CXVIII.—*The Reaction between Carbon and Oxygen at Low Pressures and Room Temperature.*

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THE adsorption of small volumes of oxygen on activated carbon at room temperature is an irreversible process; the adsorbed gas enters into chemical combination with the surface atoms, and can be recovered from the surface only as carbon monoxide and dioxide by raising the temperature (Rhead and Wheeler, J., 1910, **97**, 2178; 1911, **99**, 1140; 1912, **101**, 831, 846; 1913, **103**, 461, 1210). The adsorption is accompanied by the liberation of an amount of heat which, when expressed in terms of 1 g.-mol. of gas adsorbed, is of the same order as the heat of formation of carbon dioxide from its elements (Garner and Blench, J., 1924, **125**, 1288). There is no doubt, therefore, that we are here concerned with a reaction between oxygen and the surface carbon atoms.

Previous work (Garner and McKie, *Trans. Faraday Soc.*, 1926, **22**, 461) showed that the molar heat of reaction of oxygen with charcoal varies with the fraction of the surface covered by oxygen molecules. It is low for small surface concentrations and increases to a maximum value for a surface concentration of 1.0×10^{-5} mol. per g. of carbon. The existence of this maximum is disputed by Marshall and Bramston-Cook (*J. Amer. Chem. Soc.*, 1929, **51**, 2019), who used the ice calorimeter for the measurement of heats and obtained the maximum heat of adsorption for the smallest surface concentration. Their experimental conditions were, however, very different from those pertaining to the work of McKie, and the lack of agreement might be due to these differences. Nevertheless, it was possible that the low values obtained by Garner and McKie were due to serious defects in the thermocouple calorimeter. It was therefore necessary that the behaviour of this calorimeter should be further investigated.

The occurrence of maxima on the differential heats of adsorption curves has been found by other workers (Fryling, *J. Physical Chem.*, 1926, **30**, 818; Taylor and Kistiakowski, *J. Amer. Chem. Soc.*, 1927, **49**, 2200). In these cases either a platinum resistance thermometer or thermocouple was used to measure the rise in temperature during adsorption, and it is very likely that the maxima obtained were due to causes similar to those operating in the adsorption of oxygen on charcoal. Later investigations by Taylor and his colleagues have shown that the maxima are in many cases due to the low conductivity of the adsorbent, and to the occurrence of a lag in the transference of heat between the adsorbent and the thermocouple or resistance thermometer.

EXPERIMENTAL.

Examination of Method.

The apparatus employed was very similar to that described by McKie (J., 1928, 2871).   Fig. 1 is a diagram of the vacuum calori-

FIG. 1.
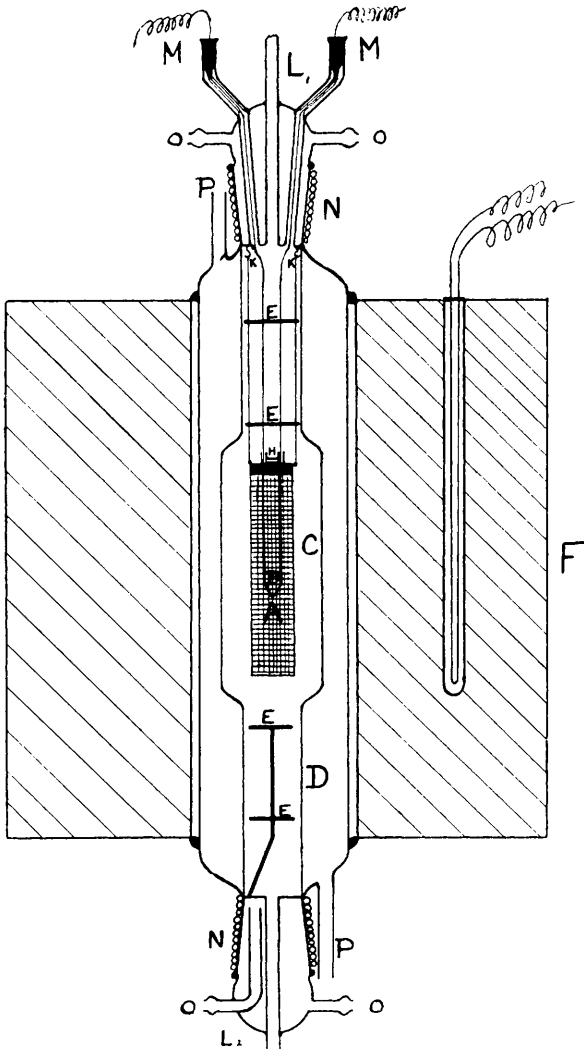
meter; this is an improvement on the earlier form in that the silica reaction vessel is double-walled.   This change makes it possible to

