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The Magnetic Susceptibility of Bromine-Graphite

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The magnetic susceptibilities of graphite and bromine-graphite have been measured. Possible structures of bromine-graphite are discussed.

INTRODUCTION

IF graphite is exposed to an atmosphere containing bromine vapor, bromine is intercalated¹ between the layer planes of the graphite lattice; the substance thus formed is known as "bromine-graphite." Rüdorff¹ has found that the bromine-graphite which is formed, at room temperature, in the presence of an atmosphere continuously saturated with bromine vapor has the empirical formula: C_6Br . If this "saturated" bromine-graphite is allowed to stand in air, more than 90 percent of its bromine is lost to the atmosphere.

Considerations based on x-ray analyses¹ of saturated bromine-graphite exclude the possibility that the greater part of the intercalated bromine is present in ionic form and this, together with the rapid decomposition of the substance in air, has lead Rüdorff to the conclusion that either atomic or molecular bromine occupies interlamellar positions in the graphite lattice.

Since the feeble diamagnetism² of molecular bromine is essentially temperature independent, and since atomic bromine should possess a strong paramagnetic susceptibility³ which is temperature dependent, it was thought that measurements of the magnetic susceptibility of bromine-graphite might lead to a more detailed knowledge of its electronic structure.

EXPERIMENTAL PROCEDURE

Apparatus

Magnetic susceptibilities were determined by the Gouy method. A partitioned Gouy tube similar to that described by Freed⁴ was used. The lower half of the tube was permanently evacuated; the upper half was packed with the sample up to a mark near the top. The tube was suspended in a Pyrex jacket filled with dry nitrogen, and nitrogen was circulated through the upper portion of this jacket to prevent the diffusion of air into the atmosphere around the Gouy tube. The jacket and its contents were surrounded by a Dewar flask which was shaped to fit between the pole pieces of an electromagnet (Consolidated Engineering Corporation's Model 23-104A). Calibrated copper-constantan thermocouples, inserted in the space between the Gouy tube and the

jacket wall, were employed to measure the temperature of the sample.

The current which passed through the magnet coils also flowed through a 0.005 ohm resistor; the potential drop due to this resistor was measured with a Rubicon potentiometer (Model 2732). It was found that a given magnet current could be reproduced with a precision of ± 0.2 percent.

Magnetic susceptibilities were calculated with the aid of the following formula:

$$X = \left[\frac{(\Delta W_p - \Delta W_N) \kappa_{H_2O}}{\Delta W_{H_2O} - \Delta W_N} - \kappa_A (1 - \rho/\rho') \right] 1/\rho,$$

where X is the gram susceptibility, ΔW_p is the apparent change in weight of the Gouy tube (upper half filled with powder) occasioned by the magnetic field, κ is the cm^3 susceptibility, ρ is the density of the powdered sample, and ρ' is the density of the solid component of the powder.

The subscripts p , N , H_2O , and A refer to the powdered sample, nitrogen, water, and air, respectively.

The Gouy tube was calibrated with water distilled through a Barnstead still and reboiled, immediately before measurement, to expel oxygen. The cm^3 susceptibility⁵ of this water was assumed to be -0.720×10^{-6} at 20°C . The calibration was checked with benzene purified according to the procedure described previously.⁶ The value obtained for the benzene, using the above value for water, was -0.706×10^{-6} at 26°C , which is in satisfactory agreement with the value -0.7020×10^{-6} at 20°C found by French and Trew.⁷

The correction for air in the powdered samples was made in the manner described by Hutchison and Elliott.⁸

Magnetic measurements were made at field strengths corresponding to potentiometer readings of 20.00 mv and 40.00 mv. These field strengths, as estimated from the data used to calibrate the Gouy tube, were 6.4 and 9.3 kilogauss respectively.⁹

⁵ P. W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York, 1943), pp. 45-46.

⁶ M. Goldsmith and G. W. Wheland, *J. Am. Chem. Soc.* **70**, 2632 (1948).

⁷ C. M. French and V. C. G. Trew, *Trans. Faraday Soc.* **41**, 439 (1945).

⁸ C. A. Hutchison, Jr. and N. Elliott, *J. Chem. Phys.* **16**, 924 (1948).

⁹ E. C. Stoner, *Magnetism and Atomic Structure* (Methuen and Co. Ltd., London, 1926), p. 40.

¹ W. Rüdorff, *Zeits. f. anorg. u. allg. Chem.* **245**, 383 (1941).

² International Critical Tables, Vol. 6, p. 354.

³ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), pp. 232-235.

⁴ S. Freed, *J. Am. Chem. Soc.* **52**, 2705 (1930).

