

Recent Determinations of the Vapor Pressure of Graphite

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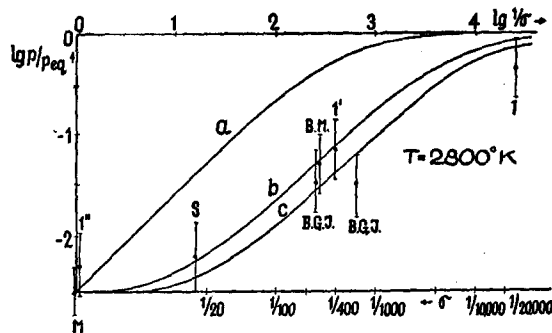


FIG. 1. Pressure p inside a Knudsen-cell vs aperture/total area ratio σ . Curve (a) (Eq. (1)); curves (b) and (c) (Eq. (2)), potential barrier of 50 and 52.5 kcal, respectively. Experimental points: (M) Marshall and Norton; (S) Simpson, Thorn, and Winslow; (BGJ) Brewer, Gilles, and Jenkins; (BM) Brewer and Mastick; (1, 1', 1'') results communicated in preceding note. Experiments (S), (BGJ), and (BM) (at lower temperatures) were plotted as $\lg p/p_{eq}$, since for large σ -values this ratio should be practically independent of temperature.

to the sticking coefficient f , and to the ratio of the aperture area to the total area σ by

$$p = p_{eq} f / (f + \sigma). \quad (1)$$

The plot of $\lg p/p_{eq}$ vs $\lg 1/\sigma$ (Fig. 1, curve (a)) gives a 45° straight line as long as $\sigma \gg f$. The intercept with the pressure axis gives practically the apparent pressure observed in rate of evaporation experiments.

The graph shows that the experimental points disagree with the theoretical curve (a). This could be accounted for if one considers that the speed of evaporation from a graphite surface is given mainly by the rate of evaporation of C_2 , whereas C_1 is predominant in the equilibrium.

The value $L_c = 141.26$ kcal we advocate, combined with $DC_2 = 83$ kcal proposed by Herzberg,⁵ yields $LC_2 = 199.5$ kcal ($LC_2 = 2L_c - DC_2$) and, using Gordon's entropy data,⁶ the vapor pressure curve of C_2 (Fig. 1, preceding note).

Some time ago, Herzberg, Herzfeld, and Teller⁷ have admitted that a potential barrier of about $L_c/3$ determines the rate of evaporation of C atoms, since two C—C bonds must be broken to evaporate the first C atom from the graphite plane and only one to evaporate the second. Hence the sticking coefficient of carbon atoms: $f_1 \approx 2 \cdot \exp[-(1/3)L_c/RT] \approx 2 \cdot \exp(-50,000/RT)$ and the apparent vapor pressure (p^*) of C atoms, as determined by rate of evaporation experiments, would be given by: $\lg p^* = \lg p_{eq} + \lg f_1$ (curve a, Fig. 1, preceding note). The evaporation of C_2 molecules, treated according to Herzberg, Herzfeld, and Teller's model, does not, on the other hand, lead to any potential barrier.

The total apparent vapor pressure determined by rate of evaporation experiments, being calculated in mass units and not as a number of particles, should thus be: $p_{ev} = p_{1eq} f_1 + 2^{\frac{1}{2}} p_{2eq}$.

This function, plotted on Fig. 1 of the preceding communication (curve b), is seen to coincide very closely with the experimental "evaporation pressures," as determined by Marshall and Norton and Simpson *et al.*² Furthermore (even though there is a great danger in using determinations of the slope of the $\lg p$ vs $1/T$ curve at such temperatures), its slope coincides very nicely with that of about 198 kcal obtained by Simpson *et al.* in their rate of evaporation experiments.

The apparent pressure determined by crucible experiments should now be

$$p = p_{1eq} \cdot f_1 / (f_1 + \sigma) + 2^{\frac{1}{2}} p_{2eq}. \quad (2)$$

The variation of $\lg p/p_{eq}$ vs $\lg 1/\sigma$ according to Eq. (2) is plotted on Fig. 1 (curves b and c) for two values of the potential barrier to C_1 evaporation (50 and 52.5 kcal, respectively). It is seen to be in excellent agreement with available experimental data.