circulate water at constant temperature around the reaction vessel through the tubes PP as well as through the double-walled stoppers OO. The calorimeter could be maintained at a constant temperature to within 0·002° by this means. By changing the temperature of the stream of water, it was possible to make the calorimeter practically adiabatic. A further improvement of the experimental conditions was attained by surrounding the reaction vessel and the furnace F by an air thermostat in which the air was circulated by a fan. This served to eliminate temperature coefficients throughout the system and the possibility of " gas effects."

The platinum–platinum-rhodium thermocouple wires entering at MM were 0·025 cm. in diameter and the sensitivity of the galvanometer thermocouple system was 3·72 ± 0·01 cm. per degree. The volume of the reaction vessel, the McLeod gauges, and the leading tubes was 876 c.c.

4—5 G. of purified carbon, 60—90 mesh and ash content 0·15%, were introduced into the platinum gauze vessel A, and heated at 950° for 2 hours under high vacuum. A vacuum of 10^{-4} cm. was obtained. Oxygen was then admitted to the carbon, and the rise in temperature measured as described in previous papers.

Position of the Thermocouple and Length of Immersion of Thermocouple Leads.—The nature of the temperature–time curves was found to vary with the position of the thermocouple, indicating that the distribution of heat was not uniform throughout the mass of carbon. When the thermocouple was placed so that its junction touched the side of the platinum vessel, it gave a different reading from that obtained when it was placed in the centre of the mass of carbon. When 0·265 c.c. of oxygen was admitted, the maximum temperature reached was about 10% lower when the thermocouple was on the side than when it was in the centre. It was found that the lower curve after application of the cooling correction gave nearly the same value for the rise in temperature as the uncorrected maximum of the higher curve, so it appeared that there was but little loss of heat from the interior of the carbon, up to the maximum on the time–temperature curve. This must be due to a lag in the distribution of heat.

It was decided to try to minimise the complexity of any temperature gradients which might be present by employing a spherical vessel 2 cm. in diameter to contain the carbon. The heats obtained with this vessel were surprisingly low. This was found to be due to the fact that only 1 cm. of the thermocouple was immersed in the carbon. It was therefore decided to return to the cylindrical vessel, and to study the effect of changing the length of the

thermocouple leads immersed in the carbon.   The results are shown below :

Length of leads covered (cm.)	0·0	0·2	1·0	2·0	3·5	4·0	6·0	10·0
Heat of adsorption (Cal./mol.)	27	35	60	83	97	98	100	97

It was thus necessary to ensure that in each experiment at least 3·5 cm. of the thermocouple were immersed in the carbon.   Fortunately, in McKie's experiments, the length of leads thus immersed was 3·5 cm.

Leads of at least 3·5 cm. in length being used, the temperature gradients in the carbon were surveyed.   They were found to be too complicated to permit of an accurate calculation of the heat of adsorption, so resort was had to an adiabatic method.

Adiabatic Method.—A second thermostat was fitted up, and water from this could be pumped round the calorimeter by means of a powerful water pump.   The temperature of the water was selected by trial so that when it was pumped round the reaction vessel after the admission of oxygen, no cooling occurred on the temperature–time records.   Since the adsorption was complete within a very short time, *i.e.*, 10—30 secs., and since the subsequent reaction occurred very quickly, the change in the temperature of the circulating water was made 5 seconds after the admission of oxygen to the carbon.   With this procedure, a thermocouple placed on the side of the gauze vessel gave the same rise in temperature as a thermocouple in the centre.   The method employed was therefore practically adiabatic.   The rise in temperature by the adiabatic method was the same to within 1—2% as that obtained with a thermocouple in the centre of the carbon when the temperature of the circulating water was kept constant.