TABLE I. Magnetic susceptibilities of graphite and bromine-graphite.

Temp. (°K)	Composition (g Br/g C)	Density (g cm ⁻³)	Approximate field strength (kilogauss)	$-\Delta W_p$ (mg)	$-X \times 10^6$
305	0	0.854	9.3	37.9	5.23
305	0	0.854	6.4	18.2	5.29
75.6	0	0.854	9.3	53.2	7.38
302	0	0.855	9.3	37.3	5.15
302	0	0.855	6.4	18.0	5.22
298	0	0.871	9.3	39.1	5.29
298	0	0.871	6.4	18.7	5.32
75.0	0	0.871	9.3	54.5	7.43
298	0.051	0.671	9.3	23.6	4.17
298	0.051	0.671	6.4	11.3	4.20
75.6	0.051	0.671	9.3	30.2	5.41
75.6	0.051	0.671	6.4	14.4	5.42
296	0.051	0.694	9.3	24.1	4.13
76.0	0.051	0.694	9.3	31.0	5.37
298	0.67	0.881	9.3	1.99	0.31
298	0.67	0.881	6.4	0.932	0.31
75.6	0.67	0.881	9.3	1.38	0.29
299	0.71	0.856	9.3	1.95	0.31
75.6	0.71	0.856	9.3	1.25	0.29

The values of ΔW_N , 0.098 mg at 6.4 kilogauss and 0.184 mg at 9.3 kilogauss, were temperature independent from 75°K to room temperature. The "tube constant," $(\Delta W_{H_2O} - \Delta W_N)/\kappa_{H_2O}$, was 4.068×10^6 at 6.4 kilogauss and 8.558×10^6 at 9.3 kilogauss.

Chemical Preparations and Analyses

Bromine-graphite samples were prepared from "SP-1" spectroscopic graphite powder obtained from the National Carbon Company. Spectrographic analysis of this powder revealed less than 1 part per million of the following elements: Ag, B, Be, Bi, Cr, Cu, Fe, Li, Mg, Mn, Ni, Sb, Sn, Ti, and V; less than 2 p/m of: Ba, Co, Na, and Si; less than 20 p/m of: Al, As, Hg, K, Pb, Sr, Zn, and Zr.

The powdered graphite was allowed to stand in a desiccator over Merck Reagent grade bromine for 24 hours; after this time the sample was transferred as rapidly as possible to a Gouy tube. The open Gouy tube was then placed for an additional 24 hours in an atmosphere saturated with bromine vapor.

When its susceptibility had been determined, the weighed sample was transferred to an open weighing bottle which was allowed to stand first in air and then over KOH until it had come to constant weight. The bromine which still remained was determined by combustion of the sample and subsequent precipitation of AgBr. It was found that the bromine-graphite samples contained approximately 0.7 g Br/g C before exposure to air and approximately 0.05 g Br/g C after standing over KOH.

RESULTS AND DISCUSSION

Experimental data and results are tabulated in Table I.

In correcting for the susceptibility of air in the various powders, the x-ray densities of graphite, bromine-graphite containing 0.05 g Br/g C, and bromine-graphite containing 0.7 g Br/g C have been assumed to be 2.25, 2.3, and 2.6 g/cm³, respectively.

The assumption that the vapor pressure of bromine above bromine-graphite is no greater than the vapor tension of liquid bromine at the same temperature enables one to neglect the contribution of bromine vapor to the magnetic susceptibility of bromine-graphite.

The values in Table I do not indicate the presence of a ferromagnetic impurity; such an impurity would cause the measured susceptibilities to be less diamagnetic at the lower field strength. That the finely powdered graphite crystals have a random, or at least a constant, orientation in the tightly packed Gouy tube is indicated by the precision of the measurements which is within the ± 2 percent usually obtainable when isotropic powders are measured by the Gouy method.

If it is assumed that all the intercalated bromine is present as free bromine molecules, the susceptibility of bromine-graphite may be calculated from Wiedmann's Law:

$$mX = \sum_i m_i X_i,$$

where m is the weight of the mixture, X the gram susceptibility of the mixture, m_i the weight of the i th component of the mixture, and X_i the susceptibility of that component. Applying the appropriate data from Table I and taking the gram susceptibility of molecular bromine² to be -0.4×10^{-6} , we obtain -3.3×10^{-6} at 298°K and -4.5×10^{-6} at 75.6°K as values of the susceptibility of a bromine-graphite sample containing 0.7 g Br/g C. These values are in serious disagreement with the observed values: -0.31×10^{-6} at 298°K and -0.29×10^{-6} at 75.6°K.

