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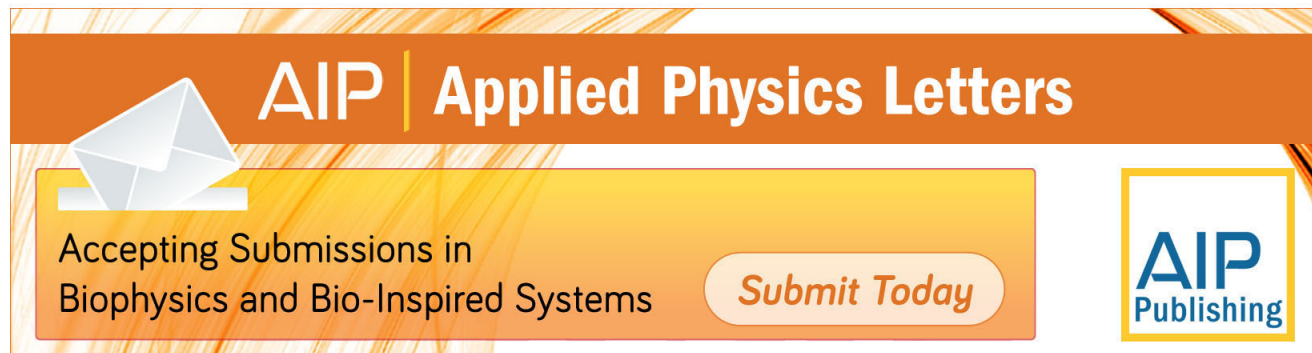
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to the mercury atom as kinetic energy, and the kinetic energy of the CH_3CO radical, as well as possibly its vibrational energy, may be appreciably lower than that of a radical produced by absorption of 2537Å radiation directly by an acetone molecule. In the absence of further information we may accept $\phi_{2537} = 1$, $a_{2537} = 0.22 \pm 0.05$ at 25°C.

In conclusion, it is well to give a summary of the various constants concerning the mechanism which have been evaluated.

The mechanism proposed in this article accounts for the following points:

- (a) The variation of the $\text{C}_2\text{H}_6/\text{CO}$ ratio with pressure, with intensity, with temperature, and with wave-length;
- (b) the increase in the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio with decreasing intensity and increasing pressure;
- (c) variation of quantum yields of C_2H_6 , CO , and CH_4 with temperature and pressure;
- (d) the effect of wave-length on the CO yield;
- (e) the formation of all known products;
- (f) qualitatively for fluorescence and its variation with temperature. This point and its relationship to primary quantum yield merit further study.

It is believed that the mechanism does not disagree with any experimental facts so far

available. In particular it agrees qualitatively with Fig. 2 of the second article by Spence and Wild,⁵ who were the first to point out that the $\text{C}_2\text{H}_6/\text{CO}$ ratio really falls on a family of curves, one for each pressure as a function of intensity.

The mechanism makes no pretense of describing acetone decomposition except in the early stages before products have been allowed to accumulate. With large percentage decomposition there must be secondary reactions which would change the composition of the gaseous products. Also the effect of the walls has not been included in detail. Such effects are almost certainly not of importance except at pressures below 50 mm and in any case could not be included easily in any quantitative theory. Many of the effects previously ascribed to the walls are undoubtedly due to variations in intensity and in pressure. The importance of obtaining data in such a fashion that the number of quanta absorbed per unit volume per second is as constant as possible is obvious from the nature of the mechanism.

The authors wish to express their appreciation to Dr. W. Davis, Jr., who first derived Eq. (32).

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The Vapor Pressure and Heat of Sublimation of Graphite*

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(Received April 19, 1948)

The heat of sublimation of graphite and the heats of dissociation of CO and C_2 , which have been the subject of much controversy in recent years, have been unambiguously established by the direct determination of the total vapor pressure of graphite by an equilibrium effusion method and by the determination of the partial pressure of $\text{C}_2(\text{gas})$ in equilibrium with graphite.

