Graphitic Oxide and Water:
Heats of Immersion and Heats of Adsorption

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RECENT investigations of graphitic oxide (*3, 4, 6*) have done much to elucidate the composition, structure, and properties of this rather peculiar substance. However, the energies involved in the adsorption of vapors and the heats of immersion have not, apparently, been investigated. The present article is a report on the adsorption of water vapor on graphite oxide surfaces and the heat liberated when graphitic oxide is immersed in water.

PREPARATION OF GRAPHITIC OXIDE SAMPLES

All samples used in this study were prepared from a Canadian graphite (Asbury Graphite Mills, Inc., Asbury, N. J.). The graphite was 99% pure flake and graded 1 through 5 according to particle size, with number 1 as the coarsest. Grades 1 and 5 only were used in this investigation.

In preparing graphitic acid from these graphites, the Brodie method of oxidation (*1*) was used. A 5.0-gram sample of graphite was added to 62.5 ml. of fuming nitric acid contained in a 125-ml. Erlenmeyer flask. After cooling this mixture in an ice bath, 25.0 grams of potassium chlorate were slowly added (over a period of about one half hour) while the mixture remained in the ice bath. After the mixture had reached room temperature, it was placed in a water bath, heated slowly to a temperature of 45° C., and kept at this temperature for 20 hours. Subsequently, the mixture was poured into 125 ml. of cold distilled water and then warmed to 70° C. to increase the solubility of humic acid, potassium chlorate, and other salts which might be present. The mixture was then centrifuged and decanted. The sample was washed three times in this manner and then dried overnight at 70° C.

The above method of oxidation was repeated eight times. After the first oxidation treatment, the product was a dark green color with some black graphite particles visible. Subsequent oxidations produced lighter greens, greenish yellow, and finally a pale yellow product. After the third oxidation treatment, examination of the samples under a microscope illuminated from below revealed the presence of only transparent particles with no traces of the original opaque graphite particles.

Following the final oxidation, the sample was washed five times with 125 ml. of distilled water, at 70° C., followed by centrifugation and decantation after each washing. A suspension of the sample was then electrodialyzed at a potential of 120 volts, in a Mattson-type cell. A continuous exchange of distilled water was maintained in the electrode compartments during the 48-hour dialysis period. At the end of the period, the mixture was again centrifuged and decanted in order to concentrate the suspension. The graphitic oxide was recovered from this suspension by 3 to 4 days of freeze drying, during which time the sample had fallen from the sides of the flask and was very light and fluffy—a decided contrast to the samples which were oven dried at 70° C. Because of their greater rate of outgassing and adsorption, the freeze-dried samples were used exclusively for adsorption and immersion studies.

The sample prepared as described above is designated as C_B^5-8-20 indicating Canadian graphite of grade 5 was given eight 20-hour oxidizing treatments by the Brodie method. Other samples were prepared by a method identical to that described above, except for the number of oxidizing treatments. In addition, one sample was prepared in a manner suggested by Selvig and Ratliff (*10*). After three oxidizing treatments, as described above, the sample was treated with 120 ml. of 6*M* sulfuric acid, cooled in an ice bath, and 25 grams of potassium permanganate were added slowly. This mixture was placed in a 45° C. water bath for 20 hours, washed, and treated with 200 ml. of 10% hydrogen peroxide to remove excess permanganate. Subsequently, the sample was washed, electrodialyzed, and freeze-dried as described previously. This sample is designated as C_B^5-3-20$^+$.

Samples were further dried over magnesium perchlorate and then analyzed for carbon, hydrogen, and oxygen. The results of these analyses are given in Table I.

EXPERIMENTAL PROCEDURE

Adsorption measurements were made in an eight-place gravimetric apparatus of conventional design using helical quartz springs with an over-all sensitivity of ±0.016 mg. For a sample weight of 0.250 gram, the weight change per gram was determined with ±0.064 mg. per gram. Pressure changes during an adsorption run were determined by means of an Apiezon B oil manometer.

Table I. Composition of Graphitic Oxide Samples

	Composition, Av. %				Atomic Ratio, Av.	
Sample	C	H	O	H_2O^a	C/O	C/O^b
C_B^5-8-20	51.89	2.50	45.11	22.30	1.52/1	2.68/1
C_B^5-6-20	51.50	2.25	46.10	21.46	1.48/1	2.54/1
C_B^5-4-20	55.36	2.66	41.53	23.75	1.76/1	3.54/1
C_B^5-3-20$^+$	56.41	2.22	41.52	19.80	1.82/1	3.02/1
C_B^1-8-20	55.51	1.62	42.87	14.49	1.72/1	2.46/1
C_B^1-6-20	56.82	2.38	40.80	21.26	1.86/1	3.46/1

[a] Per cent H_2O calculated with assumption that all H is present as H_2O.
[b] Ratio after per cent H_2O has been deducted.

