

of formation of sulfuric acid in 1.036 *M* sulfuric acid solution,²⁶ $\Delta H_{25} = -206,700$ Cal.; heat of formation of mercurous sulfate, $\Delta H_{18} = -171,580$ Cal.; heat of formation of lead sulfate, $\Delta H_{18} = -214,600$ Cal.; partial heat of formation of water in 1.036 *M* sulfuric acid solution, $\Delta H_{25} = -68,340$ Cal. Combining these to give the heat of reaction, using the value from "International Critical Tables" for the heat of formation of lead dioxide, gives $\Delta H = -46,860$ Cal. Using Millar's value for the heat of formation of lead dioxide, the heat of reaction is $\Delta H = -43,500$ Cal.

Summary

1. The conditions necessary for the preparation of reproducible lead dioxide-lead sulfate electrodes have been determined.

2. Cells of the type $\text{Hg} \mid \text{Hg}_2\text{SO}_4, \text{PbSO}_4, \text{H}_2\text{SO}_4 (xM) \mid \text{H}_2\text{SO}_4 (xM), \text{PbO}_2, \text{PbSO}_4 \mid (\text{Pt})$ have been set up and their electromotive forces have been measured over a period of seven to sixteen weeks at 25° and also at 20, 30, 35 and 40°.

3. From the results the following have been calculated: the value of E_{25}° , the electrode potential of the lead dioxide-lead sulfate electrode, the activity coefficients of sulfuric acid at various molalities, the electromotive force of the lead storage cell and the free energy change, the entropy change and the heat of reaction for the reaction $\text{PbO}_2 + 2\text{Hg} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{PbSO}_4 + \text{Hg}_2\text{SO}_4 + 2\text{H}_2\text{O}$. The last compares favorably with the value calculated from thermochemical data.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BRITISH COLUMBIA]

THE HEAT OF ADSORPTION OF OXYGEN ON CHARCOAL

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Keyes and Marshall¹ found 72,000 calories per mole for the differential heat of adsorption of oxygen on activated charcoal for initial amounts of gas adsorbed. This heat dropped slowly as the concentration increased to about 0.15×10^{-4} moles per gram of charcoal. As the concentration increased beyond this value the heat of adsorption fell off rapidly to a practically constant value of about 4300 calories per mole.

The course of the curve of differential heat of adsorption against concentration of adsorbed gas at very small concentrations is of considerable theoretical interest, particularly from the point of view of the hypothesis that adjacent carbon atoms may vary greatly in adsorptive character.

²⁶ Interpolated with the help of data of Brönsted, *Z. physik. Chem.*, **68**, 702 (1910), for the differential heat solution of sulfuric acid.

¹ Keyes and Marshall, *THIS JOURNAL*, **49**, 156 (1927).

The earlier work,¹ while emphasizing the importance of obtaining adsorptive data at small concentrations, suffered from a limitation with respect to the amount of charcoal used in the measurements. In the present work ten times the amount of charcoal was employed, making it possible to follow the relation between the heat of adsorption and concentration to very much smaller concentrations than have previously been reported.

Apparatus.—The arrangement of the apparatus is shown in Fig. 1, and is similar in many respects to that of the earlier work.¹ The chief difference lies in the arrangement of the ice calorimeter, which was supported in a silvered Dewar flask, C, after the arrangement described by Griffiths.² The interior of the Dewar flask was rendered water-tight by a large rubber stopper through which the neck of the calorimeter passed.

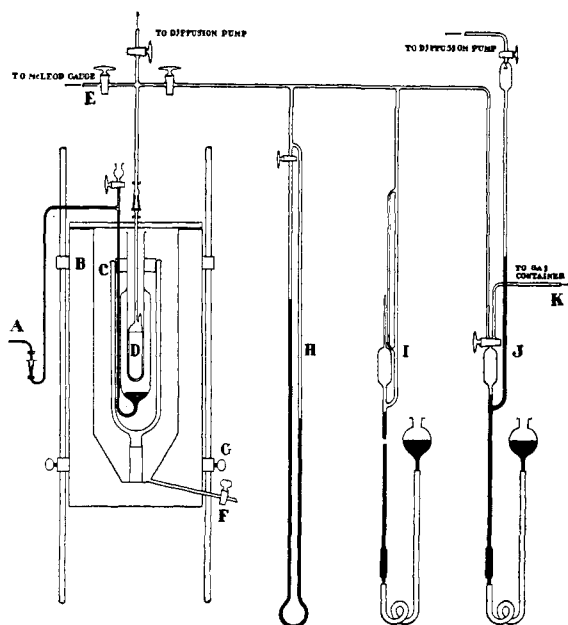


Fig. 1.

