat of adsorption, Cals./mol.		
	(i.)	(ii.)	(iii.)
0.5	60	55	32
1.0	62	53	40
1.5	70	61	41
2.0	71	45	—
2.5	71	44	—

It will be observed from Table II that repeated adsorption of oxygen at room temperature, followed by repeated activation at 950°, appeared to have no destructive effect on the activity of the charcoal. After the standard activation, the same volume of oxygen was adsorbed and the same amount of heat was evolved even after 30 such admissions and activations. All these results were closely reproducible.

It was shown that no detectable amounts of oxygen were adsorbed on the quartz, glass, platinum, etc. (see p. 2886).

In the earlier experiments of Table II the sample of gas was taken off one minute after admission of oxygen, because this was known to be the time required for the rise of temperature to reach its maximum. It was, however, suspected that adsorption might be more rapid than the temperature-time curves suggested owing to

the lag involved in the thermometric method. The gas was therefore sampled at a much shorter interval after admission, first at 30, then at 20, at 15, and finally at 10 secs. The order of the residual pressure showed that, with negligible difference, the adsorption had progressed as far in 10 secs. as in 1 min. Other measurements showed that the adsorption of the residual gas was very slow, *e.g.*, whereas 1.125 c.c. were adsorbed in 10 secs., leaving a residue of 0.175 c.c., only 0.066 c.c. of the latter was adsorbed in 48 hours. There was therefore a sudden adsorption of the bulk of gas, followed by a very slow disappearance of the residue. This rapidity of adsorption of a gas on a solid surface is in accordance with theoretical prediction and is characteristic of true adsorption. It has been observed by other workers, *e.g.*, Angus Smith (*Proc. Roy Soc.*, 1862—3, **12**, 424; 1926, *A*, **112**, 296), in the case of oxygen on charcoal; McBain (*Phil. Mag.*, 1909, **18**, 918), for hydrogen on charcoal; and Lamb and Coolidge (*J. Amer. Chem. Soc.*, 1920, **42**, 1146), for various vapours adsorbed on charcoal. In the work of these authors, however, the time periods were of the order of a few minutes. Rhead and Wheeler (*J.*, 1913, **103**, 469), in the case of oxygen on charcoal, observed a rapid disappearance of gas in the first 15 secs., followed by a much slower rate.

Attempts were made to desorb gas from the charcoal immediately after adsorption of oxygen. Such desorption would be indicated by a break in the continuity of the rearward slope, CD (Fig. 4), as shown by the broken line, FGK. For this purpose, the sampling system was employed, the procedure being as follows: A few minutes after maximum temperature had been reached, the tap T_4 was opened, and the reaction vessel rapidly evacuated. No break in the continuity of CD appeared. The adsorbed oxygen was therefore held so tenaciously by the charcoal that at room temperature it could not be removed under a vacuum of 1×10^{-4} mm.

The experiments of this series also showed that the time taken to attain maximum temperature in the case of first admissions varied with the amount of oxygen adsorbed. For admissions of 0.5 c.c. it was $2\frac{1}{2}$ mins., for those of 1.0 c.c. it was 2 mins., and for those of 1.5, 2.0, and 2.5 c.c., 1 min. The corresponding times for second and third admissions were increasingly greater than those for first admissions, but this was doubtless due to the gradual decrease in the energy of the charcoal surface.

Some Experiments with Nitrogen.—Owing to a leak occurring during one of the experiments in the series just described, nitrogen was detected in the gas which was removed from the reaction vessel, and on this occasion a break appeared in CD (Fig. 4), at a point corresponding to the time when the tap T_4 was opened, and

the dotted portion, FGK, of the curve was experimentally realised. It was subsequently found possible to reproduce this break at will by admitting mixtures of oxygen and nitrogen. When pure nitrogen was admitted, however, no such break appeared. Thus, at room temperature neither pure oxygen nor pure nitrogen could be desorbed, but some gas, which proved to be nitrogen, was desorbed after a mixture of oxygen and nitrogen had been admitted. Some of the data obtained are quoted below, all the adsorptions taking place at room temperature after activation at 950° , and all volumes being reduced to 760 mm. and room temperature.

(1) A first admission of 1.474 c.c. of nitrogen resulted in the adsorption of 0.293 c.c.; from a second admission of 1.545 c.c., 0.248 c.c. was adsorbed. The molar heat of adsorption was estimated at 38 and 19 Cals. respectively. In a third admission, of a mixture of 0.266 c.c. of nitrogen with 1.314 c.c. of oxygen, 1.028 c.c. of gas were adsorbed. A break appeared in CD.

