

samples of mercury from the following sources: cinnabar from Gölnicz, Hungary; Almaden, Spain; Palatinate, Bavaria; Idria, Dalmatia; California, United States; Santafiore, Italy; Ras el Mah, Tunis; commercial cinnabar; calomel, and mercury oxychloride from Terlingua, Texas, United States. The results agreed within 0.0004–0.0012 unit in the atomic weight.

Since the last report, evidence concerning the isotopic character of the following elements has been published.

ISOTOPES				
	Atomic number	Atomic weight	Minimum number of isotopes	Masses of isotopes in order of abundance
Be <sup>32</sup> .....	4	9.02	1	9
Al <sup>33</sup> .....	13	26.96	1	27
Ca <sup>34</sup> .....	20	40.07	(2)	40, (44)
Fe <sup>35</sup> .....	26	55.84	(1)	56, (54?)
Zn <sup>34</sup> .....	30	65.37	4	64, 66, 68, 70
Se <sup>33</sup> .....	34	79.2	6	80, 78, 76, 82, 77, 74
Sn <sup>36</sup> .....	50	118.70	7 (8)	120, 118, 116, 124, 119, 117, 122 (121)

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

### SOME PROPERTIES OF GRAPHITE

By R. M. BURNS AND G. A. HULETT

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The determination of the density of a porous solid by the liquid immersion method is affected by the ability of the liquid to penetrate the smaller capillaries of the solid. The speed of this penetration may be slow, measurable, and may result in a "drift," or increase in the weight with time after immersion in the liquid, as has been shown in the case of charcoal with a variety of liquids.<sup>1</sup> The rate of penetration was found to be proportional to the product of surface tension and fluidity of the liquids used. The attainment of a final value for the density which ordinarily might require months may be accomplished in a few hours by the application to the system of an external pressure.<sup>2</sup>

It was with a view to extending the investigation in this field that a study of the density of graphite was undertaken. The work to be described in this paper was done early in 1920.

<sup>32</sup> Thomson, *Phil. Mag.*, **42**, 862 (1921).

<sup>33</sup> Aston, *Nature*, **110**, 664 (1922).

<sup>34</sup> Dempster, *Phys. Rev.*, **19**, 431 (1922).

<sup>35</sup> Aston, *Nature*, **110**, 312 (1922).

<sup>36</sup> Aston, *ibid.*, **109**, 813 (1922).

<sup>1</sup> Cude and Hulett, *THIS JOURNAL*, **42**, 391 (1920).

<sup>2</sup> Ref. 1, p. 399.

Graphite was early recognized as a crystalline form of carbon of density intermediate between amorphous carbon and diamond and which upon oxidation, is capable of forming graphitic acids.<sup>3</sup> More recently, density alone has been considered a safe criterion for the identification of graphite.<sup>4</sup> Le Chatelier<sup>5</sup> found that the densities of a number of different natural graphites and Acheson graphite, gave the value of 2.225, after he had carefully purified them.<sup>6</sup>

Natural graphite consists of minute, hexagonal, closely adherent plates which give it a compactness which is in considerable contrast to the porous nature of charcoal. Nitric acid, however, possesses a specific power of penetrating between these plates and in the oxidation of graphite by the Brodie method, serves as an oxygen carrier in introducing the oxidizing mixture into the flake.<sup>7</sup> Luzi<sup>8</sup> has shown that natural graphites, when moistened with conc. nitric acid and heated, increase most remarkably in volume with the formation of little worm-like dendritic products. Moissan<sup>9</sup> attributed this swelling to a liberation of carbon dioxide and oxides of nitrogen between the plates of graphite, and he found, furthermore, that graphites prepared by dissolving carbon in molten metals showed this same behavior, while those obtained simply by heating amorphous carbon to high temperatures did not display it. Acheson graphite, for example, does not show this property.

In the present work samples of graphite from Ceylon, Alabama, Pennsylvania, and Acheson electrode graphite were chosen for study. These graphites were reduced to a fine state of division by grinding them in a metal ball-mill with steel balls for several hours. From 2 to 5 g. of this material was placed in a small glass bulb with a capillary exit tube which was sealed to a delivery tube leading to a large Toepler vacuum pump.<sup>10</sup> The sample was raised to 445° by surrounding the bulb with vapors of boiling sulfur, evacuated and then sealed off. It required from 2 to 6 hours to obtain a vacuum of 0.002 mm. Lowry and Hulett have shown in the case of charcoals<sup>11</sup> that adsorbed gases and vapors are completely removed when the sample of charcoal is evacuated at 184° but that the

<sup>3</sup> Berthelot, *Ann. chim. phys.*, [4] **19**, 392 (1870).