The Dewar flask was in turn supported inside the vessel B, which was provided with double walls, the space B being packed to the top with wool waste. The space C was filled with cracked ice and sufficient distilled water to fill the voids between the pieces of ice. This water did not quite reach the mouth of the calorimeter, which was closed with a thick piece of wool waste. The vessel B was covered with a piece of felt about 0.5 inch thick, which prevented a too rapid melting of the ice in C. As the ice melted, more was added every few hours, and the equivalent amount of water drained from F. The entire calorimeter could slide vertically and make contact with the fixed capillary tube at A in a manner similar to that described in the previous work.

The ice mantle was produced by the use of a mixture of solid carbon dioxide and ether contained in an open tube of slightly larger diameter than D. We found this

² Griffiths, *Proc. Phys. Soc. London*, **36**, 1 (1913).

method preferable, as the rate of freezing of the ice mantle could be easily controlled by dropping in small amounts of carbon dioxide at a time. The above arrangement of the ice calorimeter has the advantage that it can be operated for long periods of time. In the present investigation the ice mantle was found intact after being in continuous use for a week.

The oxygen was admitted to the apparatus from the gas pipet J, the bulb of which had a capacity of about 5 cc. The McLeod gage I had a low multiplying power of ten, and was used for intermediate pressures, while higher pressures were measured by the manometer H. A McLeod gage of ordinary size was connected at E for low pressure measurements when outgassing the charcoal.

The charcoal³ used was a sample of activated coconut charcoal produced by the National Carbon Company. It was washed in a Soxhlet extractor with hydrochloric acid and afterwards treated with hydrofluoric acid, the final ash content being 0.267%. Before use it was outgassed for about sixty hours at 1000°, using a platinum-wound resistance furnace. The outgassing was continued in every case down to a pressure of about 1×10^{-4} mm. After outgassing the charcoal weighed 25.792 g. During the preliminary outgassing the gas continued to come off for such long periods of time that interaction between the silica tube and the charcoal was considered possible. In the final measurements a lining of platinum foil was employed to prevent contact of the charcoal with the silica.

Experimental Procedure.—After outgassing the charcoal the calorimeter was raised into position until the quartz tube just touched the bottom of the inner tube. For the initial reading about 0.8 cc. of gas was admitted from the gas pipet. The position of the mercury thread was noted every ten minutes until the normal heat leak was resumed. Another increment of gas was added and the procedure repeated until about 250 to 300 cc. in all were added.

The data in the tables to follow give the oxygen added in moles per gram of charcoal, designated c . The quantity q is the total heat attending adsorption for the correspondingly tabulated values of c . To obtain these values of q allowance was made for the heat capacity of the gas admitted to the calorimeter, since the temperature of the former was in every case different from zero. Values of q were plotted against values of c and the slope $(\partial q)/(\partial c)$ was measured for various values of c . The quantity $(\partial q)/(\partial c)$ is the differential heat of adsorption per mole of oxygen at constant temperature, and is represented by Q . Data from two series of measurements are given in Table I. The corresponding values of Q , obtained by plotting the above q, c data suitably, are given in Table II.

The equilibrium pressures in Table I were originally measured for the purpose of correcting for unadsorbed gas in the calorimeter and connecting parts. As the low initial pressures gave negligible corrections they were not recorded. These initial pressures are, in fact, so low that they can be measured only by means of a specially sensitive McLeod gage. Such measurements are now being made in this Laboratory.

A marked discontinuity appeared in both Q - c curves at the point $c = 0.75 \times 10^{-4}$. Whether this is part of the phenomena or due to the method

³ The charcoal used previously was prepared from a sample of French gas mask charcoal. This latter charcoal was made from wood.