On the other hand, the assumption that the sample discussed in the preceding paragraph contains only atomic bromine leads, if one assumes complete quenching of the orbital contribution to the susceptibility, to the values: $+3.3 \times 10^{-6}$ at 298°K and $+21.2 \times 10^{-6}$ at 75.6°K. The differences between observed and calculated values are found to be even greater if one assumes no quenching of the orbital angular momenta.

It is believed that a qualitative explanation of the observed susceptibilities may be given in terms of the band theory of solids. Using the "tight-binding" approximation, Peierls¹⁰ has shown that an important contribution to the susceptibility of an intrinsic semiconductor, such as graphite, is dependent upon the integration, over the surface of the Fermi distribution of

¹⁰ R. Peierls, *Zeits. f. Physik* **80**, 786 (1933).

occupied energy states, of the quantity

$$\frac{1}{|\text{grad}_k E|} \left\{ \frac{\partial^2 E}{\partial k_x^2} \frac{\partial^2 E}{\partial k_y^2} - \left(\frac{\partial^2 E}{\partial k_x \partial k_y} \right)^2 \right\},$$

where, within the confines of a given Brillouin zone, the values of energy (E) which may be assumed by a conduction electron are approximated as the range of a continuous function of the wave vector k , whose components are k_x , k_y , and k_z . (The magnetic field is parallel to the z direction.) It has been re-emphasized by Wallace¹¹ that the "Peierls diamagnetism" of the graphite is strongly dependent upon those electrons which are near the top of the first zone and those near the bottom of the second zone; in addition, Wallace

calculated that the number of electrons in the second zone is only a small fraction of 1 percent of the total number of conduction electrons. One would therefore expect that the removal of these electrons from the second zone would appreciably affect the diamagnetism of graphite; thus the formation of a relatively small number of carbon-bromine covalent or ionic bonds could account for the observed susceptibilities of the bromine-graphite mixtures. This point of view is supported by the fact that the gram susceptibility at room temperature of a bromine-graphite sample containing only 0.05 g Br/g C is 20 percent lower than the susceptibility of pure graphite.

Our data together with those of Rüdorff¹ indicate the possible presence of both molecular bromine and a small number of carbon-bromine bonds in bromine-graphite.

¹¹ P. R. Wallace, Phys. Rev. 71, 622 (1947).

Argon Repulsive Potential from Collision Cross-Section Measurements

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The total collision cross section has been measured for argon atoms, with energies between 300 and 1100 electron volts, scattered in room temperature argon. In the region between 700 and 1000 volts, the cross section shows a maximum indicative of inelastic scattering, probably due to ionization by the high energy atoms.

The repulsive potential between two argon atoms has been evaluated from elastic collision cross sections (deduced from observed values of the total collision cross section) using a method which takes account of the greater probability of small angle scattering by averaging the cross section over the length of the scattering path. The results may be expressed by

$$V(r) = 4.61 \times 10^{-11} / r^{4.38} \text{ ergs}$$

or

$$V(r) = 3.66 \times 10^{-8} \exp(-6.88r) \text{ ergs}$$

for values of r between 1.37 and 1.84 Å.

HIGH velocity argon atoms, with energies in the range 300–1100 electron volts, have been scattered in room temperature argon to obtain experimental values of the total collision cross section, as part of a program for the determination of repulsive potentials at close distances of interaction.

EXPERIMENTAL

The apparatus and experimental procedure were essentially those previously described¹ in connection with the measurement of total collision cross sections of high velocity hydrogen atoms scattered in room temperature molecular hydrogen. In the present experiments, the single-junction radiation thermocouple originally used as the detector was replaced by a forty-junction thermopile kindly supplied for the purpose by Professor L.

Harris.² The receiver surface of the new detector was square, 0.254 cm on a side, and was covered symmetrically with a circular mask, 0.132 cm in diameter. The geometric average angular aperture of the detector was 2.88°, and was computed by averaging linearly, with respect to distance along the beam axis, all half-angles subtended by the detector at its fixed position, 7.738 cm from the origin of the beam. The essential features of the scattering path which determine the geometric average angular aperture are shown in Fig. 1. In calculating the average aperture, it is necessary to take cognizance of the angular limitations imposed by the tip of the second collimating channel, the lower edge of the detector mask, and the edge of the thermopile. This is done by dividing the scattering path into three sections, each characterized by a range of angle, θ_1 , θ_2 , or

¹ I. Amdur and H. Pearlman, J. Chem. Phys. 8, 7 (1940).

² L. Harris, J. Opt. Soc. Am. 36, 597 (1946).