(2) After reactivation, from 1.403 c.c. of nitrogen admitted, 0.223 c.c. was adsorbed with a molar heat of 46 Cals. In a second admission, of a mixture of 0.551 c.c. of nitrogen with 1.225 c.c. of oxygen, 1.152 c.c. of gas were adsorbed. A break was noted in CD.

(3) After reactivation, a mixture of 0.568 c.c. of nitrogen with 1.354 c.c. of oxygen was admitted. Of this, 1.284 c.c. were adsorbed. A break appeared in CD. In a second admission, of 1.567 c.c. of oxygen admitted, 0.436 c.c. was adsorbed. A break appeared in CD, which suggested that some of the oxygen adsorbed in the second admission had replaced the more firmly bound nitrogen, which pumping after the first admission had failed to desorb, and that this nitrogen could now be desorbed by pumping.

(4) After reactivation, 1.538 c.c. of oxygen were admitted, and 1.103 c.c. were adsorbed. Then 1.396 c.c. of nitrogen were admitted, and 0.265 c.c. was adsorbed. No break appeared in CD.

Consideration of the above data leads to the following comments on the respective experiments.

(1) After a total of 0.54 c.c. of nitrogen had been adsorbed, 1.028 c.c. of the mixed gases were still taken up, although the highly active fraction of the surface was already saturated with nitrogen.

(2) Although 0.223 c.c. of nitrogen had already been adsorbed, the charcoal still took up 1.152 c.c. of gas from the mixture of 0.551 c.c. of nitrogen and 1.225 c.c. of oxygen, which is more than would be expected in view of the previous admission of nitrogen.

(3) Similarly in this case, the adsorption of 1.284 c.c. is unexpectedly high.

(4) After adsorbing 1.103 c.c. of oxygen, the charcoal took up

even more nitrogen than in the case of the first admission in (2) above.

It therefore follows that (a) nitrogen, like oxygen, is adsorbed at once on a clean charcoal surface, either in first or second admissions, and cannot be removed therefrom at the temperature of adsorption; (b) when a mixture of oxygen and nitrogen is admitted, some gas can be pumped from the charcoal surface, irrespective of whether the mixture has been admitted to a clean surface or to one on which nitrogen has already been adsorbed; (c) gas can also be desorbed from the charcoal surface in the case of an admission of oxygen following an admission of a mixture of nitrogen and oxygen; (d) when nitrogen is adsorbed on a charcoal surface, on which oxygen has already been adsorbed, no gas can be pumped from the surface; and (e) the amount of gas adsorbed from a mixture of oxygen and nitrogen appears to be greater than would be expected from what is known of the separate adsorptions of these gases.

This phenomenon has not been thoroughly investigated, but the facts are sufficiently apparent. There is some change in the stability of the adsorption-complexes, formed on the surface of the charcoal, when the oxygen is diluted with nitrogen. This point has already been discussed in Part II.

Other workers have reported somewhat similar effects. De Saussure (*Ann. Physik*, 1814, 47, 113) noted cases where the presence of a second gas increased the adsorption of a first, and detected the replacement of one gas by another. The latter effect was also observed by Angus Smith (*loc. cit.*).

Heat of Adsorption of very Small Amounts of Oxygen.—The results summarised in Table III indicated a decrease in the heat of adsorption with decrease in the amount of gas admitted. To test the possibility of this heat being still less for lower concentrations of gas, very small amounts of oxygen were admitted, and attempts made to determine their heats of adsorption. The experiments showed that at these low concentrations the oxygen was adsorbed completely without, as far as this apparatus indicated, any appreciable rise of temperature. A typical result may be quoted, all volumes being at normal pressure and room temperature. After activation at 950°, 0.036 c.c. was admitted at room temperature. When the gaseous contents of the reaction vessel were sampled according to the usual method, no increase in the pressure was recorded. The McLeod gauge still registered high vacuum. A second admission of an equal amount of gas gave the same result. A third admission of 0.089 c.c. and a fourth of 0.071 c.c. gave appreciable rises of temperature, with residues of unadsorbed gas of 0.001 and 0.003 c.c. respectively. Two further experiments

confirmed this result. The first minute quantities of oxygen were therefore adsorbed with a very low heat of adsorption, which was apparently less than 5 Cals./mol.

