MAY 1, 1932 PHYSICAL REVIEW VOLUME 40

The Heat of Sublimation of Carbon

BY WILLIAM E. VAUGHAN[1] AND G. B. KISTIAKOWSKY
MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE, MASS.

(Received March 28, 1932)

By using the most likely figures for the heat of dissociation of the C_2 molecule (5.5 and 7.0 volts), it is shown that in saturated carbon vapor at temperatures from 4150 to 4700°K the partial pressures of both atoms and molecules are of the same order of magnitude. Statistical computations of the vapor pressure of solid carbon at these temperatures show that either the absolute vapor pressure as determined experimentally is entirely wrong or the pressure-temperature dependence is considerably in error. On the assumption that the absolute pressures are approximately correct, the heats of sublimation at 0°K into atoms and into molecules are 161 and 176 Cals. and 195 and 189 Cals. respectively for the 5.5 and 7.0 volt dissociation energies. The true values probably lie within these limits.

THE study of the determinations of the heats of vaporization and of sublimation of carbon has been undertaken by many workers,[2] although the data and calculations of Kohn and Guckel,[3] Fajans,[4] Rishkevich,[5] and Fajans and Rishkevich[6] are usually given the greater weight.[7] The procedure used by Kohn and Guckel was that of the measurement by photometric means of the temperature of the positive crater of a carbon arc burning in an atmosphere of an inert gas at known pressure. It was assumed that over the range of pressure studied, the vapor of carbon is in equilibrium with the added gas. The data reveal a linear trend of log p with $1/T$ over a range of 0.75 to 5.0 atm. and 4150 to 4700°K. For lower temperatures and pressures the pressure falls off very rapidly and this latter phenomenon is attributed to super-heating or variations in the emissivity of carbon. 139.2 Cals. is given as the best value for the heat of sublimation of graphite, that of diamond being 2.0 Cals. higher; a precision of 7 percent is claimed. Kohn and Guckel also attempted to calculate upon statistical bases the equilibria between solid carbon and its vapor consisting either entirely of atoms or wholly of diatomic molecules; in this they were not sufficiently equipped to utilize the multiplicities of the states and the available data used were not as precise as those now known. From the former calculation as the heat of sublimation was obtained, 141.4 Cals; from the latter, 186.0. Because of the agreement with the empirical figure it was concluded that the vapor was preponderantly monatomic and that the possible equilibrium was far shifted to the one form. Fajans,[4]

---

[1] National Research Fellow in Chemistry.

[2] For a bibliography of the more reliable work, see *Intern. Crit. Tab.* II, p. 205.

[3] Kohn and Guckel, Zeits. f. Physik **27**, 305 (1924); Naturwissen. **12**, 139 (1924).

[4] Fajans, Zeits. Elektrochem. **31**, 63 (1925).

[5] Rishkevich, Ibid., **31**, 54 (1925).

[6] Fajans and Rishkevich, Naturwissen. **12**, 304, 578 (1924).

[7] Marshall in Taylor's *Treatise of Physical Chemistry*, New York, Van Nostrand, 1931, Vol. I, pp. 326–7, gives a good summary of the present status of the problem.

has critically corrected the data of Kohn and Guckel for the heat of fusion of carbon, since their experiments were performed at much higher temperature than the melting point of carbon (3800 ± 100°K). He has obtained a value for the heat of sublimation of diamond at 293°K of 147.3 Cals.

The summarizing vapor pressure equation in *International Critical Tables*[2] corresponds to a logarithmic slope equivalent to 129 Cals. for the interval from 4150 to 4700°K; this when corrected according to Fajans gives 143 Cals.

The heat of sublimation may also be calculated from the following data:

		ΔH_0(volts)
CO	$\rightarrow$C(gas)+O	10.35[8]
C(solid)+$\frac{1}{2}$	$O_2 \rightarrow$CO	-1.14[9]
O	$\rightarrow \frac{1}{2}$ O_2	-2.54[10]
C(solid)	$\rightarrow$C(gas)	6.67 volts (153.5 Cals.)

The upper limit of 11.18 volts for CO→C+O results in a value of 173 Cals., but this dissociation energy of CO is undoubtedly too high.

The problem may be attacked from another viewpoint, as sufficient data are now available to permit a statistical calculation of the equilibrium in carbon vapor and its effect upon the heat of sublimation.