The graphitic acid samples were kept at 51% relative humidity by storing them over a saturated solution of calcium nitrate. Approximately 0.250 gram of the sample was then placed in a small bucket made from tin foil which had been previously weighed. The container was then placed in a weighed glass weighing bottle and stored at 51% relative humidity for another 24 hours. Before removing the samples from the constant humidity environment, the bottles were stoppered. Weighings were then made to within 0.2 mg.

The samples were next placed in the adsorption columns, and a zero point reading was taken. The system was evacuated very carefully to prevent loss of sample from the containers. After outgassing at room temperature for 24 to 36 hours at 10^{-5} mm. of mercury, the samples were outgassed at 70° C. for another 24 hours. They were then brought to the temperature of the desired isotherm and water vapor was introduced into the system in small increments. After approximately 8 hours, no noticeable change in weight or pressure occurred. Therefore, from 8 to 12 hours were allowed for each adsorption point. Adsorption runs were made at 5°, 25°, and 45° C.

For the heats of immersion measurements, a calorimeter previously described (*11*) was used. Samples were prepared for use in the calorimeter by outgassing weighed amounts (125 to 150 mg.) of graphitic oxide which had been stored at 51% relative humidity. The samples were outgassed at room temperature for 24 hours, then at 70° for another 24 hours. Tubes for each sample were then sealed off, while the remainder were exposed to various water vapor pressures at 25° C. before being sealed.

EXPERIMENTAL RESULTS

The adsorption and desorption of water vapor on the six graphitic acid samples produced typical *S*-shaped isotherms characterized by a definite hysteresis upon desorption over the entire range of vapor pressures. However, at the end of a desorption run, the samples could be returned to within 0.3 mg. of their initial weights by outgassing at 70° C. for another 24 hours.

The B.E.T. equation (*2*) was used to determine the amount of adsorbent required to produce a monolayer. Results for the 25° C. isotherms are shown in Table II. A value of 10.6 Å^2 was used for the area occupied by a water molecule. Isosteric heats of adsorption were determined by use of an equation similar to the Clausius-Clapeyron equation:

Table II. Surface Areas of Graphite Oxides

Sample	Wt. Adsorption for Monolayer w_m, Mg./G.	Surface Area, Sq. Meter/G.
C_B^5-8-20	92.0 ± 0.6	331
C_B^5-6-20	99.4 ± 0.5	358
C_B^5-4-20	96.7 ± 0.6	348
C_B^5-3-20$^+$	94.9 ± 0.2	342
C_B^1-8-20	87.3 ± 0.6	314
C_B^1-6-20	87.0 ± 0.9	313

$$\left(\frac{d \ln p}{dT}\right)_\gamma = \frac{\Delta H_q}{RT^2} \quad \text{or} \quad \ln \frac{p_2}{p_1} = \frac{-\Delta H_q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Where p is the pressure of the water vapor over the solid, ΔH_q is the isosteric heat of adsorption, and γ is the amount of vapor adsorbed.

The isosteric heats of adsorption are shown in Figure 1. The amount of vapor required for a monolayer, as determined from the B.E.T. equation, was used to obtain the fraction of monolayer of adsorbent at different pressures. Because these systems did not show strictly reversible adsorption and desorption, the validity of the calculations of isosteric heats of adsorption was tested by making calculations from both the adsorption and the desorption isostere data. Heats calculated from desorption data, for example, are shown for sample C_B^5-8-20 in Figure 1 as half-filled circles.

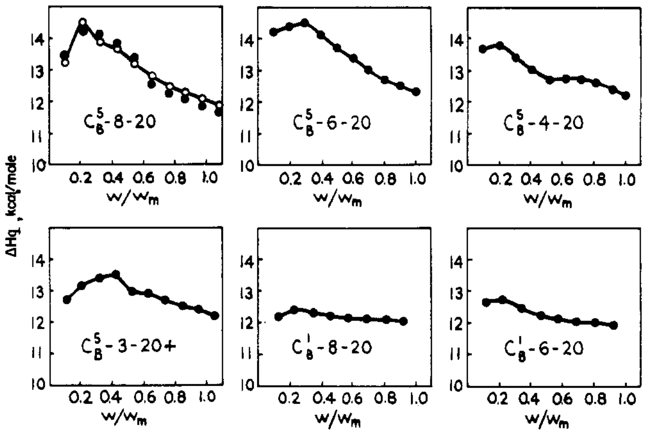

Figure 1. Isosteric heats of adsorption of water on graphitic oxide at 25° C.

Heats of immersion are shown in Figure 2. When more than one measurement was made on samples exposed to the same water vapor pressure, the average value of the heat of immersion is plotted. The relative pressures required to produce a monolayer as determined from the B.E.T. equation are indicated by dotted lines. A correction of 0.22 cal. for the heat of breakage and entry of water into the sample tubes was made to all immersion measurements.

