correct the increase in the $C^{13}O^{18}$ concentration would be explained if the extent of the exchange is greatest on the portions of the surface where the CO is most strongly bonded. In this case the $C^{13}O^{18}$ concentration in the desorbed gas would not be the same as in the gas remaining on the surface.

If the exchange proceeds uniformly over the entire surface and the increase in $C^{13}O^{18}$ concentration is due to the increases in temperature, the $C^{13}O^{18}$ concentration in the desorbed gas would represent the concentration in the gas remaining on the surface. Since the CO_2 formed during carbiding is in isotopic equilibrium with the carbon monoxide pumped off simultaneously, it appears that at 60° or above, the $C^{13}O^{18}$ concentration in the desorbed carbon monoxide is the same as that in the gas remaining on the surface. This is based on the assumption that the oxygen exchange and carbide formation are independent processes so that one would not expect them to be in isotopic equilibrium unless the CO_2 was formed from carbon monoxide which had the same $C^{13}O^{18}$ concentration as the carbon monoxide pumped off.

The effect of a gas phase in markedly increasing the extent of exchange could be due to two factors. The gaseous phase could simply provide a means of transporting chemisorbed carbon monoxide from inactive to active parts of the surface. It is known that under these conditions exchange of CO molecules between the gaseous and chemisorbed phases is rapid and complete.[9] The second factor is the maintenance of a fully covered surface by the gaseous phase. On a sparsely populated surface there are few pairs of adjacent molecules and exchange depends upon surface migration. According to this concept the apparent exchange rate would become slower as coverage decreased even on a uniform surface. By increasing the gas phase pressure the full coverage rate is maintained at the higher temperatures. At present there are not enough data to clearly differentiate between the transport and full coverage mechanism. The full coverage mechanism appears more plausible because it is consistent with the uniform surface concept indicated by the formation of CO_2 in isotopic equilibrium with the CO.

It is apparent that the discovery that oxygen exchange occurs in chemisorbed CO poses more questions than it answers. Despite the difficulties found in trying to arrive at unreserved conclusions it appears that the oxygen exchange will prove to be valuable in the study of how the nature of CO is modified by chemisorption.

We are grateful to Dr. L. C. Roess for his interest and encouragement and to J. H. Shively and M. S. Donovan who carried out the mass spectrometric analyses.

BEACON, N. Y.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Low Temperature Heat Capacity of Ceylon Graphite

BY WARREN DESORBO

RECEIVED DECEMBER 3, 1954

Low-temperature specific heat data are presented in the temperature region 17 to 300°K. for a Ceylon natural graphite. The data and the thermodynamic functions derived therefrom are compared with those previously reported for a graphite sample having a smaller crystallite size.

Introduction

There can be a considerable difference in particle size between natural and artificial graphites.[1] What influence this variation in crystallite size has on the specific heat has not been reported. The problem is complicated by the fact that the specific heat of graphite is very small at low temperatures, and the substance can easily become contaminated by various gaseous adsorbates. Furthermore, lattice irregularities (presence of turbostatic structures, faulting, twinning, edge effects on the crystallites, lattice strain, etc.) and the presence of intergranular, non-graphitic carbon can also influence a graphite's thermal properties. Discrepancies in the low temperature specific heat[2] and thermal conductivity[3] of graphite have been reported recently. The theoretical aspects of specific heat of graphite have recently been summarized by Newell.[4]

The present experiment was undertaken to find out if a particle-size effect on the specific heat of graphite could be measured. The specific heat of a Ceylon natural graphite is reported and compared with the results obtained earlier[5] on an Acheson graphite, CS grade. These two samples differed in their crystallite size, as evidenced by X-ray analysis. Both samples had been purified earlier by an identical method.

Experimental

The high-purity Ceylon natural graphite studied in this investigation was obtained from the Great Lakes Corporation.[6] Approximately 84 g. (6.974 gram-atoms) of large "foliated" crystals were selected and sealed in the copper calorimeter. The calorimeter cryostat and accessory equipment used in this work have been described previously.[7] Identical techniques were employed, as in the study on the CS grade sample.[5]

Between liquid hydrogen temperature and the ice point the accuracy of the measurements is about 0.5%. In the liquid hydrogen temperature region, the data are accurate to approximately 4 to 5%. Higher drift rates than those

---

[1] J. P. Howe, *J. Am. Ceramic Soc.*, **35**, 275 (1952) (contains bibliography on structure of graphite).