TABLE I
 EXPERIMENTAL DATA

Press., mm.	$c \times 10^4$	q	Press., mm.	$c \times 10^4$	q
	Series 1			Series 2	
....	0.0151	0.124	179.2	2.606	4.595
....	.0361	.272	271.5	3.488	4.999
....	.0793	.558	382.2	4.599	5.436
....	.097	.650	0.0136	0.119
....	.115	.7660405	.324
....	.151	1.0090849	.647
....	.193	1.286152	1.095
....	.232	1.542	0.05	.222	1.575
....	.287	1.905	.40	.354	2.409
0.20	.326	2.201	6.85	.545	3.009
.34	.404	2.468	20.25	.796	3.609
3.25	.501	2.913	43.50	1.113	3.840
7.40	.611	3.247	128.2	2.153	4.472
14.73	.779	3.567	259.0	3.463	5.072
35.60	1.122	3.833	374.0	4.530	5.521
83.40	1.532	4.095	513.9	5.586	5.963
140.00	2.206	4.421			

 TABLE II
 VALUES OF Q

$c \times 10^4$	0.00	0.01	0.02	0.03	0.04	0.05	0.10		
Q	89600	81400	74400	71700	70200	69900	69400		
$c \times 10^4$	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	
Q	66800	58900	40800	32200	25300	21300	7690	7570	
$c \times 10^4$	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.5
Q	7390	6050	5140	4690	4430	4250	4220	4180	4180

of experimentation is not known at this time so the curves were drawn to follow the data obtained. The resulting values of Q are plotted in Fig. 2 and the curve so obtained is smoothed at this point as shown.

Interpretation of Results

Like the curve of Keyes and Marshall, the present curve shows a tendency to flatten in the vicinity of 70,000 calories. Instead of ending abruptly at 72,000 calories, however, the data indicate a rapidly increasing differential heat not differing much from 89,600 calories for zero concentration. The final heats of adsorption at large values of c are practically the same as those of Keyes and Marshall. The numerical accord between the earlier work and the present indicates that the general adsorptive characteristics of wood and coconut charcoal are not different, at least as far as the adsorptive heats of oxygen are concerned.

With few exceptions the Q - c curves obtained by other investigators have shown a maximum value of Q at zero concentration. This can be ex-

plained in terms of the hypothesis suggested by Langmuir⁴ for adsorption and Taylor⁵ for contact catalysis, that the surface atoms are of unequal activity. The gas would be expected to adsorb on the more active atoms first, and assuming that the heat of adsorption is an approximate measure of the activity of the surface atoms, a maximum differential heat of adsorption would be obtained at the lower concentrations. In the case of the adsorption of hydrogen on metal catalysts, which forms an exception to the above rule,⁶ it must be assumed that here the heat of adsorption is not a measure of the activity of the surface atoms.

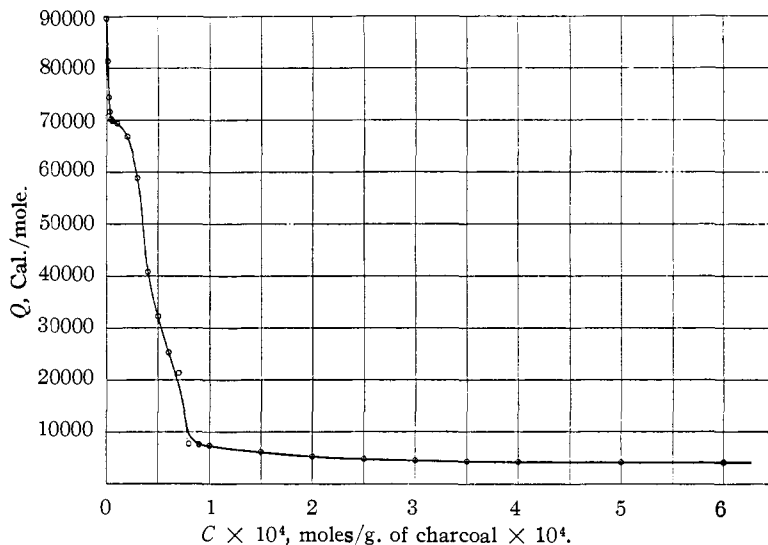


Fig. 2.

