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Figure 1

Figure 1: Figure 1

Abstract

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DIFFERENTIAL HEATS OF ADSORPTION OF OXYGEN AND WATER VAPOR ON THE SURFACE OF GRAPHITE

(Presented by Academician M. M. Dubinin on 26 XII 1961)

Earlier ($^{1-3}$), the high reactivity of the surface of a fresh cleavage of graphite, obtained by dispersing it in an atmosphere of an inert gas, was investigated. Adsorption studies and chemical-analysis data (^{3}) made it possible to identify some functional groups that arise on the surface of a fresh cleavage after the successive adsorption of oxygen and water.

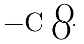
To elucidate the mechanism of formation of surface functional groups, studies of differential heats of adsorption are very valuable, since they make it possible to determine the energy of adsorption interaction at different stages of surface filling. Studies of the heats of chemical adsorption of oxygen on coals and graphite evacuated at high temperatures were carried out in works ($^{4-6}$). Results of measurements on the surface of a fresh cleavage of graphite and of the adsorption of water on an oxidized, but not hydrated, carbon surface have not been reported in the literature.

Fig. 1. Differential heats of adsorption *(a)* and adsorption isotherm *(b)* of oxygen on the surface of a fresh cleavage of graphite. Different symbols denote independent series of measurements.

In this work, a sample of highly dispersed graphite with a specific surface area $S = 350$ m^2/g, obtained by vibromilling natural graphite in an argon atmosphere (^{3}), was used. Measurements of heats of adsorption were carried out on an automatic calorimeter with constant heat exchange (^{7}); measurements of oxygen adsorption were carried out by the volumetric method, and adsorption of water vapor by the method of independent weighing with the use of magnesium perchlorate ([7]). The results of measurements of adsorption and of the heats of adsorption of oxygen on the surface of a fresh cleavage of graphite are given in Fig. 1.

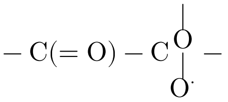
As follows from this figure, the initial heats of adsorption are very large (110 kcal/mol) and close to the corresponding values determined on samples of coal ([4]) and graphite ([6]) activated at high temperatures. When the surface is filled with about 0.5 μM/m^2 of oxygen, the differential heat begins to fall, and at adsorption of 1 μM/m^2 its value decreases almost by half. Further decrease of the heat proceeds more smoothly. In the initial region, the magnitude of the main period of the calorimetric run did not exceed 1 hour. In the region of higher fillings, a slowing of the kinetics of heat evolution was observed (up to 5-6 hours). The data of Fig. 1 show good reproducibility of the state of the surface of a fresh cleavage of graphite; points corresponding to measurements on samples of different milling fit well on a single curve.

High values of the heats in the region of initial fillings possibly correspond to the formation of carbonyl groups*, as well as radicals and groups of the type:



$$-\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}^{\cdot}}\quad (157\ \mathrm{kcal}/M),\qquad -\mathrm{C}-\mathrm{O}-\mathrm{O}-\mathrm{C}-\qquad (111\ \mathrm{kcal}/M)$$

or



$$\text{or}\qquad -\mathrm{C}(=\mathrm{O})-\mathrm{C}\overset{|}{\underset{\underset{\mathrm{O}^{\cdot}}{|}}{\mathrm{O}}}-\qquad (105\ \mathrm{kcal}/M).$$

Probably, the formation of these groups is preceded by the appearance on the surface of peroxide radicals $\mathrm{R}-\mathrm{O}-\mathrm{O}^{\cdot}$ ([8]), some of which then pass into valence-saturated oxygen complexes. Rupture of the double bond of an oxygen molecule with formation of a biradical under these experimental conditions is unlikely. It should be noted that the mean values of the heats of formation given in parentheses are extremely approximate. As is known ([9]), in a system of conjugated bonds, owing to equalization of the electron density, considerable variations in the energy of single bonds are possible. It follows from Fig. 1 that in the region of high heats of adsorption (up to $0.5\,\mu M/\mathrm{m}^2$) the adsorption isotherm rises practically vertically; the main amount of oxygen at this stage is chemically bound to the surface. With increasing adsorption the heat of adsorption falls sharply (Fig. 1), and the adsorption isotherm undergoes an inflection. Analysis of the composition of the gas phase, carried out during measurement of adsorption and desorption, showed no presence (more than 0.5%) of any gases other than oxygen. Thus chemisorption ([10]) did not occur at room temperature. As

Figure 2: Differential heats of adsorption of water vapor on an oxidized but not hydrated graphite surface (open points) and on a hydrated surface (black points). 1 and 2—independent series of measurements.