[2] U. Bergenlid, R. W. Hill, F. J. Webb and J. Wilks, *Philosophical Mag.*, **45**, 851 (1954).

[3] A. W. Smith, *Phys. Rev.*, **95**, 1095 (1954).

[4] G. F. Newell, "Specific Heats of Lamellar Crystals," Technical Report Contract No. Nonr-562 (08), Brown University, December 15, 1954.

[5] W. DeSorbo and W. W. Tyler, *J. Chem. Phys.*, **21**, 1660 (1953).

[6] Sample loaned to the writer by Dr. W. W. Tyler, Knolls Atomic Power Laboratory, now with the General Electric Research Laboratory.

[7] W. DeSorbo, THIS JOURNAL, **75**, 1825 (1953).

experienced in the study of the CS grade graphite gave an uncertainty in the measurements of about 2% in the room temperature region.

Results and Discussion

The observed data are given in Table I. The temperature difference, ΔT, in the measurements has a value of approximately two degrees at the lowest temperatures, increasing to approximately five degrees at 100°K. Above the ice point the value of ΔT is less than four degrees. In Table II are listed the values of the thermodynamic functions obtained from a smooth curve of large plots of specific heats *vs.* T and of specific heats *vs.* log T with the aid of Simpson's rule. These functions have been evaluated at convenient intervals of temperatures up to 300°K.

TABLE I

SPECIFIC HEAT OF CEYLON NATURAL GRAPHITE

Mean temp. (°K.)	C_p, cal. (g.-atom. deg.)$^{-1}$	Mean temp. (°K.)	C_p, cal. (g.-atom. deg.)$^{-1}$
17.70	0.0135	143.90	0.679
18.46	.0174	148.51	.721
21.65	.0200	156.69	.790
23.45	.0233	169.88	.863
25.47	.0267	178.12	.954
27.92	.0314	189.64	1.034
31.25	.0434	195.16	1.046
33.31	.0538	202.28	1.117
35.76	.0603	208.75	1.172
38.64	.0767	216.79	1.238
41.63	.0863	223.28	1.284
44.75	.0975	229.27	1.315
47.87	.106	233.61	1.380
51.66	.122	235.64	1.376
55.67	.144	241.62	1.412
59.78	.171	242.02	1.411
63.94	.193	247.78	1.477
68.06	.204	249.61	1.491
72.14	.231	253.36	1.510
76.11	.266	260.20	1.570
83.14	.304	261.54	1.586
88.05	.327	265.40	1.573
93.06	.362	265.42	1.637
97.88	.378	270.77	1.635
102.48	.409	271.08	1.641
106.86	.442	276.41	1.713
111.16	.468	279.62	1.694
115.93	.507	281.47	1.716
120.92	.536	287.75	1.777
125.96	.560	290.87	1.824
130.37	.600	293.29	1.822
134.89	.623	294.69	1.844
139.32	.651	295.78	1.829
		300.45	1.905

TABLE II

THERMODYNAMIC FUNCTIONS OF CEYLON NATURAL GRAPHITE BASED ON THE SMOOTH CURVE OF HEAT CAPACITY

T, °K.	C_p, cal. (g.-atom. deg.)$^{-1}$	$H^0 - H_0^0$, cal. (g.-atom.)$^{-1}$	S^0, cal. (g.-atom. deg.)$^{-1}$	$-\left(\frac{F^0 - H_0^0}{T}\right)$ cal. (g.-atom. deg.)$^{-1}$
16	0.0162	0.0664	0.0062	0.0021
25	.0260	.2395	.0147	.0051
50	.1215	1.9395	.0578	.0191
75	.2528	6.5804	.1316	.0438
100	.4010	14.720	.2243	.0771
125	.5566	26.684	.3305	.1170
150	.7297	42.697	.4469	.1622
175	.9123	63.201	.5730	.2118
200	1.101	88.350	.7072	.2655
225	1.291	118.245	.8482	.3227
250	1.486	152.957	.9946	.3828
275	1.684	189.222	1.1456	.4575
298.16	1.874	230.030	1.2895	.5180
300	1.889	233.462	1.3010	.5228