The heat of sublimation of graphite to $\text{C}(\text{g})$ is found to be $\Delta H_0 = 170.39 \pm 0.20$ kilocalories per mole at 0°K. The heat of sublimation of graphite to $\text{C}_2(\text{g})$ is found to be $\Delta H_0 = 233.1 \pm 7$ kilocalories per mole. The heats of dissociation of C_2 and CO have been shown to be 4.7 ± 0.3 and 11.109 ± 0.01 electron volts, respectively. The accommodation coefficient of carbon gas on graphite at high temperatures is found to be about 0.3 and vaporized carbon gas is shown to be in the 3P ground electronic state.

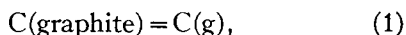
* Abstracted in part from the thesis submitted by Paul W. Gilles in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of California. Presented before the Inorganic and Physical Division of the American Chemical Society at the 113th National Meeting at Chicago, April 19, 1948.

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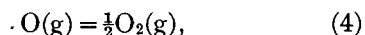
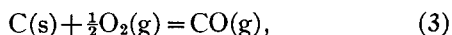
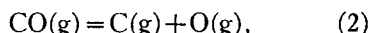
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INTRODUCTION

THE vapor pressure of graphite and the heat for the reaction



have been the subject of considerable controversy for a great many years.¹ The sum of the reactions



yields reaction (1) and the sum of the heats of these reactions must be the heat of reaction (1). Herzberg² showed in 1937 that a consideration of various predissociations in carbon monoxide leads to several definite values, one of which must be the heat of dissociation of this molecule. It was not possible for him to make an unequivocal choice from these values. Since the heats of reactions (3) and (4) are accurately known, each possible value for the heat of dissociation of CO leads to a possible value for the heat of sublimation of graphite. The purpose of this work has been to obtain data that make possible the correct choice of the value for the heat of sublimation of graphite, and incidentally thereby, the proper choice for the CO dissociation energy.

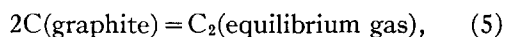
Previous values for the heat of sublimation calculated from vapor pressure data obtained from rates of vaporization of graphite filaments and rings have been criticized on the grounds that sublimation may have taken place to an excited gaseous state, that the accommodation coefficient may have been very low, and that the relative gaseous concentrations of C(gas) and C₂(gas) were unknown.¹ The value obtained in the present work is not subject to these same objections since the vapor pressure measurements were obtained by an equilibrium method, that of the effusion of a gas through a small knife-edged orifice. As is indicated by the constancy of the vapor pressure values with variation of hole size, the vapor pressure determined by this

method is not dependent on the accommodation coefficient. This method also insures that the gas will be in its equilibrium state. Also the independent measurement of the C₂(gas) partial pressure has eliminated any uncertainties due to C₂. The determination of this last quantity along with the heat of formation of C₂(gas) will be discussed first.

THE HEAT OF FORMATION OF C₂(GAS)

The process of the formation of gaseous diatomic carbon from the solid can be studied independently of the formation of monatomic carbon vapor, by spectroscopic observations of the intensities of the molecular bands of C₂.

If one measures the intensity of a single spectral line, he has a quantity that is proportional to the total rate of decay of the excited state of the molecule and therefore to the concentration or pressure of the molecules in this excited state. If he measures the temperature coefficient of this intensity, he has a measure of how rapidly the pressure of the excited species is varying with temperature, a quantity that is related to the heat of formation of the excited gaseous state. The heat of formation of the equilibrium gaseous state of C₂ can be calculated from the heat of formation of the excited state and can be used with values of the free energy function, $(\Delta F - \Delta E_0)/T$, for the reaction,



to calculate the pressure of C₂(gas) in equilibrium with graphite.

Experimental

For the production of the C₂ vapor, a special high temperature graphite tube resistance furnace, shown in Fig. 1, was constructed somewhat similar to one made by King.³ The innermost part of the furnace was a hollow graphite tube of either National Carbon C-18 graphite or National Regular Spectroscopic Electrode Material, AGKS-ANJ-889.