If some value c_0 is considered to represent the concentration at which the surface is covered, we can plot $c_0 - c$ against the corresponding values of Q and obtain an integral distribution curve giving values of Δc equal to those from Fig. 2, but with a positive sign. From the slopes of this last curve at various values of Q we obtain $d(c_0 - c)/dQ = -dc/dQ$. These values of $-dc/dQ$ were accordingly obtained from Fig. 2 by measuring graphically at various values of Q the slopes of the curve, and their sign was then changed. These results are given in Table III and plotted in Fig. 3.

This last curve (Fig. 3) is a distribution curve of the type used to describe the distribution of gas velocities. In such curves the area under the

⁴ Langmuir, THIS JOURNAL, 40, 1361 (1918).

⁵ Taylor, Proc. Roy. Soc. London, 108A, 105 (1925).

⁶ (a) Beebe and Taylor, THIS JOURNAL, 46, 43 (1924); (b) Fryling, J. Phys. Chem., 30, 818 (1926); (c) Kistiakowsky, Florsdorf and Taylor, THIS JOURNAL, 49, 2200 (1927).

TABLE III
RESULTS

Q	89600	80000	75000	72000	71000	70000	69800	69600	69400	
$-dc/dQ \times 10^9$	0.110	0.132	0.175	0.464	0.594	1.795	12.595	9.443	6.431	
Q	69000	68000	66000	60000	50000	40000	30000	20000	8000	
$-dc/dQ \times 10^9$	5.224	3.484	1.868	0.899	0.462	0.850	1.370	1.524	0.242	0.000 ^a

^a The choice of this value is explained below under the heading "Thickness of the Adsorbed Layer."

curve between any two energy values represents the fraction of the total number of molecules present having energy values between these limits. In the present case, because the number of molecules required to cover the surface is still a matter for debate, we have preferred to choose our variables

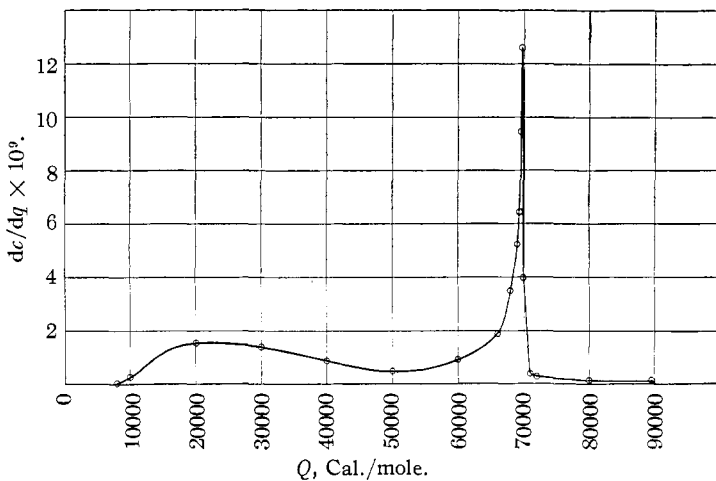


Fig. 3.

to make the area between any two values of Q equal to the number of moles of oxygen per gram of charcoal with heats of adsorption between these limits. That is, $\int_{Q_1}^{Q_2} dc/dQ \cdot dQ = \int_{c_1}^{c_2} dc$. As pointed out previously, this change of c between Q_1 and Q_2 can be obtained from Fig. 2. These integral values of c can be regarded as equivalent to Langmuir's elementary spaces per gram of charcoal. It is difficult to discuss the relative activities of individual carbon atoms, as all the surface atoms probably cannot hold the same amount of oxygen. Furthermore, one carbon atom can represent two different heats of adsorption, a high heat for the first addition of oxygen, and a lower heat for a later second addition.