Spectrographic analysis[8] of the CS material shows it to contain silicon and bismuth in "trace" amounts plus magnesium in "slight trace." The same analysis carried out on the Ceylon natural sample revealed the presence of magnesium in "trace (slight)" only. Total ash content was found to be 0.2% for the CS sample and 0.06% for the Ceylon material.[9] The results of the X-ray analysis on both samples were obtained by Roth.[10] His report reads in part that "the Ceylon natural graphite is pure graphite and gives sharp three-dimensional diffraction maxima. There is no detectable broadening of the lines under our experimental arrangement, which means the crystals are larger than 400 Å. The CS sample, 'high purity Acheson,' also is pure graphite and gives a three-dimensional diffraction pattern. There is slight broadening of the 00.L maxima, corresponding to a crystallite size in the C direction of about 230 Å."[10]

A definite difference in the specific heat between the CS grade and the Ceylon natural graphite has been detected in the temperature region 120 to 300°K. In this region the specific heat of the CS graphite is larger than that of the Ceylon natural graphite. The difference is larger than the experimental precision of both experiments and cannot be accounted for by the small difference in ash content. A comparison of the smooth C_p data of this paper with those reported earlier for the CS graphite[5] shows that a maximum in $\Delta C_p/C_p$ occurs at approximately 250°K. ($\Delta C_p/C_p$ = 0.090.)[11] For CS grade graphite, $(H^0 - H_0^0)_{298.16°\text{K.}} = \pm 251$ 2 cal. (g.-atom)$^{-1}$ and $S^0_{298.16} = 1.372 \pm 0.005$ cal. (g.-atom deg.)$^{-1}$, while for Ceylon natural graphite $(H^0 - H_0^0)_{298.16} = 230 \pm 4$ cal. (g.-atom)$^{-1}$ and $S^0_{298.16} = 1.29 \pm 0.01$ cal. (g.-atom deg.)$^{-1}$. The evaluations of entropy and enthalpy increments between absolute zero and the lowest experimental point in each case have been approximated by assuming a heat capacity proportional to T^3.

At present, not much information is available on how various factors influence the specific heat of graphite. However, it is noteworthy that the above results do resemble in part those on specific heats and size effect recently reported by Dugdale, Morrison and Patterson.[12,13]

---

(8) Carried out by L. B. Bronk of our laboratory.

(9) These results were obtained by digesting sample with concentrated HNO_3 and H_2SO_4 followed by ignition at 1000° (as reported by E. L. Simons of our laboratory).

(10) W. L. Roth, private communication.

(11) Smooth values of C_p for CS graphite presented in Table II of a previous paper[5] contain two typographical errors. At 200°K., C_p should read 1.190 instead of "1.180" and at 225°K., C_p should read 1.406 instead of "1.461."

(12) J. S. Dugdale, J. A. Morrison and D. Patterson, *Proc. Roy. Soc.* (*London*), **A224**, 228 (1954).

(13) If the difference in the specific heat of graphite reported here

is due to the difference in crystallite size only, then one could possibly calculate "crystallite boundary" tension, energy and entropy of graphite provided that certain essential information is also available. Further data necessary would be the difference in surface area of the crystallites in the two samples and the difference in the heats of combustion.[14] If the surface area measurements on the CS grade graphite and the average heats of combustion between Ceylon natural graphite and the CS material reported by Bupp and associates[15] are used, the crystallite boundary entropy of graphite is roughly 4.8 ergs cm.$^{-2}$ deg.$^{-1}$ g-atom.$^{-1}$. The value of heat content for the crystallite surface is 1950 ergs cm.$^{-2}$, while the crystallite boundary tension is 530 ergs cm.$^{-2}$.

Acknowledgments.—The author wishes to thank A. J. Peat, Mrs. E. L. Fontanella and A. C. Wilson, Jr., for their assistance in the operation of the calorimeter and data computation. Discussions with W. L. Roth are also gratefully acknowledged.

These values are probably reliable only as to order of magnitude.

(14) G. Jura and C. W. Garland, THIS JOURNAL, **74**, 6033 (1952).

(15) L. P. Bupp, private communication.

SCHENECTADY, N. Y.