The tube was supported at each end by a split graphite bushing, bored so that the tube fitted snugly. The outside of the bushing was tapered

¹ F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, New York, 1936), p. 230, gives early references; L. H. Long and R. G. W. Norrish, *Nature* **158**, 238 (1946) gives later ones.

² G. Herzberg, *Chem. Rev.* **20**, 145 (1937).

³ A. S. King, *Trans. Am. Electrochem. Soc.* **56**, 97 (1929).

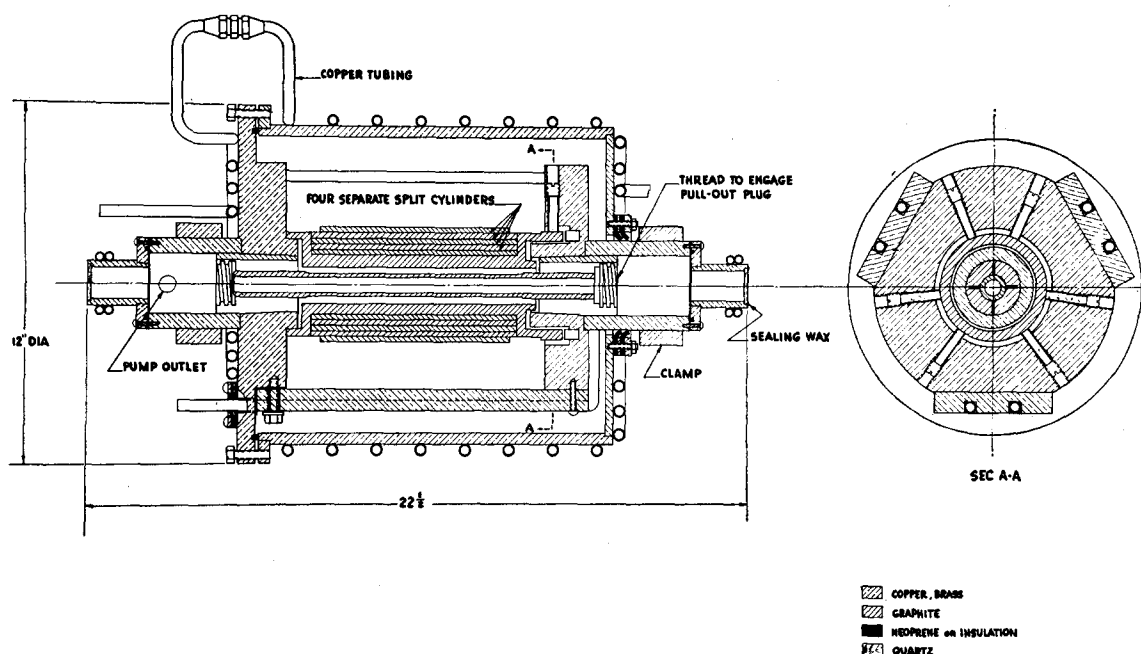


FIG. 1. High temperature carbon tube furnace.

so that when it was forced into the tapered copper end-plate it tightened on the tube, giving good electrical contact. This shape and position of the bushing permitted longitudinal thermal expansion and contraction of the graphite tube without destroying the electrical contact. The other parts of the furnace were for insulation, cooling, and sealing purposes. The furnace was designed and constructed in such a way that the tube could be heated in a vacuum or in a gaseous atmosphere at any pressure less than one atmosphere. The outstanding feature of the design of this furnace is the ease with which a burnt-out tube can be replaced. By removing the window holders and inserting a threaded piece of aluminum into the square threads on the bushings, one can remove a spent tube in a very few minutes.

The tube is heated by low voltage alternating current led in by the massive copper clamps. Furnace currents of about 700 to 800 amp. were obtained from a 90 amp., 220-volt, 60-cycle source through a step-down transformer.