There are three band spectra attributed[11,12] to the C_2 molecule: the singlet system, ${}^1\Pi_g \rightarrow {}^1\Pi_u$($\nu_e = 3.2$ volts); the Swan bands, ${}^3\Pi_g \rightarrow {}^3\Pi_u$ ($\nu_e = 2.4$ volts); and the high pressure system, ${}^3\Pi \rightarrow {}^3\Pi$. The two former are the more complete. The ${}^3\Pi_u$ is the lowest definitely known energy state of C_2 and in all probability is the normal state. The products of dissociation of all electronic states between ${}^3\Pi_u$ and ${}^3\Pi_g$, which includes the ${}^1\Pi_u$, are, in all likelihood, two normal ${}^3P$ carbon atoms. Mulliken[12] has estimated and lists the relative energies of some of the electronic states of C_2. There appears in the literature two figures for the energy of dissociation of C_2 into two ${}^3P$ atoms: 7.0 volts is given by Weitzel and this embodies all earlier work; 5.5 volts is advanced by Mulliken. On the assumption of Mulliken's electronic excitation values and by using the Birge-Sponer method it is found that the lower state of Swan bands, ${}^3\Pi_u$, corresponds to a dissociation energy of 7.02 volts; the upper state, ${}^3\Pi_g$, to 7.42; the lower state of the singlet system, ${}^1\Pi_u$, 8.28; the upper state, ${}^1\Pi_g$, 6.78; the high pressure system, ${}^3\Pi$, 6.97 (average of all, 7.29). Thus it seems likely that the figure of 7.0 is the more correct value. Since the Birge-Sponer method usually gives too high a figure for the heat of dissociation by some 15 to 30 percent, it is entirely possible that the values obtained are too high. However, in order to arrive at a figure of 5.5 volts, the electronic excitation of ${}^1\Pi_u$ must be assumed to be considerably less than suggested. For the purposes of this paper, as extremes, the values of 7.0 and 5.5 will be utilized and a comparison of the data obtained will be made.

---

[8] Weitzel, *Bandenspektren*, Leipzig, Akad. Verlags. 1931, p. 354.

[9] Lewis and Randall, *Thermodynamics*, New York, McGraw-Hill, 1923, p. 171.

[10] Weitzel, reference 8, p. 369.

[11] Weitzel, reference 8, p. 333 ff.

[12] Mulliken, Rev. Mod. Phys. **4**, 65–7 (1932).

The free energy at constant pressure of the atoms of a monatomic gas is expressible by the equation:

$$-\frac{f_c{}^p}{kT} = -\frac{\epsilon_c{}^0}{kT} + \frac{3}{2}\ln\frac{2\pi mkT}{h^2} + \ln\frac{V}{N_c} + \ln g_e + \ln g_n \tag{1}$$

wherein $f_c{}^p$ is the free energy at constant p per atom, k and h the Boltzmann and Planck constants, T the absolute temperature, $\epsilon_c{}^0$ the "zero point" energy N_c the number of molecules in the volume V, m the atomic mass, and g_e and g_n the multiplicities of the electronic and nuclear states respectively. These latter two terms are easily evaluated for the carbon atom in a ^3P state. There is no nuclear spin; and g_n is 1. The electronic multiplicity, g_e, may be set equal to 9, since the multiplet separations are very small and the temperature to be considered, very high.

Similarly may be expressed the analogous term for diatomic molecules, in which case

$$\begin{aligned}-\frac{f_{c_2}{}^b}{kT} = -\frac{\epsilon_{c_2}{}^0}{kT} + \frac{3}{2}\ln\frac{2\pi(2m)kT}{h^2} + \ln\frac{V}{N_{c_2}} + \ln\sum_i g_{i_e}e^{-\epsilon_{ie}/kT}\\ + \ln\sum_i g_{i_r}e^{-\epsilon_{ir}/kT} + \ln\sum_i g_{iv}e^{-\epsilon_{iv}/kT}\end{aligned} \tag{2}$$

wherein the three summations respectively represent electronic, rotational and vibrational energies of the molecule, on the assumption of negligible interaction between these three terms. The electronic multiplicity term is that of a $^3\Pi$ molecule; thus 5 may be used, as again the separations are small. The rotational energy term may be evaluated[13] as $8\pi^2JkT/2h^2$ wherein J is the moment of inertia; this for the case at hand may be computed from the value of the distance between the atoms, which is 1.31×10^{-8} cm.[14] The vibrational term may be written approximately as $(1-e^{-h\nu/kT})^{-1}$, ν being the vibrational frequency in the lowest state. This for the Swan bands is 1629.88 wave numbers.[15]

For equilibrium one may write $2f_c{}^p/kT = f_{c_2}{}^p/kT$ and after putting $V/N = kT/p$ an expression for $\log_{10}K = \log_{10} p_c^2/p_{c_2}$ is readily obtained.