It is evident that the curve, as a whole, does not resemble a probability curve in form. Probability distribution in the present curve would be most likely to exist above 70,000 calories, although the probability function

$y = 2h/\sqrt{\pi} \times e^{-(hx)^2}$ could not be made to fit the curve over this range. The present curve shows a much more uniform distribution in this region than the error curve. It is evident that a slight relative error in the values of q in the extremely low concentration range would alter the shape of the distribution curve (Fig. 3) considerably, so that a large amount of exact experimental data is necessary before a decision can be reached regarding the application of such distribution functions. A knowledge of the distribution of surface activities is very desirable, as it would enable a study of catalyzed reactions to be made under controlled conditions of surface activity and distribution.

That a similar distribution of the more active centers occurs on some other adsorbents as well is shown by the Q - c curve of Beebe⁷ for carbon monoxide on a copper catalyst, and a similar curve for carbon dioxide on charcoal by Magnus and Kälberer,⁸ which resemble the present curve in the particular that the curve becomes almost parallel with the Q axis as c approaches zero. Even for the heat of adsorption of hydrogen on nickel, where the initial heat is abnormally low, Fryling^{6b} assumes that extrapolation of the final portion of the curve back to small values of c would cause it to approach the Q axis in the same manner.

The flattening of the Q - c curve, similar to that at 70,000 calories for the previous work¹ and the present investigation, is not so common. Polanyi and Welke⁹ obtain Q - c curves for sulfur dioxide on charcoal which increase rapidly with decreasing c and show a tendency to flatten at the same molecular concentration ($c = 0.1 \times 10^{-4}$) as the present curve. The resulting maximum in the distribution curve (Fig. 3) at about 70,000 calories possibly represents some definitely recurring state or position of the surface carbon atoms.

Thickness of the Adsorbed Layer.—Keyes and Marshall have found linear relations between the final heats of adsorption at high concentrations and certain constants of the normal molecule which led them to the conclusion that the final heats of adsorption resulted from adsorption on previously adsorbed layers. If, then, we assume for the time being that the entire extent of the Q - c curve represents the formation of multiple layers, the point at which a single primary layer is completed would in general be represented by a zero or a minimum value of $-dc/dQ$, provided that extensive overlapping of layers does not occur. There are two points on the Q - c curve which approach this condition, first, the steep part of the curve at $c_a = 0.35 \times 10^{-4}$, and second, the inflection resulting from smoothing of the discontinuity at $c_b = 0.78 \times 10^{-4}$. If the data were followed strictly $-dc/dQ$ at c_b would be zero, as can be seen from the

⁷ Beebe, *J. Phys. Chem.*, **30**, 1538 (1926).

⁸ Magnus and Kälberer, *Z. anorg. Chem.*, **164**, 345 (1926).

⁹ Polanyi and Welke, *Z. physik. Chem.*, **132**, 371 (1928).

position of the points in Fig. 2. For the construction of the distribution curve (Fig. 3) this zero slope at c_b has been used, although in the actual Q - c curve (Fig. 2) we have given $-dc/dQ$ a small positive value at this point, as zero slope would not be expected experimentally either at c_a or c_b due to some overlapping of layers.

Three possible explanations occur to us for the peculiar form of the distribution curve (Fig. 3). (1) The range to $c_b = 0.78 \times 10^{-4}$ represents the formation of a monomolecular or monatomic layer. Fig. 3 gives the variation in activity of the elementary spaces on the surface. (2) As c_b is about twice c_a , the point c_a could represent the completion of a primary layer and c_b a second layer. (3) Adsorption of oxygen on one elementary space would tend to decrease the activity of an adjacent space. Thus it can be shown that the heat evolved when an atom of oxygen combines with an atom of gaseous carbon to form carbon monoxide is several times as great as that evolved when an atom of oxygen combines with a molecule of carbon monoxide to form carbon dioxide. This decrease in the activity of adjacent spaces might create a preponderance of elementary spaces having the lower heats of adsorption, and possibly cause a deficiency among the spaces with intermediate heats. Such a state of affairs would produce the minimum found on the curve (Fig. 3) at intermediate Q values, thus showing the characteristics of a second layer.