<sup>4</sup> Charpy, *Compt. rend.*, **148**, 920 (1909). Arsem, *Trans. Am. Electrochem. Soc.*, **20**, 105 (1911).

<sup>5</sup> Le Chatelier, *Compt. rend.*, **146**, 49 (1908).

<sup>6</sup> Le Chatelier's method of determining the density of graphite was to place the sample in ethylene bromide and then add ether until the density of the liquid mixture became equal to that of the graphite sample. Gases were removed from the graphite by boiling for some time in this liquid mixture.

<sup>7</sup> Kohlschutter and Haenni, *Z. anorg. Chem.*, **105**, 121 (1919).

<sup>8</sup> Luzi, *Ber.*, **24**, 4085 (1891); **25**, 214 (1892).

<sup>9</sup> Moissan, "Le Four Electrique," 1897.

<sup>10</sup> For apparatus and method employed see Ref. 1.

<sup>11</sup> Lowry and Hulett, *THIS JOURNAL*, **42**, 1393 (1920).

"fixed" oxygen held in a carbon-oxygen complex is not all pumped off even at 1400°. The evacuated bulb was weighed in the air, then immersed in a pure, air-free liquid, generally water, and the capillary tip broken, thereby permitting the liquid to enter.<sup>12</sup> After 5 to 10 minutes' interval allowed for the disappearance of temperature effects, the sample was weighed in the liquid. Successive observations were made at later intervals so long as an increase in weight occurred. In order to hasten completion of the "drift," an external pressure of several hundred atmospheres was applied to the liquid after transferring the bulb containing the sample to a steel cylinder into which a tight-fitting piston was pressed. The sample bulb was then compressed in the liquid which was used for the immersion.

All values given for density are referred to water at 4°, that is, mass/volume.

**Ceylon Graphite.**—Two different samples of Ceylon graphite containing 3.5% of ash when opened under water gave densities of 2.312 and 2.285. These samples showed practically no increase in weight with time, that is, no "drift." Even applications of external pressure of 660 atmospheres in the first case, and 8500 atmospheres in the second failed to increase these density values. The ash content of this graphite was then reduced to 0.80% by digestion for several hours in hydrofluoric acid. Five minutes after it was opened under water this material gave a density of 1.951 which increased to 2.058 after 9 days and to 2.238 after the application of a pressure of 1600 atmospheres. Further purification of this graphite was accomplished by prolonged treatment with fuming nitric acid followed by digestion with hydrofluoric acid. Analysis of this product gave 0.40% ash. When it was heated, the graphite greatly increased in volume with an apparent evolution of oxides of nitrogen, the reaction first observed by Luzi.<sup>8</sup> When opened under water, carbon tetrachloride and carbon disulfide, this swelled graphite was found to display a marked "drift." Table I shows its increase in density with time when opened under water. These results together with those for all samples of Ceylon graphite are plotted in the form of curves in Fig. 1.

TABLE I

Time after opening under water Min.	Weight of system in H <sub>2</sub> O G.	Density	Time after opening under water Min.	Weight of system in H <sub>2</sub> O G.	Density
5	4.4500	1.047	290	5.3080	1.560
10	4.5500	1.089	380	5.3420	1.590
20	4.6490	1.133	2000	5.4318	1.678
80	5.0550	1.363	4880	5.4660	1.714
140	5.1800	1.450	14 days	5.4880	1.743

After application of 1780 atmospheres' pressure, the weight of the system in water was 5.8225, and the density, 2.207.

<sup>12</sup> For details see Ref. 1, p. 394.

It will be observed that the application of pressure was necessary for the attainment of the final value for the density. Reference to Curves V and VI in Fig. 1 will show that a similar drift was displayed by this graphite when opened under carbon tetrachloride and carbon disulfide. It will be seen that the final value for density in carbon tetrachloride was 2.160,