Table I gives the numerical results at several temperatures for $D_0 = 5.5$

TABLE I.

T	p_t (atms.)	K (atms.)		p_c (mm)	
		5.5 volts	7.0 volts	5.5 volts	7.0 volts
4153	0.84_1	0.63	0.88×10^{-2}	362	62.0
4303	1.35_6	1.05	1.67×10^{-2}	591	108
4503	2.83	2.24	4.36×10^{-2}	1240	249
4703	5.24	4.23	9.77×10^{-2}	2320	505

---

[13] Gibson and Heitler, Zeits. f. Physik **49**, 465 (1928).

[14] Mulliken, reference 12, p. 81.

[15] Weitzel, reference 10, p. 370.

and 7.0 volts ($D_0 = \epsilon_{c_2}{}^0 - 2\epsilon_c{}^0$). p_t is the total pressure as computed from the equation in *International Critical Tables*; p_c shows the two sets of partial pressures due to carbon atoms. If these latter two sets of data are employed in a determination of the heat of vaporization into atoms, 130 Cals. is obtained on the basis of 5.5 volts dissociation energy, and 147 Cals. on the basis of 7.0 volts; the former of these two values is equal to that obtained neglecting the presence of molecules; the latter is, on the other hand, considerably higher. If both are reduced to heat of sublimation at room temperature, one finds 144 and 161 Cals. respectively.

With the now available data on the equilibrium between atoms and molecules, it should be possible to verify the experimental vapor pressure curve by statistical methods. For the present problem the equation for the free energy at constant pressure of the monatomic gas is already known (1). The analogous expression for the solid may be formulated as

$$-\frac{f_s{}^p}{kT} = -\frac{\epsilon_s{}^0}{kT} + \frac{1}{R}\int_0^T \frac{dT}{T^2}\int_0^T C_p dT. \tag{3}$$

The symbols have their usual significance and the subscript s merely refers to the solid state. The specific heat of carbon (diamond) is accurately known to 1169°K,[16] and is well expressed by the Debye equation. Beyond this the data are infrequent. Fajans[17] has given a series of average values for high temperatures: 5.04 for 293 to 2370°K; 6.5 for 2370 to 3800°; and 8.0 for 3800 to 4380°. Thus, from these two sources it is possible to determine by graphical integration the values of the double integral.

In order to eliminate the possibility of an error involved in the heat of fusion (10 Cals. according to Fajans) the *International Critical Tables* vapor pressure equation was extrapolated from 4153 to 3800°K, the melting point of carbon ±100°. K's were also determined for this temperature and partial pressures computed. These data are given in Table II.

TABLE II. $p_t = 149.3$ mm at 3800°K.

	5.5 volts	7.0 volts
p_c	84.2 mm	11.7 mm
p_{c_2}	65.1	137.5

The total pressure is within fair agreement of the approximate figure of Fajans and Rishkevich[18] of 1/4 atm. for the equilibrium pressure at this temperature, indicating a well-founded extrapolation.

By combining (1) and (3) for the equilibrium and putting $V/N_c = kT/p_c$ there is obtained:

---

[16] Jellinek, *Lehrbuch der physikal. Chem.*, Stuttgart, F. Enke, 1915, Vol. II, p. 595.

[17] Fajans, reference 4, pp. 67–8.

[18] Fajans and Rishkevich, reference 6, p. 304.

$$\frac{\lambda_c{}^0}{2.3kT} = -\log_{10} p_c - \frac{1}{2.3R}\int_0^T \frac{dT}{T^2}\int_0^T C_p dT + \frac{3}{2}\log_{10}\frac{2\pi m}{h^2} + \frac{5}{2}\log_{10} kT + \log_{10} 9 \tag{4}$$

$$(\lambda_c{}^0 = \epsilon_c{}^0 - \epsilon_s{}^0).$$

The term involving the specific heat of the solid equals 1.623 for 3800°K. Evaluation of $\lambda_c{}^0$, the heat of sublimation of carbon into atoms, gives 176 and 161 Cals. respectively for the 7.0 and 5.5 volt dissociation energy values. It is significant that by this method both cases give figures larger than the value now used.