The author wishes to thank Professor Goldfinger for continued interest and valuable help received during this research. He is

indebted to the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture and to the Centre National Belge de Chimie Physique Moléculaire for grants which allowed him to carry out this work.

¹ Doehaerd, Goldfinger, and Waelbroeck, preceding note.

² A. L. Marshall and F. J. Norton, *J. Am. Chem. Soc.* **72**, 2166 (1950); Simpson, Thorn, and Winslow, *AEC*, 2680 (1949).

³ P. Goldfinger and W. Jeunehomme, *Third Symposium on Combustion, Flame, and Explosion Phenomena*, Minneapolis (1948); Brewer, Gilles, and Jenkins, *J. Chem. Phys.* **16**, 797 (1948); L. Brewer and D. F. Mastick, *UCRL*, 572 (1949).

⁴ Although an experimental confirmation of Eq. (1) is not known to us.

⁵ G. Herzberg, *Phys. Rev.* **70**, 762 (1946).

⁶ A. R. Gordon, *J. Chem. Phys.* **5**, 530 (1937).

⁷ Herzberg, Herzfeld, and Teller, *J. Phys. Chem.* **41**, 325 (1937).

Recent Determinations of the Vapor Pressure of Graphite

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DOEHAERD, Goldfinger, and Waelbroeck¹ have greatly extended the range of measurements of the vapor pressure of graphite. If the details of their complete paper can confirm that the variation of vapor pressure with ρ , the ratio of orifice to evaporating area, is real, their work will be the definitive determination. However, certain internal inconsistencies are apparent in the information presented which cause one to be cautious in the acceptance of these new data and which indicate that well-established experimental errors may readily account for the observed variation.

The previous vapor pressure measurements²⁻⁵ cover a range of values of ρ from 1 to 1/700. If f , the condensation coefficient, were small enough to allow reconciliation of these data with $L_c = 141$ kcal, a pronounced dependence of vapor pressure upon ρ would have been observed as indicated by curve (a) of Waelbroeck's letter.⁶ Such a variation is not found, indicating that f cannot be very small. Also the direct determination^{3,5} of the condensation coefficient of carbon vapor gives f greater than 0.1. The preceding authors^{1,6} agree that one must accept a high f value for the range of ρ -values previously studied. They claim, however, that upon even further reduction of ρ , one finds a dependence indicating an extremely low f value. These observations are reconciled by assuming that the main species escaping when ρ is small is C_2 and that this species has a high f value. At very low ρ -values the concentration of C atoms, which have an extremely low f value, can build up, and the atomic beam consists largely of C atoms.

One can present arguments against C_2 playing such a role, but the significant point of the argument is that two species are present with vastly different condensation coefficients, and we need not debate here the possible nature of such species. Such an unusual situation is entirely possible. However, if this is the true situation in the case of graphite, it does not appear possible that the method used by the preceding authors^{1,6} could indicate it. They⁷ used the same method as that of Simpson, Thorn, and Winslow³ and have indeed used the values of the absorption coefficient of carbon deposits and of the condensation coefficient of carbon vapor on such deposits determined by Simpson, Thorn, and Winslow. However, their hypothesis requires that Simpson's atomic beam, for which a high f value of 0.2 was obtained, consists largely of C_2 . With a much smaller orifice and therefore presumably a beam largely of C atoms, with their very low f value, only a small fraction of the beam should condense. The carbon deposit would be due essentially only to the C_2 molecules in the beam and the C atoms should reflect off the carbon deposit. Thus the method used will not give appreciable detection of a species with an extremely low f value even when the atomic beam consists largely of that species. It would seem that some other explanation must be responsible for the abnormally high vapor pressure reported for the low ρ -value of 1/24,000. All the other

new data reported lie as close to or closer to $L_C=170$ than to $L_C=141$ kcal.