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was pointed out earlier ([3]), part of the oxygen at these pressures could be adsorbed molecularly through a stronger (quasi-chemical) bond ([11]) with radicals or on regions of the surface deformed in the basal plane ([12]). On the other hand, part of the oxygen could be adsorbed chemically with the formation of oxygen bridges ([15])

$$-\mathrm{O}-\mathrm{O}-\mathrm{O}-$$

$$(53\ \mathrm{kcal}/M)\quad \text{and peroxide radicals}\quad -\mathrm{C}\ -\mathrm{O}-\mathrm{O}^{\cdot}\quad (26\ \mathrm{kcal}/M).$$

Fig. 2. Differential heats of adsorption of water vapor on an oxidized, but **not** hydrated, graphite surface (open points) and on a hydrated surface (black points). *1* and *2*—independent series of measurements.

The presence of peroxide radicals on the surface of carbon-containing substances was confirmed by studies of electron paramagnetic resonance ([11,13,14]).

It is hardly possible to explain unambiguously the fall in the differential heat only from the standpoint of energetic heterogeneity of the surface. In the system of conjugated bonds forming the structure of graphite, one cannot ignore changes in adsorption activity associated with induction effects during the formation of chemisorbed complexes ([8]). In this sense the heat of adsorption must change with filling, as is the case in chemical adsorption on semiconductors ([16]).

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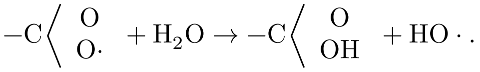
* The presence of carbonyl groups on the surface has been confirmed ([3]).

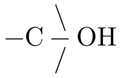
As the next stage of the investigations, it was of interest to measure the heats of adsorption of water vapor on the oxidized graphite sample. For this purpose, after completion of the cycle of measurements with oxygen, the graphite sample (without contact with air) was evacuated to a vacuum of 10^{-5} mm Hg and brought into contact with water vapor. The results of measuring the differential heats of adsorption of water are given in Fig. 2, from which it is seen that the initial heats (40 kcal/M) considerably exceed the heats of physical adsorption of water and apparently characterize the formation of hydroxyl groups on the graphite surface. As the coverage increases, the heat decreases and, at coverages of 0.5–0.6 $\mu M/m^2$, approaches the heat of condensation. As was shown earlier (3), the magnitude of the irreversible adsorption of water on this graphite was 0.4 $\mu M/m^2$, which agrees well with the region of the most significant heat values characteristic of the occurrence of chemical adsorption. It is necessary to note the very slow kinetics of heat evolution in this region of coverages (4–5 h). At higher coverages, physical adsorption predominated for the most part; the kinetics of heat evolution accelerated considerably and amounted to 1-1.5 h. The good agreement of the data obtained on different samples indicates the reproducibility of the processes under study.

The interaction of a water molecule with the oxygen groups of graphite probably leads to the formation of hydroxyl groups, for example:



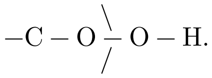
$$-C\left\langle{O \atop O\cdot}\right. + H_2O \rightarrow -C\left\langle{O \atop OH}\right. + HO\cdot\,.$$

The hydroxyl radical can form phenolic and alcoholic groups



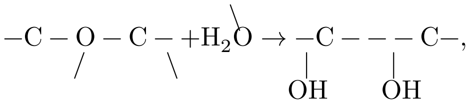
$$-C\overset{\diagdown}{\underset{/}{-}}OH \qquad (3)$$

or hydroperoxide groups



$$-C-O\overset{\diagdown}{\underset{/}{-}}O-H.$$

In the region of lower heat values, hydration of oxygen bridges is possible:



$$-C-\underset{/}{O}-C\underset{\diagdown}{-}+H_2\overset{\diagdown}{O}\rightarrow -\underset{\substack{|\\ OH}}{C}---\underset{\substack{|\\ OH}}{C}-,$$