Immediately following these experiments with small quantities, and after re-evacuation, 1.5 c.c. of oxygen were admitted. In all cases the normal value was obtained for the heat of adsorption, and no reduction in the adsorptive capacity of the charcoal was apparent beyond that due to the amount of gas already adsorbed.

A test was made to determine whether the small amounts of oxygen had been removed by the platinum, quartz, etc. The charcoal was taken out of the apparatus and the process of activation carried out in its absence; 0.036 c.c. of oxygen was then admitted, and the volume of the apparatus was calculated from the resulting pressure as recorded by the McLeod gauges, but did not differ by more than the experimental error from the known volume, and thus showed that these small amounts of oxygen were adsorbed on the charcoal and not on any of the parts of the apparatus.

Heat of Adsorption of Oxygen on Charcoal from Room Temperature to 200°.—In Table IV are the values obtained for the heat of adsorption of oxygen on charcoal at various temperatures from room temperature to 200° after activation at 950° in each case. The same sample of charcoal was used throughout the experiments of this series: it was not so active as that used previously, e.g., at 20°, of 3.0 c.c. (N.T.P.) of oxygen admitted, only 1.4 c.c. were adsorbed. The heat of adsorption had, however, the same value as that previously found for that temperature.

The increment of temperature recorded in the table is the net increment of temperature due to adsorption, i.e., the difference between the (corrected) rise of temperature observed and that due to the "gas effect." The correction for the latter varied from 0.25° to 0.30°, i.e., it was of the order of 10% approximately. The values given for the heat evolved are corrected for the heat of formation of the amounts of oxides of carbon found by analysis, except in the experiments at 60° and 100°, in which analyses were not made. This correction in the experiments at 150° and 200° amounted to 5% of the heat evolved. In Experiments 60 and 62 the residual pressure was not read until some minutes after adsorption had occurred, and in both these cases the tap T₅ was left open, not for 10 seconds as in the usual case, but for several minutes until a constant pressure was recorded by the McLeod gauges.

In these experiments it was found that at the higher temperatures the adsorption required about 1 min. for completion and therefore was not so rapid as at room temperature, where the adsorption

TABLE IV.

Heat of Adsorption of Oxygen on Charcoal from Room Temperature to 200°.

Expt	Temp. of charcoal.	Temp. of room.	Oxygen admitted, c.c.	Pressure of sample (mm.),		Oxygen adsorbed, c.c.	Rise of temp.	Heat evolved, g.-cals.	Heat of adsorption, Cals./mol.
				obs.	corr.				
55	20°	20°	3.035	0.298	0.342	1.397	3.48°	4.04	70
56	57	19	1.073	0.009	0.023	0.964	2.81	3.71	92
57	57	21.5	1.066	0.011	0.027	0.938	2.63	3.47	89
Mean = 91									
58	96	14	1.066	0.0008	0.0023	1.055	3.33	5.00	112
59	97	16.5	1.059	0.001	0.003	1.045	3.28	4.92	112
60	97.5	19.5	1.130	—	0.020	1.036	2.89	4.34	101
61	97.5	18.5	1.123	0.003	0.009	1.081	3.22	4.83	107
62	97.5	18.5	0.995	—	0.012	0.939	2.83	4.25	108
Mean = 108									
63	150	18	1.038	0.004	0.012	0.982	2.92	4.68	114
64	200	21	1.073	0.010	0.024	0.962	2.67	4.57	115
65	200	20	1.059	0.0078	0.020	0.967	2.67	4.65	116
66	200	20.5	1.066	0.0078	0.020	0.974	2.71	4.72	117
Mean = 116									

Note.—Mass of charcoal = 5.45 g. Mass of platinum = 6.665 g. All volumes are referred to normal pressure and room temperature.

here studied was complete in less than 10 secs. This may possibly be due to the blanketing effect of the oxides of carbon evolved.

Gaseous Products of the Adsorption of Oxygen on Charcoal.—The results of the analyses carried out in the experiments at 18°, 150°, and 200° were as follows :

Temp. of adsorption.	Gaseous products.
18°	Oxygen; trace of CO ₂ ; no CO.
150	5% Oxygen; 95% CO ₂ ; trace of CO (?).
200	9% Oxygen; 82% CO ₂ ; 9% CO.