Because of the heat losses through the graphite bushings to the copper parts at the ends, a tube with straight outer walls showed a short hot zone in the center and a large temperature gradient

out toward the ends. To equalize the temperature along the length of the tube and to make it thus suitable for equilibrium measurements, the outer diameter of the tube was decreased in certain places to such a degree that the temperature was nearly constant over a long region and then fell off quite rapidly through cylindrical graphite diaphragms inserted into the tube near its ends. The tendency for a loss of carbon vapor by diffusion out the ends was counteracted by adjusting the diameter of the tube so that the temperature just inside the diaphragm was about 30° to 50° higher than in center of the tube. The diaphragms, in addition to defining the hot zone, also helped to decrease the diffusion loss because of their small, $\frac{1}{4}$ -inch opening. The temperature used in the calculations was that of the long center zone. This procedure was shown experimentally to be correct in several early runs in which the temperature differences between ends and center increased during the course of the experiment. The C_2 spectral intensities taken with the large temperature differences agreed with those taken with small differences if central temperatures were used.

Argon was added to the furnace as an inert gas in order to decrease diffusion of carbon out

TABLE I. Experimental intensity data and their Σ -treatment.

Exposure	Temp. (°K)	I	$4.576 \log I$	$-2600 \Delta C_p$ T	$-2.303 (\Delta C_p - R)$ $\log T$	Σ
4	2683	2.4	1.739	7.559	77.267	-86.565
3	2733	5.9	3.528	7.420	77.448	-88.396
5	2793	18.2	5.766	7.261	77.660	-90.686
2	2828	31.0	6.823	7.171	77.782	-91.775
6	2858	51.9	7.843	7.096	77.885	-92.828
1	2918	72.1	8.502	6.950	78.089	-93.541
7	2963	289.	11.262	6.844	78.238	-96.343

the ends of the tube and in order thereby to lengthen the life of the tube. Argon was chosen rather than helium because its large molecular weight helped prevent loss of carbon vapor by thermal diffusion. Despite the presence of gas in the furnace, at high temperatures rapid volatilization occurred, leading ultimately to arcing within the tube and subsequent breaking. Arcing was always detectable as soon as it started because of a drop in current of about 50 percent.

An experiment was performed to show that the argon which was added only decreased the diffusion out of the tube and did not alter the equilibrium pressure of diatomic carbon vapor inside the tube. Two spectrograms were taken at the same temperature of 2850°K, one with an argon pressure of 48.5 cm and the other with a pressure of 9.1 cm. The intensities were the same in the two exposures to within the limit of measurement of the tracings, which was about one percent. This experiment also showed that the effect of pressure broadening of lines was negligible. Self-absorption of emitted light by the vapor was considered and found to be negligible in these experiments. For example, if the number of dispersion electrons per molecule, or the f value, is taken as unity for C_2 , the maximum error caused by self-absorption can be calculated to be 10^{-6} percent. The f value would not be expected to be appreciably greater than unity and is probably less than 0.1.

After the tube had been prepared to give the desired temperature distribution, the furnace was heated for a few minutes in a vacuum to above 2500°C to rid the tube of gaseous impurities. Then argon was added to the desired pressure. The current through the furnace was increased until the desired temperature was reached, following which ten to fifteen minutes was allowed for the furnace to reach equilibrium. After

temperature measurements had been made with an optical pyrometer at different points along the tube, a five minute exposure was taken. Temperature measurements were made after each exposure as well as before. The current was then raised or lowered and the process repeated for another exposure. Since temperature equilibrium existed within the furnace no discrete lines would be observed if light from the wall of the furnace was allowed to enter the spectrograph. A thin piece of metal with a $\frac{1}{16}$ -inch hole was placed between the furnace and spectrograph and it diaphragmed out any light from solid material in the furnace. Since the work was done in a darkened room, only light from the gas inside the tube entered the spectrograph.

