

Isotopic effect in the binding of helium in graphite

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The binding of helium isotopes by graphite has been studied. The thermal desorption of helium after it is introduced into the graphite obeys an Arrhenius law. The desorption activation energies are 8.1 ± 1.0 kcal/mole for ^3He and 21.0 ± 1.3 kcal/mole for ^4He . The isotopic effect observed here is explained on the basis of a model of an encapsulation of helium atoms in the volume between graphite layers. The characteristic amplitudes and frequencies of the vibrations of the encapsulated atoms are found.

Although the wetting of graphite by helium has been studied in detail,¹ no compound of helium with graphite has yet to be produced. Using a method involving the acceleration of atoms, we have been able to implant from 0.1 to 3 at. % of helium. In an effort to determine the method by which the He is incorporated in the graphite lattice, we have studied the thermal desorption of helium atoms.

If the helium atoms are isolated from each other as in cellular compounds (clathrate compounds), the desorption should be characterized by an activation energy which is independent of the temperature. If the helium atoms are instead arranged in groups or layers which alternate with layers of carbon, as in interlayer (intercalated) compounds, the activation energy will depend on the number of atoms in a group, i.e., will vary with the temperature. The desorption energy remains constant. Proof that a compound is a clathrate compound has also been found from estimates of the isotopic effect during the binding of ^3He and ^4He in graphite.

The process by which helium desorbs from the samples was studied by means of a mass spectrometer connected to a specially designed quartz reactor,² in which the samples were heated. Portions of 0.2–0.5 g were placed in the reactor. We used two measurement methods: a quasisteady method and a kinetic method. In the quasisteady method we determined the total amount of gas which was evolved at the given temperature. The temperature was changed in steps after saturation was reached in the preceding measurement at a lower temperature. In the kinetic method, the reactor was continuously evacuated through the ion source of the mass spectrometer, and the helium ion current was measured as a function of the temperature. Figure 1 shows the results. We see that the plot of the logarithm of the ion current versus the reciprocal temperature is linear, as it characteristically is for true inclusion compounds (clathrate compounds). Within the experimental error, the two types of measurements yield the same values for the activation energy for each isotope. There is a huge isotopic effect:

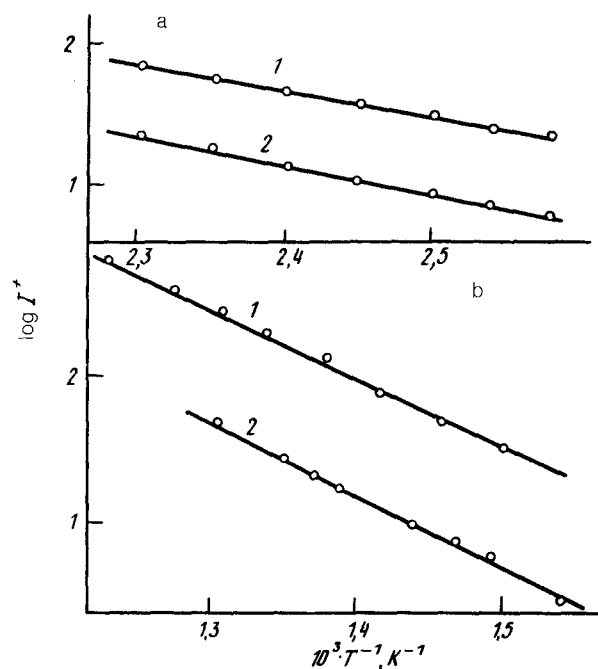


FIG. 1. Temperature dependence of the intensity (I^+) of the He ion current during desorption from graphite. a— ^3He ; b— ^4He . 1) "Quasistatic" method; 2) "kinetic" method.

The activation energy for the desorption of ^4He is nearly three times that for ^3He (21.0 kcal/mole and 8.1 kcal/mole, respectively). A macroscopic manifestation of this difference in "binding" energies is that the outgassing of graphite with ^3He occurs in the temperature range 70–300 °C, while that of graphite with ^4He occurs in the range 300–700 °C. The weight loss of the samples during the outgassing corresponds to maximum helium concentrations from 0.1 to 3 at. %.

In the clathrate model, the He atoms should lie in the volume between graphite layers, deforming the lengths and angles of C–C valence bonds, as shown in Fig. 2. The He atom vibrates in the cavity which is formed. The vibrations of the C atoms can be ignored because of the substantial difference between the masses of the helium and carbon atoms (this is the adiabatic approximation). The vibrational levels of the He atoms then correspond to the instantaneous position of the helium term in the force field of the carbon atoms of the slightly deformed graphite lattice. Under these assumptions, the vibration frequencies can easily be estimated from the results of experiments on thermal desorption. In the harmonic approximation we would have $\omega_{1,2} = (K/M_{1,2})^{1/2}$, where K is the formal "rigidity" of the system which stems from the repulsive potential of the cavity walls, and $M_{1,2}$ are the masses of the ^3He and ^4He atoms, respectively. The rigidities obviously do not depend on the masses of the atoms: $(K_1 - K_2)/K_{1,2} \approx m/M_{1,2}$, where m is the mass of an electron. For this reason, the difference in desorption activation energies found experimentally, Δ , expressed per atom, is related to the frequencies $\omega_{1,2}$ by $\Delta = \hbar(\omega_1 - \omega_2)$. The vibration amplitude $x_{1,2}$ is found from the condition $\hbar\omega = Kx^2/2$. Substituting in the values of the constants and $\Delta = 0.52$ eV, we find $\omega_1 = 6.3 \times 10^{15} \text{ s}^{-1}$, $\omega_2 = 5.4 \times 10^{15} \text{ s}^{-1}$, $x_1 = 0.18 \times 10^{-8} \text{ cm}$, and $x_2 = 0.17 \times 10^{-8} \text{ cm}$. An independent estimate based on the potential-box model combined with the uncertainty relation, yields a lower estimate on the vibration amplitude: $x \gtrsim 0.1 \times 10^{-8} \text{ cm}$, in agreement with the calculation above.

The vibration frequency of the He atoms is far higher than the limiting Debye

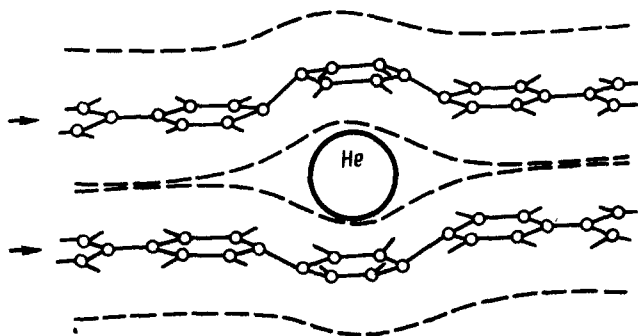


FIG. 2. "Encapsulated" He atom in graphite. The arrows show graphite layers.

frequency in graphite ($\omega_{\text{lim}} = 3 \times 10^{14} \text{ s}^{-1}$; Ref. 3). This circumstance would probably prevent a free migration of the implanted helium atoms in the volume between graphite layers.

We wish to thank M. V. Éntin for a discussion of these questions.

¹G. Zimmerly and M. H. W. Chan, *Phys. Rev. B* **38**, 8760 (1988).

²P. P. Semmyannikov *et al.*, in: *Proceedings of the Twelfth All-Union Conference on Chemistry, Thermodynamics, and Calorimetry*, Gorki, 1988, p. 224.

³B. Wunderlich and G. Baur, *Heat Capacity of Linear Polymers* [Russian translation], Mir, Moscow, 1972, p. 306.

Translated by Dave Parsons