Similarly by doubling (3) and combining it with (2) one finds

$$\frac{\lambda_{c_2}{}^0}{2.3kT} = -\log_{10} p_{c_2} + \frac{3}{2}\log_{10}\frac{2\pi m}{\mathrm{h}^2} + \frac{1}{2}\log_{10} 2 + \log_{10} 5 + \frac{7}{2}\log_{10} kT + \log_{10}\frac{8\pi^2 J}{h^2} + \log_{10}\frac{1}{1 - e^{-h\nu/kT}} - \frac{2}{2.3R}\int_0^T \frac{dT}{T^2}\int_0^T C_p dT \tag{5}$$

$$(\lambda_{c_2}{}^0 = \epsilon_{c_2}{}^0 - 2\epsilon_s{}^0)$$

Computation gives for $\lambda_{c_2}{}^0$, the heat of sublimation into molecules, 189 and 195 Cals. respectively for the 7.0 and 5.5 volt cases. Proper combinations of $\lambda_c{}^0$ and $\lambda_{c_2}{}^0$ give 7.0 and 5.5 volts for the dissociation energies, showing the absence of gross arithmetical errors.

If one uses the presumably more correct experimental value of the heat of sublimation (corrected *I.C.T.* value), 143 Cals., and calculates the theoretical vapor pressure, there is obtained a figure of approximately 1000 mm as the partial pressure of atoms alone which is six times the total measured vapor pressure.

Analysis of the possible discrepancies in the methods employed reveals several potentialities for error. For the specific heat term of the solids was utilized a figure which was at best approximate. No account was taken of the possibility of specific heat due to electronic motion or anharmonicity of vibrations in the crystal. Allowing for as much as 25 percent error in this term and increasing it by that amount, 169 Cals. is found for the heat of sublimation into atoms for the 7.0 volt case and 154.5 Cals. for the 5.5 volt case. This allowance certainly should exceed the maximum error from this cause.

Another factor which might prove serious is that of the neglect of the possible presence of electronic states of the atom other than the ^3P and of the molecule other than the $^3\Pi_u$. The carbon atom has three low energy forms, ^1S, ^1D and ^5S. Disregarding ^5S and again, as a first approximation, neglecting the energy separations, the presence of the other two of these states would increase the g_e term to 15; by Eq. (4) this would give results of 180 and 165 Cals. for the respective 7.0 and 5.5 volt cases. Again, considering only the states of the molecule predicted by Mulliken and of those only the three with less than 2 volts excitation energy above the $^3\Pi_u$ state, $^3\Sigma_g{}^-$, $^1\Delta_g$ and

$^3\Sigma_g{}^+$, for the electronic multiplicity term is found approximately 11 instead of 5. This change gives an increased heat of sublimation into molecules of 195.5 and 201 Cals. for the 7.0 and 5.5 volt energy conditions. The combined changes would not greatly disturb the equilibrium constant, K, for $2\ C \rightleftarrows C_2$, as calculated. The chance of the existence of polyatomic carbon molecules has also been ignored. If such molecules are present in appreciable concentrations, all calculated heats of sublimation should be further raised.

Upon examination of all of these possible errors, it still seems apparent that the calculated heats of sublimation are considerably larger than the measured value. Thus either the experimental vapor pressures are erroneous or the pressure-temperature dependence is wrong. The second possibility is much more likely, as indicated by the observations that at low pressure the observed slope is quite different from that at higher concentrations. It must be concluded, thus, that the procedure of Kohn and Guckel in discarding the low pressure portion of their measurements is questionable, although no indication of the source of error can now be advanced.

If the assignment of electronic excitation for $^1\Pi_u$ by Mulliken is assumed to be correct, it seems entirely likely that the 7.0 volt value for the heat of dissociation is the more accurate figure and that the heat of sublimation of carbon at 0°K is 176 Cals. This is much larger than the currently accepted value and renders imperative the recalculation of certain thermochemical data, such as "bonding energies". If on the other hand, the excitation energy is questioned, the figure of 5.5 volts seems fairly satisfactory, and $\lambda_c{}^0$ (sublimation) $=161$ Cals. This is substantiated by the calculation using the heat of dissociation of the CO molecule. This, likewise, is larger than the current value.

An independent experimental method of measuring the heat of sublimation of carbon is offered by determination of the heat of dissociation of cyanogen, $(CN)_2$ into 2 CN groups, since all other necessary thermochemical data are here available. It has been found in this laboratory that in cyanogen vapor heated to 1000°C there is absorption due to CN groups (the violet bands). Experiments to determine the heat of dissociation by a method analogous to that of Bonhoeffer and Reichardt[19] are now in progress.

---

[19] Bonhoeffer and Reichardt, Zeits. phys. Chem. Abt. A, **139,** 75 (1928).