There was thus residual oxygen over the whole range of temperature of these experiments. Carbon dioxide increased up to 150°, and then decreased while the monoxide increased.

The "Active" Fraction of the Surface of Charcoal.—The "active" fraction of the surface of the charcoal used in these experiments may be estimated from the results of Table II. Its total surface was determined, from the isotherms of straight-chain alcohols adsorbed thereon (Garner, McKie, and Knight, *J. Physical Chem.*, 1927, **31**, 641), as 66 sq. m. per g. The volume occupied by an atom of carbon in charcoal is $1/D \div N/12$, where D is the density, and N the Avogadro number, 6.062×10^{23} . On insertion of the value for D obtained by Cude and Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 391), *viz.*, 1.9, it is found that this volume is 1×10^{-23} cm.³. If, as a first approximation, this space be assumed cubical, the

cross-sectional area corresponding to every atom of carbon is 4.64×10^{-16} cm.². The number of atoms on the surface of 1 g. of charcoal is, therefore, $66 \times 10^4 / 4.64 \times 10^{-16} = 1.4 \times 10^{21}$. The total number of atoms in 1 g. of charcoal = $N/12 = 5.05 \times 10^{22}$. Therefore, the ratio of surface atoms to total atoms = $1.4 \times 10^{21} / 5.05 \times 10^{22}$, or 1 to 36.

Table II shows that at the most 2 c.c. (N.T.P.) of oxygen can be adsorbed by 5.6 g. of charcoal with a molar heat of adsorption of the order of 70 Cals. On the assumption that every molecule of oxygen is adsorbed on one atom of carbon only, and since the number of molecules in 1 c.c. (N.T.P.) of oxygen is 2.7×10^{19} , the number of atoms per gram of charcoal giving a molar heat of adsorption of 70 Cals. = $2 \times 2.7 \times 10^{19} / 5.6 = 1.0 \times 10^{19}$ (nearly). If these are regarded as active atoms, the ratio of active to total atoms is $1.0 \times 10^{19} / 5.05 \times 10^{22}$, or 1 in 5000, and the ratio of active atoms to surface atoms is $1.0 \times 10^{19} / 1.4 \times 10^{21}$, or 1 in 140.

This value for the active fraction of the surface is in qualitative agreement with the general results obtained by Langmuir, who found that these fractions were generally small, and that they increased with the temperature at which the surface was cleaned. Table I confirms this latter effect for the charcoal employed in this work, for it is there shown that the proportion of oxygen adsorbed at room temperature from a constant volume admitted increased steadily with the temperature of activation. The amount of gas adsorbed will depend, however, on two factors: (1) the temperature of activation, and (2) the efficiency of the process for removal of adsorbed gases.

The activity of the charcoal used in these experiments may be compared with that of the charcoal used by Keyes and Marshall (*J. Amer. Chem. Soc.*, 1927, **49**, 156). From the curve obtained by plotting the heat of adsorption against the surface concentration of oxygen, these authors calculated that the active surface of their charcoal was 5100 cm.² per g. This value is in good agreement with that obtained in this work, *viz.*, 4700 cm.² per g. Keyes and Marshall, however, concluded that, at the highest concentration at which they worked (4.5×10^{-4} mol. per g.), many layers of gas were present. Their highest concentration is equivalent to $4.5 \times 22400 \times 10^{-4}$ c.c. of oxygen per g. of charcoal, *i.e.*, 10 c.c. per g. From the value here recorded for the total surface area of 1 g. of charcoal, the number of molecules of oxygen necessary to form a unimolecular layer thereon is $66 \times 10^4 / \pi \times (1.81 \times 10^{-8})^2$, since the radius of the oxygen molecule is 1.81 Å. (Jeans, "Dynamical Theory of Gases"); but the number of molecules in 1 c.c. (N.T.P.) is 2.7×10^{19} , hence the volume of oxygen required to form a uni-

molecular layer = 24 c.c. per g. of charcoal, or more than twice the highest concentration measured by Keyes and Marshall. There is thus no evidence in their work of the formation of a second adsorbed layer, or even of the completion of a first layer. Moreover, their experiments did not indicate that their charcoal was saturated.

Summary.

A method is described for measuring the heats of adsorption of gases on solid surfaces, and is applied to the study of the adsorption of oxygen and of nitrogen on charcoal.

Details of a specially devised apparatus and furnace are given.

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