The only other investigation which shows an inflection at c_b is that of Fryling^{6b} for hydrogen on nickel, while a minimum value of $-dc/dQ$ corresponding to that at c_a is more common. Consequently c_a most probably represents the limit of the primary layer. This rarity of occurrence does not necessarily mean that the c_b inflection is due to experimental errors. It is evident that an overlapping of layers would obscure both inflections, but that at c_b more readily than that at c_a . This would be particularly true for vapors or easily condensable gases whose initial heats of adsorption are low. The above considerations favor (2) or (3) but cannot distinguish between them. The authors consider that more data are necessary before forming a definite hypothesis, and the above statement of possibilities is presented with the hope that it will assist in the production of such data.

It is difficult to utilize the Q - c data below c_b for the construction of a distribution curve of the type represented by Fig. 3, because of the comparatively small variation of Q with c . Considerations of kinetic equilibrium would require the formation of an equipotential surface as the layers increase in thickness, the concentration of adsorbed gas being greatest around the most active centers. Over this region the surface would be of uniform activity, which is in accordance with the small variation in Q actually obtained.

Applicability of the Theory of Monomolecular Layers.—From the point of view of the monomolecular layer theory we must assume that

oxygen is adsorbing on elementary spaces of the free carbon surface, even at $c = 5.0 \times 10^{-4}$. Examination of the Q - c curve shows that at least 85% of the total elementary spaces have heats of adsorption below 8000 calories. Investigations covering other adsorbents and adsorbates show similar almost constant final heats. The curve of Keyes and Marshall shows practically the same proportion of elementary spaces below 8000 calories as that quoted for the present results. Outgassing of the charcoal between runs should alter considerably this abnormal distribution of elementary spaces by removing some of the carbon atoms as oxides of carbon. The steep part of the Q - c curve would be affected to a much smaller degree, as the distribution over this range is more in accord with probability. In accordance with this possibility, we have noted during our experiments slight variations about a mean of the shape of the curve in this region. On the other hand, the position of the sharp change in slope at c_b varied so little that the proportion of low activity spaces could be considered to remain practically constant. The sum total of evidence at hand seems to show that the position of this change of slope depends mainly on the specific surface of the charcoal, which in turn is a function of the material from which the charcoal is made.

We might, of course, assume that only the more active carbon atoms can activate the oxygen molecule, causing a kind of surface chemical combination, and that the low final heats are due to combination of oxygen molecules with less active carbon atoms by secondary valence only. This would explain the constancy of the low final values, but the hypothesis is still open to the previous objection that it should be possible to shift considerably the position of the change of slope at c_b by heat treatment. Consequently, comparing the assumptions involved in the two opposing views, we believe that the phenomena herein described receive a more plausible explanation from that form of the multimolecular layer theory suggested by Keyes and Marshall.

Calculation of the Specific Surface.—Calculation of the specific surface of the adsorbent from the amount of gas adsorbed is always uncertain, as some assumption must be made regarding the manner in which the molecule is adsorbed. Assumption of a monatomic layer would give the largest surface, while assumption of orientation normal to the surface would give the smallest. As a mean between the two extremes we will consider the total number of molecules which can be packed in a single layer on 1 sq. cm. of surface to be 0.77×10^{15} , as computed by Langmuir from the molecular volume of liquid oxygen. Assuming completion of the first layer at $c = 0.35 \times 10^{-4}$, we have $(0.35 \times 10^{-4} \times 6.06 \times 10^{23}) / (0.77 \times 10^{15}) = 2.8 \times 10^4$ sq. cm. per gram of charcoal. If, on the other hand, we assume the surface layer to be complete at $c = 0.78 \times 10^{-4}$, the specific surface would be 6.1×10^4 sq. cm. per gram.

Other Investigations.—Ward and Rideal¹⁰ have obtained curves for the heat of adsorption of oxygen on four varieties of charcoal. They did not measure initial values of Q , although the curves shown resemble corresponding parts of the present curves. They object to the multimolecular layer theory of Keyes and Marshall because of the dye adsorption work of Paneth,¹¹ and because the pressure increases indefinitely with the concentration and does not tend to a limiting value at constant temperature. We feel that much work must still be done before the conclusions of Paneth regarding the specific surface of charcoal can be accepted without question. The mode of variation of p with c can hardly be quoted in support of the monomolecular layer theory, as it can be made to fit either theory by making appropriate assumptions regarding the mechanism of the adsorption. The question of layer thickness is reviewed by Rideal.¹²