Rate at which the Heat reaches the Thermocouple.—The rate of rise to the maximum temperature obeyed Newton's law, which would apply if the rate of reaction were very rapid compared with the rate of heating of the thermocouple.   In order to determine if there was a serious lag in the equalisation of temperature between the carbon and the thermocouple, a coil of fine platinum–iridium resistance wire was embedded in the carbon, and heat supplied electrically to cause a rise in temperature of about 0·5°.   The rate of attainment of thermal equilibrium depended on the pressure of the gas in the calorimeter.   At a pressure of 1×10^{-4} cm. the time required was approximately 4—5 mins., which was greater than that required to reach thermal equilibrium in an actual experiment.   This would be expected, since there will be a lag in the transference of heat from the heated coil to the carbon.   There is thus bad thermal contact between the carbon grains and the thermocouple under the conditions of the experiments.

Surface Concentration and Heat of Adsorption.—With the improved apparatus, measurements were made on the effect of surface concentration on the heat of adsorption. The low values for the heat of reaction previously obtained at low surface concentrations were confirmed by several series of experiments. Some of the results obtained are in Table I, in which are recorded the position of the

TABLE I.

The Heat of Adsorption of Oxygen on Charcoal as a Function of Surface Concentration.

Series VII (Adiabatic).

Weight of charcoal = 4·420 g.   Temp. of expt. = 20°.   Evacuation at 950°.
Thermocouple sensitivity = 3·72 cm. per degree.

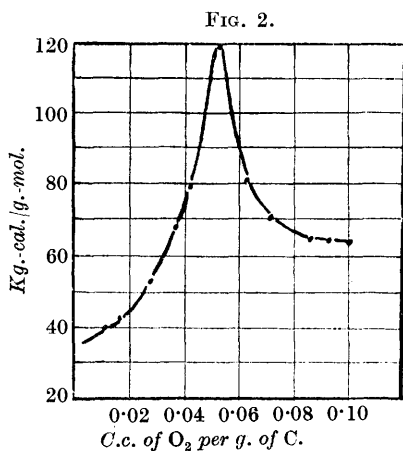| Expt. No.	Adm.	Posn.	Residual press., 10^{-4} cm.	Vol. not adsd., c.c.	Vol. adsd., c.c.	Galv. defln., cm.	Heat of adsorp.	Total vol. adsd., c.c.	Mean heat.
283	i	s	0·0	0·0000	0·0116	0·06	34		
284	ii	s	0·5	0·0006	0·2110	2·72	85	0·2226	82
264	i	s	0·0	0·0000	0·0455	0·36	52		
267	i	c	0·0	0·0000	0·0464	0·37	52		
268	ii	c	1·5	0·0020	0·2120	2·98	92	0·2584	85
269	i	c	0·5	0·0010	0·1050	1·14	71		
270	ii	c	5·0	0·0060	0·2010	2·67	87	0·3060	82
273	i	s	0·5	0·0010	0·1090	1·16	70		
274	ii	s	3·4	0·0040	0·2040	2·64	85	0·3130	80
271	i	c	1·2	0·0010	0·1490	1·80	79		
272	ii	c	10·0	0·0100	0·1970	2·50	84	0·3460	82
279	i	s	1·0	0·0010	0·1540	1·82	78		
280	ii	s	3·2	0·0040	0·2060	2·67	85	0·3600	82
262	i	c	1·5	0·0020	0·2090	2·66	83		
263	i	s	0·6	0·0010	0·2110	2·62	82		
289	i	c	9·6	0·0100	0·3380	4·45	86		
290	ii	c	20·4*	0·0820	0·1400	1·87	86	0·4780	86
281	i	s	25·3*	0·1020	0·5390	7·08	87		
282	ii	s	69·3*	0·2790	0·1560	2·05	87	0·6950	87

* With the bottle.

thermocouple (*i.e.*, whether on the side *s*, or at the centre, *c*), the volume adsorbed, and the heat of reaction (as kg.-cals./mol.) for a number of admissions of oxygen varying in volume from 0·01 to 0·5 c.c. For each experiment numbered i, the charcoal was previously heated in a vacuum for 2 hours at 950°; those numbered ii were second admissions to a charcoal which had already adsorbed one volume of gas. If the results be plotted, it will be seen that the nature of the rise in molar heat with surface concentration is the same for the inner and the outer thermocouple. The maximum heat of adsorption found was 87 kg.-cals./g.-mol.

The total heat liberated after two admissions of oxygen was the same as that which would have been obtained had the gas adsorbed been admitted in one volume (last two columns of Table I). There-

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fore, if there be any energy loss during the measurement, which is not accounted for, it is practically the same for one admission as for two.