A possible clue to this explanation is given in the manner of presentation of the data given in the figures of the preceding letters. All of the determinations of Brewer, Gilles, and Jenkins² are presented out of context as if they were equivalent. Actually most of these pressures varying over a factor of ten were given by experiments designed to emphasize the error due to the "tar effect." Long heatings at very high temperatures are necessary to obtain graphite samples which do not give spuriously high vapor pressure values.^{2,4,6} Their method of presentation of the data would indicate that the preceding authors might have overlooked this effect. Proper representation of the data gives much poorer agreement with curves *b* and *c* (reference 6). The figure of reference 1 presents two groups of data for $\rho=1/2400$ labeled *D* and *GJ*. The details of the *GJ* determinations are available.⁸ The highest heating reported for the samples was 2100°K which would be much too low to have eliminated the "tar effect." Brewer and Mastick⁵ have made a study of the various serious sources of errors involved in the determination of the vapor pressure of graphite. These cannot be reviewed here. However, the detailed paper of Doehaerd, Goldfinger, and Waelbroeck will be awaited with great interest to determine if these various errors have been adequately appraised. Because of the severe experimental difficulties inherent in these measurements, it is a difficult and time consuming task to carry out the experiments necessary to evaluate all the important variables. Doehaerd, Goldfinger, and Waelbroeck have greatly extended the available data and techniques and it is hoped that their work will soon lead to an unambiguous determination of this very important quantity.

¹ Doehaerd, Goldfinger, and Waelbroeck, *J. Chem. Phys.* **20**, 757 (1952).

² Brewer, Gilles, and Jenkins, *J. Chem. Phys.* **16**, 797 (1948).

³ Simpson, Thorn, and Winslow, Argonne National Laboratory Declassified Report ANL-4264, May 6, 1949.

⁴ A. L. Marshall and F. J. Norton, *J. Am. Chem. Soc.* **72**, 2166 (1950).

⁵ L. Brewer and D. F. Mastick, paper submitted to *Journal of Chemical Physics*; based in part upon University of California Radiation Laboratory Declassified Report UCL-572, November, 1949.

⁶ F. Waelbroeck, *J. Chem. Phys.* **20**, 757 (1952).

⁷ See reference 3 of Doehaerd, Goldfinger, and Waelbroeck letter.

⁸ P. Goldfinger and W. Jeunehomme, *Rev. de l'Institut Fr. du Pétrole* **4**, 427 (1949); Third Symposium on Combustion, Flame and Explosion Phenomena, pp. 618-621, Minneapolis (1948).

The Structure of the Molecules PH_3 , AsH_3 , and SbH_3 *

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THE two nearly coincident vibration frequencies ν_1 and ν_3 and the overlapping bands ν_2 and ν_4 (Herzberg's notation) of the molecules PH_3 , AsH_3 , and SbH_3 are coupled, respectively, by Coriolis interactions. It is possible to show in the case of ν_1 and ν_3 that the interaction is so slight that it may satisfactorily be taken into account in the effective moments of inertia of the molecule. Standard methods, where use is made of combination relations, may therefore be employed in the analysis of these bands. The Coriolis coupling between ν_2 and ν_4 in such molecules is not small, however, and since ν_2 and ν_4 are nearly alike, the interaction must be calculated by the use of degenerate perturbation methods.¹

It may be shown, however, that for values of the quantum number K equal to J and K equal to $J-1$ (i.e., where the rotation of the molecule classically is almost entirely about the axis of symmetry) the perturbation is small enough so that the corresponding term values in the first excited state ν_4 may be obtained by an expansion of the secular determinant. One may show by this method that the frequency interval between two $^R R$ lines, $^R R(J, K)$ and $^R R(J+1, K+1)$ is equal to $\Delta\nu=2[(1-\xi_4)C+2\xi_2, 4^2 B^2/\Delta]$ where $B=h/8\pi^2 I_{xx}C$, $C=h/8\pi^2 I_{zz}C$, I_{xx} and I_{zz} being the two moments of inertia, ξ_4 is the degenerate Coriolis coefficient coupling the angular momentum associated

with ν_4 to the rotation of the molecule, $\xi_2, 4$ is the Coriolis coefficient coupling the incipient angular momentum of ν_2 and ν_4 to the rotation of the molecule and where $\Delta=\omega_4-\omega_3$. Similarly one may show that the frequency interval between two $^R R$ lines $^R R(J, K-1)$ and $^R R(J+1, K)$ is equal to $\Delta\nu'=2[(1-\xi_4)C+4\xi_2, 4^2 B^2/\Delta]$. One has, therefore, a direct means of determining the magnitude of the perturbation from the experimental data if the above lines can be identified.