DISCUSSION OF RESULTS

The maximum isosteric heat of adsorption is less than 1.5 times that of the heat of condensation of water vapor, indicating that the process is definitely one of physical adsorption. The maximum heat of adsorption varies with the sample investigated over a range of 14.5 to 12.4 kcal. The heats at a monolayer coverage are within a range of 11.9 to 12.3 kcal. This is from 1.4 to 1.8 kcal. greater than the 10.5 kcal. for the molar heat of condensation of water vapor at 25° C.

Surprisingly the heat of adsorption shows a maximum at a range of 0.2 to 0.4 fraction of a monolayer. The usual case is for the more active sites to be covered first, resulting in a maximum heat of adsorption at the lowest w/w_m values with continually decreasing heats of adsorption as the amount of adsorption increases. Others have occasionally reported maxima in heat of adsorption curves, such as Greyson and Aston (*5*) who found maxima in the heat of adsorption of neon on graphitized carbon black.

Several investigators (*7–9*) have shown that graphitic oxide swells in water and that the distance between the graphite layers is increased. This spreading of the graphite layers would require energy and could thus reduce the heats of adsorption as long as spreading occurs. However, DeBoer and Van Doorn (*4*) have shown that graphitic oxide can adsorb up to 4.2% water without swelling. This amount of water is present in the samples under investigation at less than 0.13 w/w_m which would not account for the lower heats of adsorption at the low w/w_m values.

A second possibility is that the more active sites are present between layers of graphitic oxide flakes rather than on the edges of particles. Although the graphitic oxide layers are not separated at low water content, the water molecules first adsorbed at the edges have a tendency to gradually separate the layers to the extent that water molecules subsequently adsorbed could reach the more active sites between layers. It is proposed that the lower heats of adsorption obtained for the graphitic oxides prepared from coarser graphite flasks are associated with the progressive penetration phenomenon indicated above.

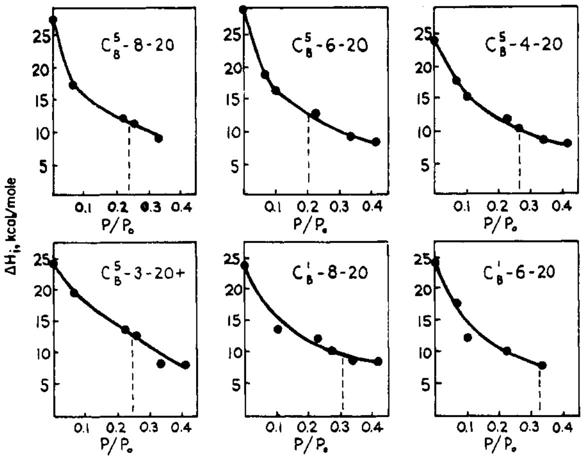

Figure 2. Heats of immersion of graphite oxide in water at 25° C.

------ Monolayer coverage with water vapor

Consequently, larger graphitic oxide flakes, although similar in composition to oxides made of finer flakes, would lead to lower heats of adsorption because of the greater energies required to separate the layers as adsorption progresses.

The heats of immersion decrease continually as the amount of water vapor previously adsorbed is increased. The difference between the heats of immersion of the dry sample and those obtained after exposure to a given vapor pressure should give a measure of the heats of adsorption of that amount of water vapor. By applying this procedure at vapor pressures necessary to give a monolayer as determined by use of the B.E.T. equation, heats of adsorption in kilocalories per mole of water adsorbed were calculated. These, together with the isosteric heats, are shown in Table III. Subtraction of the heat of liquefaction of water vapor from the isosteric heats of adsorption gave the values listed in the last column of the table. A comparison of the calorimetric heats of adsorption to the last column shows the calorimetric values to be from 0.8 to 1.5 kcal. greater. However, the isosteric heats are differential heats of adsorption, while the heats determined calorimetrically are integral heats of adsorption, which in this case would be larger. Within the limits of experimental errorm the comparison appears valid.

Table III. Immersional and Isosteric Heats of Adsorption

Sample	ΔH, Calorimetric[a], Kcal./Mole	ΔH, Isosteric[b], Kcal./Mole	$\Delta H_q - \Delta H_l$
C^5_B-8-20	-2.8 ± 0.2	-12.0 ± 0.1	-1.5 ± 0.2
C^5_B-6-20	-3.2 ± 0.2	-12.3 ± 0.3	-1.8 ± 0.2
C^5_B-4-20	-2.5 ± 0.1	-12.2 ± 0.2	-1.7 ± 0.1
C^5_B-3-20	-2.5 ± 0.2	-12.3 ± 0.3	-1.8 ± 0.2
C^1_B-8-20	-2.8 ± 0.2	-11.9 ± 0.3	-1.4 ± 0.2
C^1_B-6-20	-2.8 ± 0.3	-11.9 ± 0.3	-1.4 ± 0.3

[a] Heats of adsoprtion for monolayer coverage calculated from heats of immersion.

[b] Isosteric heats of adsorption calculated at monolayer coverage.

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