The time–temperature curves of the side and centre thermocouple for the first small volumes of oxygen are very different in shape. For admissions of 0·04 c.c. of oxygen, an outer thermocouple showed increase in temperature immediately the oxygen was admitted and gave a sharp maximum. On the other hand, a thermocouple with its junction in a central position showed a lag of $\frac{1}{2}$—1 min. before it responded to the heat liberated. This shows that adsorption of the first small volumes of gas occurs almost entirely in the outer layers of the carbon mass. The outer thermocouple did not indicate higher temperatures than the inner thermocouple, but this is probably due to the heating up of the platinum gauze vessel, which must occur very rapidly when oxygen is adsorbed on the outside carbon layers.


FIG. 2.

Differential Heat of Adsorption.—If successive quantities of oxygen of approximately equal volume are added to an activated charcoal, the heat measured increases throughout a series to a maximum value and then diminishes (Fig. 2). This confirmed the experiments of McKie (*loc. cit.*), and the curves are similar in type to those obtained by Taylor and his co-workers for the adsorption of gases on metallic oxides.

Since the experiments recorded above indicated that adsorption in the case of the early admissions occurs solely on the outside layers of carbon, it was possible that the maximum on the curve in Fig. 2 was due to an abnormal loss of heat from the surface. Adopting a suggestion by Dr. Marshall, we tried the effects of admission of gas to the centre of the carbon, using a new platinum container consisting of a tube of platinum foil closed at each end, but with a cylindrical tube of platinum gauze down the centre. Two small holes for admitting the carbon and the thermocouple were made at one end. The cylinder was 2 cm. in diameter and 8 cm. long. With this apparatus, since the gas was admitted to the centre of the carbon, there should be little possibility of loss of heat by radiation from the carbon until the whole mass of carbon and platinum had been

warmed.   Actually, no maxima were found on the differential curves. The form of the curves agreed with those obtained by Marshall and Bramston-Cook (see Fig. 3).   A typical series of results is given in Table II, which shows the residual pressure at the moment of the removal of gas, the galvanometer deflexion, and the heat of adsorption in kg.-cals./g.-mol.   In these experiments the pumps were not applied.

FIG. 3.

C.c. of O_2 per g. of charcoal.
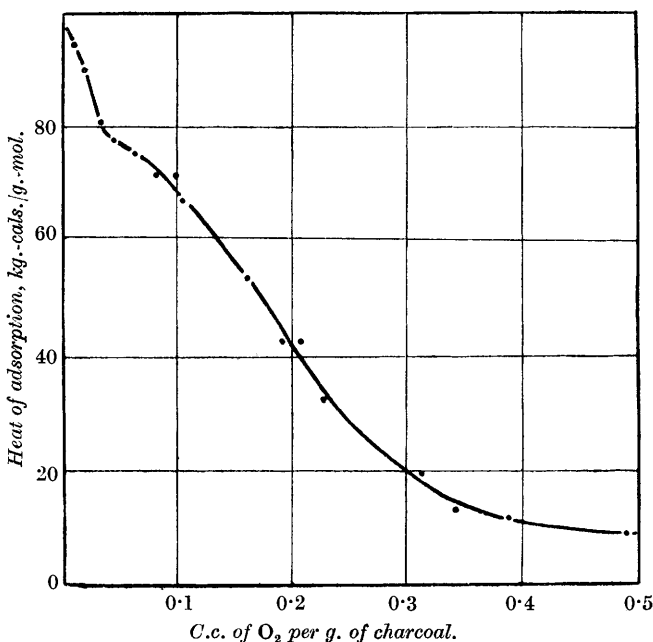
Defects of the Thermocouple Method.—The above investigation shows that the thermocouple method as used in the earlier investigations has serious defects.   Not only is heat distributed very slowly among the carbon grains at low pressures, but also, when small volumes of gas are adsorbed, the adsorption occurs on the outside layers of carbon and energy from these layers is lost at an abnormally rapid rate to the walls of the calorimeter.   By admitting gas into the interior of the mass of carbon, these defects are removed.

The addition of helium to 0·001 cm. pressure did not obviate the trouble, for the energy loss was practically the same as without it.

Another cause of difficulty with this method arises when the temperature of various parts, stoppers, etc., of the reaction vessel is not uniform.   The admission of an inert gas like hydrogen, which is not adsorbed by charcoal at low pressures, causes a modification

TABLE II.

Series 24. Temp. = 20°.