The term values of ν_3 where $K=0$ (i.e., where the molecule is tumbling) may also readily be obtained from the secular determinant. Moreover, the frequency positions of the corresponding lines in the P branch are given by a rather simple equation. Here also the frequency interval between two lines in the P branch where $K=0$ gives a measure of the value $\xi_2, 4^2 B^2/\Delta$.

When applied to the PH_3 molecule,² this method leads to the values $2\xi_2, 4B=4.77\text{ cm}^{-1}$, $B=4.4460\text{ cm}^{-1}$, $(1-\xi_2)C=3.8360\text{ cm}^{-1}$, and $(1-\xi_4)C=5.5425\text{ cm}^{-1}$. Recalling that $\xi_2+\xi_4=(B/2C-1)$,³ the rotational constant C is determined and one may calculate the size and the shape of the molecule. For the H-P-H angle (α) we obtain the value $93^\circ 50'$, and for the PH distance (r_0) we find 1.424 \AA . When the method is applied to the data on AsH_3 , the following values are found $2\xi_2, 4B=4.999\text{ cm}^{-1}$, $B=3.723\text{ cm}^{-1}$, $(1-\xi_2)C=3.883\text{ cm}^{-1}$ and $(1-\xi_4)C=4.800\text{ cm}^{-1}$. These lead to the values $\alpha=91^\circ 35'$ and $r_0=1.523\text{ \AA}$. The data on the SbH_3 molecule⁴ treated in the same manner give these values: $2\xi_2, 4B=3.28\text{ cm}^{-1}$, $B=2.935\text{ cm}^{-1}$, $(1-\xi_2)C=2.975\text{ cm}^{-1}$, and $(1-\xi_4)C=3.950\text{ cm}^{-1}$. These give for α and r_0 the values $\alpha=91^\circ 30'$ and $r_0=1.711\text{ \AA}$.

The values of α and r_0 arrived at from infrared bands are, therefore, in substantial agreement with the value of these constants as determined from microwave spectra.⁵ The values of α and r_0 given by Loomis and Strandberg for PH_3 , AsH_3 , and SbH_3 are, respectively, $\alpha=93^\circ 5$, $r_0=1.419\text{ \AA}$; $\alpha=92^\circ 0$, $r_0=1.523\text{ \AA}$; and $\alpha=91^\circ 5$, $r_0=1.712\text{ \AA}$.

The values of $2\xi_2, 4B$ obtained from the bands ν_3 and ν_4 were, in each of the above cases, in good agreement.

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² V. M. McConaghie and H. H. Nielsen, *Proc. Natl. Acad.* **34**, 455 (1948).

³ M. Johnston and D. M. Dennison, *Phys. Rev.* **48**, 868 (1935).

⁴ W. Haynie, Doctoral dissertation, Ohio State University, Columbus, Ohio (1951).

⁵ C. C. Loomis and M. W. P. Strandberg, *Phys. Rev.* **81**, 798 (1951).

Erratum: Ultrasonic Absorption in the Critical Temperature Region

[*J. Chem. Phys.* **18**, 1300 (1950)]

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VALUES of the sound velocity given in the above communication should be divided by two and the absorption coefficients per wavelength (as defined previously) divided by two. These corrections also apply to a later paper.¹

The corrections are necessitated by a recent observation that on the recording of the resonance peaks of the double crystal acoustic interferometer every other peak was missing. This behavior can be accounted for by the presence of a superimposed emf having the same frequency as the resonant frequencies of the quartz crystals. At temperatures well below the critical temperature, where the sound attenuation is small, all the resonance peaks can be recorded with but a slight alternation of amplitude. As the critical temperature is approached, this alternation becomes very marked, alternate peaks appearing as small satellites. Very close to the critical temperature, where the sound absorption is very high, these "satellites" are completely obscured. This interpretation and the correct sound velocity was verified by employing a pulsing technique and measuring the transit time of a sound pulse between the two crystals at a known distance apart.