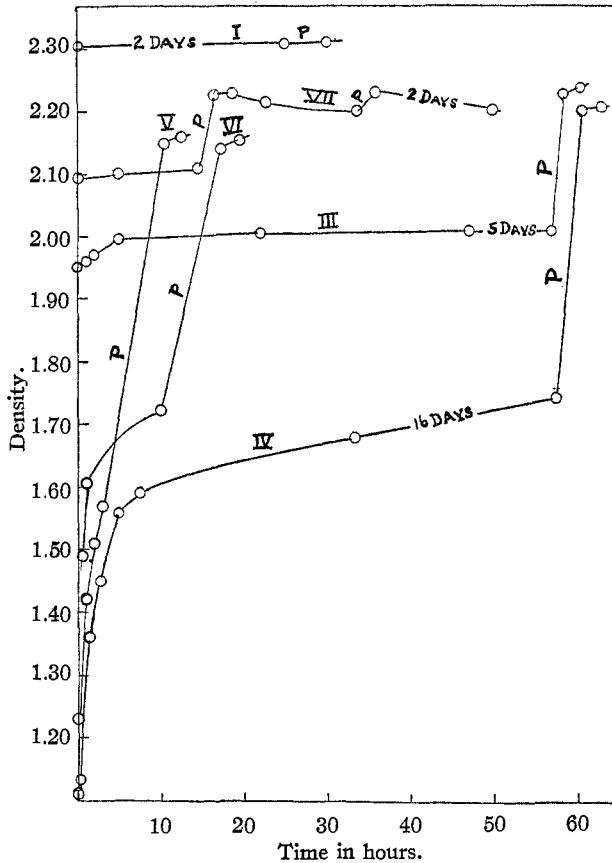


Fig. 1.—I. Original material containing 3.5% ash, opened under water. III. Material in which ash was reduced to 0.8%, opened under water. IV. Swelled material, ash 0.45%, opened under H<sub>2</sub>O. V. Material of IV opened under CCl<sub>4</sub>. VI. Material of IV opened under CS<sub>2</sub>. VII. Material of IV compressed by pressure of 4400 atmospheres, ash 0.45%, opened under H<sub>2</sub>O. P indicates application of pressure of approximately 1500 atmospheres.

and in carbon disulfide, 2.165, both less than that in water. These observations show that when evacuated samples of these swelled graphites are opened under liquids, their behavior is analogous to that of charcoal, and it seems, therefore, that the swelling of graphite is accompanied by an enormous increase of volume (porosity). In an attempt to decrease the

extent of this porosity, a portion of the swelled material was placed in a small steel cylinder with a piston and subjected to a compression of approximately 4400 atmospheres.

A subsequent density determination made in water showed that the drift previously displayed had been largely destroyed by this compression. Compare Curve VII with Curve IV in Fig. 1.

The determinations made in water indicate that 2.20 is the best value for the density of this Ceylon graphite containing 0.4% of ash.

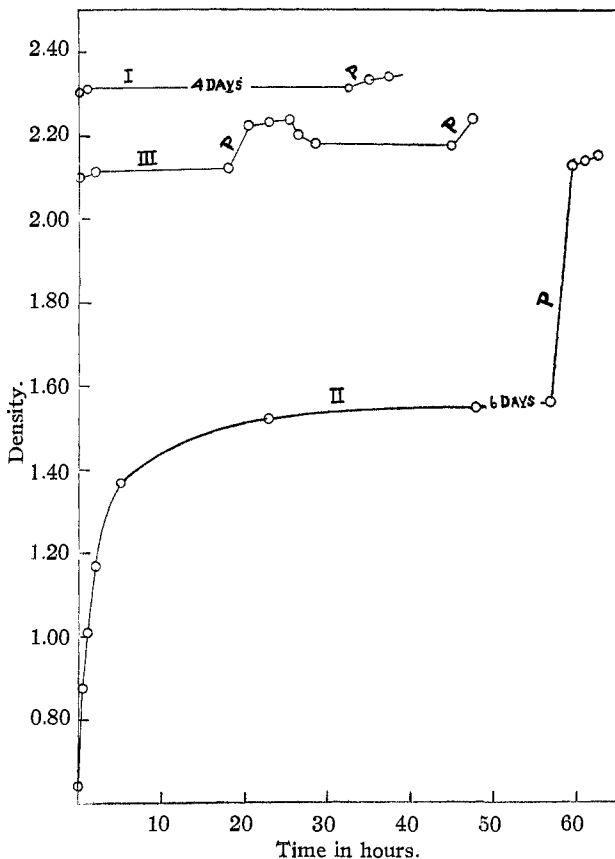


Fig. 2.—I. Original material, ash 4.0%, opened under water. II. Swelled material, ash less than 1.0%, opened under water. III. Swelled material compressed by 4400 atmospheres, opened under water. P indicates application of pressure of approximately 1500 atmospheres.

**Alabama Graphite.**—Alabama graphite containing 4% of ash gave a density of 2.339 and displayed only a slight drift when opened under water, which was only slightly affected by pressure. The data for Alabama graphite are given in the form of curves in Fig. 2. After being subjected to the

swelling treatment this graphite showed a pronounced drift which, like that displayed by Ceylon graphite, was practically destroyed by compressing the swelled material previous to the density determination. Curve III in Fig. 2 shows the maximum value of 2.24 for density immediately after release of the external pressure from the system, and that after 2 hours it had declined to an equilibrium value of 2.176. The same phenomenon was shown by Ceylon graphite after similar treatment.