Garner and McKie¹³ report a heat of adsorption for oxygen on charcoal of 5000 calories per mole at 18° between $c = 0.001 \times 10^{-4}$ and $c = 0.006 \times 10^{-4}$, jumping to 60,000 calories at $c = 0.04 \times 10^{-4}$, and then increasing slowly to 71,000 calories at $c = 0.15 \times 10^{-4}$. The present results show no evidence of this low initial value. We could not, of course, investigate the region between $c = 0.001 \times 10^{-4}$ and 0.006×10^{-4} , but from $c = 0.01 \times 10^{-4}$ to $c = 0.04 \times 10^{-4}$ our values are abnormally high rather than abnormally low, as required by the curve of these authors. Further, between $c = 0.0136 \times 10^{-4}$, our lowest measured concentration, and $c = 0$ the slope of the q - c curve shows a marked tendency to increase as it approaches the origin, which is a real point on the curve. Finally, we note that these authors report only one really low value, no heat values between 5000 calories and 60,000 calories having been measured. Since completion of this paper, McKie¹⁴ has described their experimental method in detail. It would be desirable to repeat the above measurements with thermocouples placed at different points throughout the mass of the charcoal and so arranged that the average temperature of the charcoal could be obtained by integration of the results.

Summary

1. The differential heat of adsorption of oxygen on activated coconut charcoal has been measured as a function of the gas concentration on the charcoal, special attention being paid to these values at low concentrations. The maximum heat of adsorption at zero concentration was found to be 89,600 calories per mole of oxygen.

¹⁰ Ward and Rideal, *J. Chem. Soc.*, **130**, 3117 (1927).

¹¹ Paneth and Vorwerk, *Z. physik. Chem.*, **101**, 445 and 480 (1922); Paneth and Thimann, *Ber.*, **57**, 1215 (1924); Paneth and Radu, *ibid.*, **57**, 1221 (1924).

¹² Rideal, "Surface Chemistry," Cambridge University Press, pp. 139-145, 150-151.

¹³ Garner and McKie, *J. Chem. Soc.*, **130**, 2451 (1927).

¹⁴ McKie, *ibid.*, **130**, 2870 (1928).

2. Similarity of the resulting curve, of heat of adsorption against gas concentration on the surface, to that obtained in previous investigations emphasizes the specific nature of the adsorption and the constancy of the charcoal surface.

3. A distribution curve is obtained showing the apparent distribution of activities of the elementary spaces on the carbon surface. Several possible explanations are advanced for the shape of this curve.

4. From a comparison of the shapes of the initial portions of various $Q-c$ curves certain regularities are noted and it is concluded that there is a possibility of obtaining a mathematical expression for the distribution of the more active elementary spaces on the surface.

5. The conclusion is reached that the results support best that form of the multimolecular layer theory previously suggested by Keyes and Marshall.

6. The specific surface of the charcoal is estimated to lie between 2.8×10^4 and 6.1×10^4 sq. cm. per gram.

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GERMANATE GELS OF THE ALKALINE EARTHS

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The soluble salts of the alkaline earths cause no precipitation in neutral or acid solution of germanium dioxide but when such solutions are made alkaline with ammonium hydroxide most of the germanium is thrown down as a bulky gelatinous mass. Under such circumstances, however, it is not easy to form homogeneous or firmly set gels owing to the flocculating influence of the ammonium salt simultaneously produced. If calcium hydroxide solution be substituted for the salt of the same base the reaction with aqueous germanic acid takes on a surprisingly different character, for the precipitate then assumes the form of a firm, transparent gel even in highly dilute solutions. The direct formation of calcium, strontium and barium germanates by neutralization of aqueous germanic acid results in the formation of insoluble or difficultly soluble salts under conditions most favorable to colloid formation, as water is the only by-product in the reaction. At the same time this reaction is peculiarly characteristic for germanium, for all of the other semi-metallic dioxides in the fourth periodic group are quite insoluble in water.

It is the purpose of this paper to describe the alkaline earth germanates when prepared in the form of highly dispersed systems with particular attention to the calcium salt, which appears to give permanent gels of extraordinary water content,