Expt. No.	Volume of oxygen, c.c. Admit.	Adsorb.	Residue.	Residual press., × 10⁴.	Defln., cm.	Heat.	Total oxygen adsorbed, c.c./g.
323	0·0655	0·0630	0·0025	2·0	0·58	84·9	0·0135
324	0·0583	0·0576	0·0007	0·6	0·50	80·0	0·0259
325	0·0515	0·0510	0·0005	0·4	0·43	77·8	0·0368
326	0·0518	0·0510	0·0008	0·7	0·42	76·0	0·0477
327	0·0512	0·0505	0·0007	0·6	0·40	73·1	0·0585
328	0·0505	0·0499	0·0006	0·5	0·40	73·9	0·0692
329	0·0564	0·0555	0·0009	0·7	0·42	69·8	0·0811
330	0·0706	0·0694	0·0012	1·5	0·54	71·8	0·0960
331	0·0536	0·0518	0·0018	1·7	0·39	69·5	0·1071
332	0·0640	0·0609	0·0031	2·7	0·45	68·2	0·1201
333	0·0588	0·0541	0·0047	3·9	0·39	66·5	0·1317
334	0·0700	0·0671	0·0029	2·4	0·45	61·8	0·1461
335	0·0822	0·0814	0·0008	3·1	0·46	52·1	0·1635
336	0·0756	0·0735	0·0021	4·9	0·39	48·9	0·1793
337	0·0585	0·0534	0·0051	4·3	0·34	58·7	0·1907
338	0·0780	0·0709	0·0071	10·3	0·35	45·6	0·2059
339	0·0961	0·0850	0·0111	19·7	0·41	44·5	0·2241
340	0·0788	0·0589	0·0199	36·5	0·21	33·0	0·2368
341	0·0960	0·0864	0·0096	44·6	0·20	21·4	0·2552
342	0·0894	0·0734	0·0160	58·1	0·16	20·2	0·2710
343	0·2216	0·1361	0·0855	120·3	0·30	20·3	0·3009
344	0·4506	0·1906	0·2600	340·0	0·38	18·5	0·3410

of the temperature gradients, and the thermocouple embedded in the mass of charcoal may indicate a change in temperature.   The rise or fall in temperature may be as much as 0·05° on the addition of an inert gas, even when the adiabatic arrangement is employed. This effect can only be eliminated by surrounding all parts of the reaction vessel in a thermostat at constant temperature.   These gas effects only become appreciable when the final pressure exceeds 10^{-3} cm., so that the heats of adsorption of oxygen on charcoal as determined by the thermocouple method are satisfactory if the final pressure does not exceed this value.   For higher residual pressures, a thermostat must be employed.

Slow Changes in the Adsorbed Gas Layers.—The values of the heat of adsorption which are obtained by the addition of successive small volumes of oxygen are not entirely independent of the interval between successive admissions.   Up to 0·04 c.c. per g. of oxygen adsorbed, the heat is independent of the interval between successive admissions, but for greater surface concentrations, evidence of the presence of a very slow change is obtained.   Usually, the interval adopted was 20—30 mins.   If the interval is extended to 12 hours, the rate of adsorption and the heat liberated are greater than is the case after an interval of 30 mins.   Thus, for example, after the adsorption of 0·22 c.c. of gas in fourteen successive amounts at intervals of 30 mins., the heat of adsorption fell from 94·8 Cals. to

32·6 Cals. After the charcoal had been left over-night in a high vacuum, further admissions were commenced; the first value obtained was 58·1 Cals. The same effect is seen in Table II at Expt. 337. The carbon surface appears to become more active on standing. This must be due either to molecularly adsorbed oxygen diffusing into the interior of the grains or to a slow reaction occurring between the adsorbed gas and the surface. We are unable to decide between these two possibilities.

The step on the differential heat curve (Fig. 3) is of interest, especially as it occurs also on the curve of Marshall and Bramston-Cook.

Rate of Adsorption.—As already mentioned (p. 842), the adsorption of oxygen by a mass of activated carbon grains enclosed in a gauze cylinder has been shown to occur first on the outside layers of carbon. The rate of adsorption is so rapid that, with small volumes of gas, no oxygen penetrates through the interstices between the grains to the carbon round the thermocouple. The same process, but on another scale, must also occur in each carbon grain. On account of the rapidity of adsorption, the surfaces of those capillaries lying nearest to the surface will be first saturated with oxygen. Those capillaries which are not readily accessible or which are of small diameter will not be reached by the first small admissions of gas. In such circumstances, it will be seen that the rate of adsorption on activated carbon grains will be a very complex function of the pressure.