[CONTRIBUTION NO. 1296 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

On the Detailed Mechanism of a New Type of Catalase-like Action

BY JUI H. WANG

RECEIVED APRIL 18, 1955

A model catalyst was constructed for the catalytic decomposition of hydrogen peroxide. The detailed mechanism of this new type of catalase-like action was studied with respect to ligand specificity, metal ion specificity, inhibition and activation by other ions and the isotope-effect. Comparison of the model catalysts with natural catalases was made and the similarities were briefly discussed.

The elucidation of the detailed mechanisms of enzyme action is a problem of common interest to physico- and bio-scientists. At the present time the major difficulty of this problem seems to be due to our lack of knowledge on the detailed structure of enzyme molecules. While the complexity of the detailed structures of these molecules shows little promise of their complete elucidation in the near future, this important problem of enzyme action may meanwhile be approached from a new angle, *i.e.*, by constructing and studying small model molecules with enzyme-like activity. This paper presents some first results obtained in a research project planned in this direction. The general method of approach in this project may be summarized as follows. Firstly, with the help of our knowledge on the structure of the substrate molecule, properties of the corresponding enzyme and the nature of the chemical bond, small model molecules with possible enzyme-like activity are designed, synthesized and tested for their catalytic activity. Secondly, detailed kinetic and structural studies will be carried out on those synthetic molecules with outstanding catalytic activity. Finally, attempts will be made to improve the catalytic activity of these model molecules by modifying their structure and by incorporating them, if necessary, into the structure of macromolecules. It is the hope of the present writer that the results obtained in this direction could accelerate our present pace of progress toward the understanding of enzyme action.

The decomposition of hydrogen peroxide is catalyzed by a large variety of substances.[1] But molecule for molecule, none can compete with catalases for catalytic efficiency. Even hematin and hemoglobin are about 10^7 times less efficient as compared to catalases according to Lemberg and Legge.[2]

It was reported in a recent communication that a very efficient model catalyst for the decomposition of hydrogen peroxide can be made by combining triethylenetetramine (TETA), $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, with ferric ion.[3] The results of a more extensive study on the catalytic action of this model catalyst, $(TETA)Fe(OH)_2^+$, and related compounds are given below.

The Catalytic Mechanism.—It was pointed out earlier[3] that steric considerations show that it is energetically improbable to have the four N atoms and the Fe^{III} ion in $(TETA)Fe(OH)_2^+$ located in one plane, but that the structure with one primary amine N atom above and the other below the plane determined by the two secondary amine N atoms and the Fe^{III} ion is stable. The detailed mechanism of the catalytic action of $(TETA)Fe(OH)_2^+$ for the decomposition of hydrogen peroxide is illustrated in Fig. 1. The configuration of $(TETA)Fe(OH)_2^+$ is depicted by structure I in Fig. 1. In the presence of hydrogen peroxide the two attached OH^- ions in compound I may be replaced by an OOH^- ion, yielding compound II. But since the O–O bond length in OOH^- is only about 1.3 Å., compound II is unstable and tends to stretch the O–O bond until compound III is formed. Direct splitting of the O–O bond in an isolated H_2O_2 molecule requires about 35 kcal. of activation energy per mole. But in the above reaction mechanism the energy consumed in splitting the O–O bond is partially compensated by the energy gained through the formation of more stable Fe–O bonds, because the O atom and the OH^- ion are now separate ligands and can orient themselves for maximum overlapping with the two vacant octahedral d^2sp^3 hybrid atomic orbitals of the Fe^{III}. The binding between the O atom and Fe^{III} in compound III is probably not a single covalent bond. It probably involves a considerable amount of a one-electron bond (depicted by the dotted line in Fig. 1) in addition to an ordinary electron-pair bond. Compound III can then readily react with a second OOH^- ion to yield O_2 and regenerate compound I. This cyclic mechanism was

---

(1) For reference to the literature see a comprehensive review by J. H. Baxendale in "Advances in Catalysis" (Edited by W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal), Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 31.

(2) R. Lemberg and J. W. Legge, "Hematin Compounds and Bile Pigments," Interscience Publishers, Inc. New York, N. Y., 1949, p. 402.

(3) J. H. Wang, THIS JOURNAL, **77**, 822 (1955).