similar to what was assumed in the hydration of graphite oxide (17). In this case the heat values are small and are to a certain extent determined by the strain of the bonds. Any accurate calculations here are likewise impossible because of the above-mentioned induction effect in the conjugated system of bonds. The differential heats of secondary adsorption, measured on a graphite sample after prolonged exposure in an atmosphere of saturated water vapor, differ little even in the initial region from the heat of condensation and characterize the physical adsorption of water. Earlier (10, 18) the view was expressed that water is adsorbed on the oxygen complexes of carbon through a hydrogen bond. In a number of works (10, 18, 20, 21) a strong dependence was shown of the adsorption and heats of adsorption of water vapor on the degree of oxidation of coals and carbon blacks. However, in most of these works (19, 20) the adsorption measurements and measurements of heats of adsorption were not accompanied by analysis of the surface of the adsorbents studied. M. M. Dubinin and V. V. Serpinsky (10) proposed an adsorption equation that describes well the adsorption of water on carbon adsorbents and makes it possible to estimate the number of primary adsorption centers a_0. The calculation carried out in (3) led to a value of $a_0 = 5\ \mu M/m^2$, which is close to the value of irreversibly adsorbed oxygen ($4.5\ \mu\mathrm{E}/m^2$) (3).

The heats of adsorption on oxidized and hydrated graphite are close to the heat of condensation (Fig. 2). Water molecules form, on average, two hydrogen bonds with oxygen groups and hydroxyls on the surface. Apparently, adsorption on isolated hydroxyl groups is slight.

probable. Because of the poor transparency of graphite bodies, it is still difficult to obtain any reliable data on the adsorption mechanism by means of infrared spectroscopy. At present we are attempting to use the method of nuclear magnetic resonance for this purpose.

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REFERENCES

1. G. G. Fedorov, Yu. A. Zarif' yants, V. F. Kiselev, DAN, **139**, 1166 (1961).
2. Ju. A. Zarifianz, V. F. Kiselev, G. G. Fedorow, Proc. of the Fifth Intern. Symp. on Free Radicals, University of Upsala, Sweden, 1961.
3. Yu. A. Zarif' yants, G. G. Fedorov, V. F. Kiselev, N. N. Lezhnev, DAN, **143**, No. 6 (1962).
4. M. J. Marshall, H. E. Bramston-Cook, J. Am. Chem. Soc., **51**, 2019 (1929).
5. A. Lendle, Zs. Phys. Chem., A **172**, 77 (1935).
6. H. J. Bull, M. Hall, W. E. Garner, J. Chem. Soc., **1931**, 837.
7. T. S. Egorova, Yu. A. Zarif' yants, V. F. Kiselev, V. V. Murina, ZhFKh, No. 6 (1962).
8. N. N. Semenov, *On Certain Problems of Chemical Kinetics and Reactivity*, Publishing House of the USSR Academy of Sciences, 1958, p. 219.

9. V. N. Kondrat' ev, *Structure of Atoms and Molecules*, Moscow, 1959, p. 508.

10. M. M. Dubinin, in: *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 9.

11. D. Ingram, *Electron Paramagnetic Resonance in Free Radicals*, Moscow, 1961, p. 269.

12. J. Koutezký, H. Tomachek, Phys. Rev., **120**, 1212 (1960).

13. Yu. D. Tsvetkov, S. Lebedev, V. V. Voevodskii, Vysokomolek. soed., **1**, 1634 (1959).

14. Yu. D. Tsvetkov, Yu. N. Molin, V. Voevodskii, Vysokomolek. soed., **1**, 1805 (1959).

15. S. Lewina, A. Frumkin, A. Lunew, Acta Physicochim. USSR, **3**, 397 (1935).

16. F. F. Vol' kenshtein, *Electronic Theory of Catalysis on Semiconductors*, Moscow, 1960.

17. J. H. DeBoer, A. B. C. van Doorn, Proc. Koninkl. Akad. Wett., B**61** (3), 160 (1958).

18. M. M. Dubinin, E. D. Zaverina, DAN, **92**, 111 (1953).

19. C. Pierce, R. N. Smith, J. W. Wiley, H. Cordes, J. Am. Chem. Soc., **73**, 4551 (1951).

20. N. N. Avgul' , *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 34.

21. M. M. Dubinin, E. D. Zaverina, Izv. AN SSSR, OKhN, **1956**, 1038.

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