**Pennsylvania Graphite.**—Pennsylvania graphite containing about 4% of ash showed densities of 2.385 and 2.318 when determined in water. After being treated with acids and swelled, this material displayed a drift analogous to that shown by Ceylon and Alabama graphites and gave a value of 2.065 in water.

**Acheson Graphite.**—Acheson electrode graphite ground to a fine powder and containing 0.1% of ash was opened under water and gave an initial value of 2.246, for density. One day later this had drifted to 2.247, while a density observation made immediately after an application of 2000 gave a value of 2.310.

**Carbon from Graphitic Acid.**—When graphitic acid is heated it explodes with the formation of a large volume of an extremely finely divided and fluffy material described in the literature as *amorphous* carbon. The density of this material was determined in the usual way by opening a tube of it under water and was found to drift from 1.820 to a final value of 2.215, after an application of a pressure of 660 atmospheres to the system. It seems certain, therefore, that this material is graphite and not amorphous carbon, as has been assumed from its light fluffy nature and extremely fine state of division.

Natural graphites in spite of their plate-like structure seem to show no drift, or slow penetration of liquid between the plates. But in each case, after the ground material has been extracted with acids to remove impurities and heated to produce the large volume increase first shown by Luzi, the product shows a marked drift, and a final value of approximately 2.20 for density.

This value is probably very close to the density of graphite since it is in agreement with the value (2.215) shown by the exceedingly finely divided and pure graphite obtained by exploding graphitic acid.

### Summary

1. The densities of natural graphites from Ceylon, Alabama, and Pennsylvania, Acheson electrode graphite, and carbon produced by the explosion of graphitic acid, were determined by the liquid immersion method.

2. The density of pure natural graphite appears to be about 2.20, and that of Acheson graphite about 2.30.

3. Carbon produced by the explosion of graphitic acid showed a density of 2.215, and is, therefore, probably graphite.

4. Samples of the graphites originally showed no "drift" or increase in weight with time after immersion in the liquid. The natural graphites, however, after being swelled, or increased in volume by treatment with fuming nitric acid and heat, displayed remarkable drifts. Pressure was used to hasten completion of the drift.

5. The tendency to drift was largely destroyed by a severe compression of the swelled material previous to the density determination.

PRINCETON, NEW JERSEY

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY,  
No. 398]

## THE VAPOR PRESSURES OF CERTAIN HYDRATED METAL SULFATES

BY CLIFFORD D. CARPENTER AND ERIC R. JETTE

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A review of the literature not only reveals a striking incompleteness in the experimental data on the vapor pressure of hydrates, but considerable discrepancy in much of the corresponding data given.

Soon after Vogel<sup>1</sup> observed that blue vitriol effloresces rapidly over sulfuric acid Watson<sup>2</sup> made what appears to be the first attempt to measure the vapor pressure of a hydrate. Since that time many investigators have made such measurements, but as Wilson<sup>3</sup> has recently pointed out, the work "prior to 1875 had little scientific value owing chiefly to the hazy notions which prevailed as to the nature of the phenomenon." Although Gibbs<sup>4</sup> formulated the phase rule in 1877, it does not seem that investigators in this field realized its merits until about 15 years later. It is interesting to note that Andrae,<sup>5</sup> apparently unfamiliar with the phase rule 14 years after its proposal, interpreted the results of some vapor-pressure measurements of hydrates in accordance with the requirements of those of the phase rule. It is also evident that some of the other investigators of this period understood the general nature of the requirements for defining the point of equilibrium between the various phases.

Although much of the earlier data is unsatisfactory, considerable progress was made in developing methods for the measurement of vapor pressures. It will not be necessary, however, to discuss these methods in detail, for extensive bibliographies and discussions of the more important investigations have been given by Johnston<sup>6</sup> on hydroxides and carbonates, by Smith and Menzies<sup>7</sup> on general methods as applied to all phases of the subject, by Menzies<sup>8</sup> on "Apparent Anomalies Outstanding in the Results of

<sup>1</sup> Vogel, *Schweigger's J.*, **22**, 160 (1818).

<sup>2</sup> Watson, *J. prakt. Chem.*, **14**, 112 (1838).

<sup>3</sup> Wilson, *THIS JOURNAL*, **43**, 704 (1921).

<sup>4</sup> Willard Gibbs, *Trans. Connecticut Acad.*, **1874-1878**.

<sup>5</sup> Andrae, *Z. physik. Chem.*, **7**, 241 (1891).

<sup>6</sup> Johnston, *ibid.*, **62**, 330 (1908).

<sup>7</sup> Smith and Menzies, *THIS JOURNAL*, **32**, 898, 907, 1412, 1434, 1449, 1541 (1910).

<sup>8</sup> Menzies, *ibid.*, **42**, 1951 (1920).