When the carbon surface has been partially saturated with 0·2—0·3 c.c. of oxygen per g. of carbon, the rates of adsorption are measurable. It is found that the rate of adsorption for oxygen pressures below 2×10^{-3} cm. is given by $dp/dT = kp +$ const. (Fig. 4). This simple relationship is probably due to the fact that the exteriors of the carbon grains have been saturated with oxygen and the rate which is measured is that of the diffusion of oxygen into the less accessible capillaries in the carbon. At such low pressures, the mean free path is much greater than the size of the capillaries. There is no hindrance to molecular movement by collisions between the gas molecules and diffusion occurs at a rate proportional to the pressure.

The fact that the curves in Fig. 4 give an intercept on the pressure axis at $1—2 \times 10^{-4}$ cm. is of interest. Perhaps this is the equilibrium pressure of oxygen adsorbed on the carbon surface. The magnitude of the intercept increases as the carbon becomes saturated with oxygen.

Adsorption of Hydrogen on Carbon.—On the addition of 0·01 c.c. of hydrogen per g. of carbon, none was adsorbed, neither was there

any reaction observed when hydrogen was admitted to a carbon surface to which oxygen had previously been added.

Summary.

The maxima previously found on the curves for the differential heats of adsorption of oxygen on charcoal have been shown to be due to defects in the thermocouple calorimeter. These defects arise

FIG. 4.
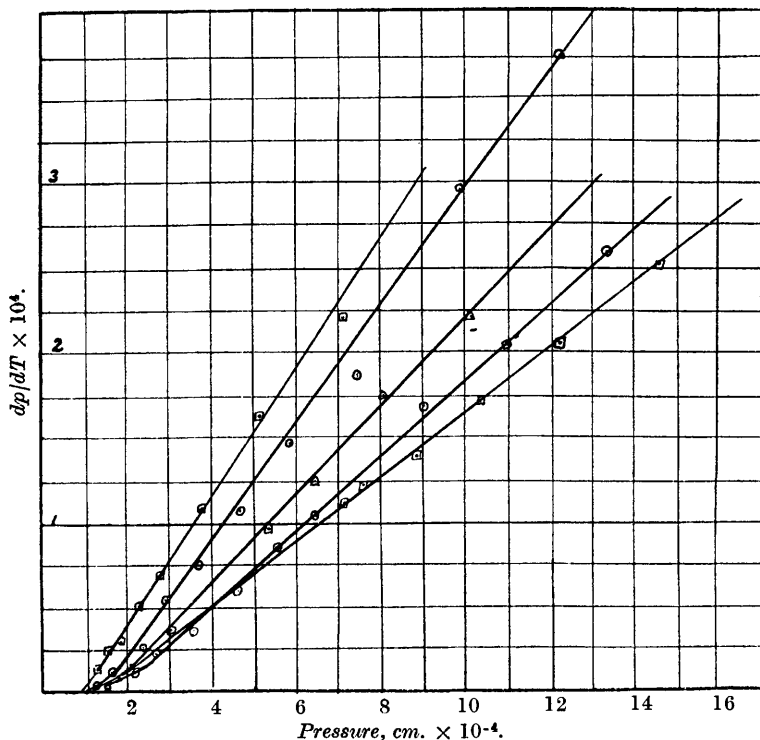
from (a) the slow conduction of heat between the carbon grains and from the carbon to the thermocouple at low pressures, and (b) the lack of uniformity in the adsorption of oxygen by the various layers of the carbon; they are eliminated by employing a new type of container which permits of the admission of gas into the middle of the bulk of the carbon grains. The results obtained by Marshall and Bramston-Cook, which give the highest value for the heat of adsorption for the smallest volumes admitted, have been confirmed by this method.

Another defect which is observable when the residual gas pressures

exceed 10^{-3} cm. may be eliminated by surrounding the reaction vessel by a thermostat kept at constant temperature.

The rate of adsorption of oxygen is determined by the rate of diffusion into the carbon grains.   At low pressures, adsorption on a partially saturated carbon surface is given by $dp/dT = kp + \text{const.}$ Slow changes occur in the adsorbed gas film owing either to diffusion of the adsorbed oxygen into the interior of the grains or to a slow reaction occurring between the gas film and the surface.

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