All spectrograms were taken with a small Hilger glass constant-deviation spectrograph of 50-cm focal length and a dispersion of from 20 to 200Å/mm Eastman Number 33, Panchromatic, and 103a-F plates were used. Developing was done with Eastman M-Q developer for one to two minutes. The plates were calibrated by means of a tungsten bulb running at constant current from storage batteries and screens calibrated for transmission. The screens were placed some distance in front of the slit of the spectrograph and were rocked in an apparatus in an

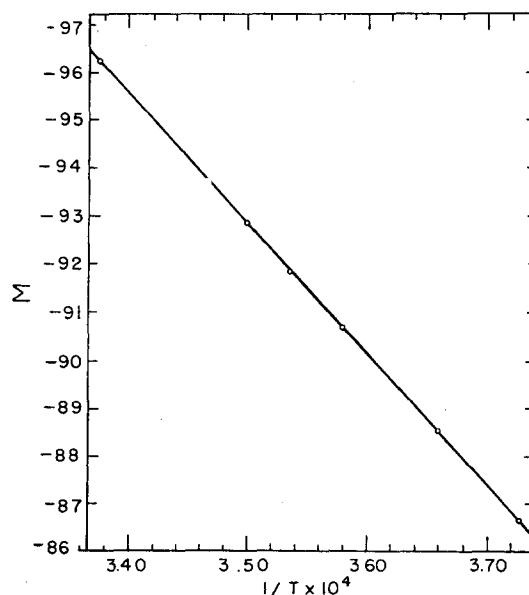


FIG. 2. Σ vs. $1/T$ plot for the reaction $2C(\text{graphite}) = C_2(^3\Pi_u \text{ excited state})$.

TABLE II. Pressure of $C_2(g)$ above graphite.

$T^\circ K$	$\left(\frac{F-E_0}{T}\right)_{\text{graphite}}$	$\left(\frac{F-E_0}{T}\right)_{C_2}$	$\left(\frac{\Delta F - \Delta E_0}{T}\right)_{2gr=C_2}$	$\frac{\Delta E_0}{T}$	$\frac{\Delta F}{T}$	$\log P$	$P(\text{atmos.})$
2000	-5.38	-56.331	-45.57	116.5	71.0	-15.5	3×10^{-16}
3000	-7.38	-59.666	-44.91	77.7	32.8	-7.16	7×10^{-8}
4000	-8.92	-62.102	-44.26	58.3	14.0	-3.06	9×10^{-4}
5000	-10.20	-64.032	-43.63	46.6	2.98	-0.65	2.2×10^{-1}

elliptical motion so that an average transmission was obtained. Photographic densities were measured with a Zeiss recording microphotometer.

Calculations and Results

In the experiments, the resolving power of the apparatus was insufficient, and the intensity was too low to allow the measurement of an individual band line in the spectrum. In this work the peak intensity of the 0-0 head of the C_2 Swan bands at $\lambda 5165$ was used. The furnace spectra were examined to see if lines arising from impurities lying close to the head could contribute to the intensity and thereby cause an error. None was found.

The uncertainties arising when one uses the head of the band are due to the possibility of inclusion of a different number of lines in the

head at different temperatures of the furnace, to the change of the line of maximum intensity with temperature, and to the uncertainty as to what state one takes as his "average" upper state in the calculation of the excitation energy.

The microphotometer tracings of the heads of the C_2 bands indicated that the number of lines included in the heads did not change with the temperature. A calculation of the line of maximum intensity at the extreme temperatures indicated that it changed by only one rotational quantum number. None of the above effects was considered to cause an appreciable error.

In the 0-0 band the head occurs at a J' value of about 13. At 3000°K the line of maximum intensity is $J'=24$. Within 1.5Å of the head are found lines corresponding to $J'=5$ through $J'=21$ which are the only lines to contribute appreciably to the peak intensity as determined by measuring the contour of individual atomic lines. The rotational energies in the excited state corresponding to the rotational quantum numbers of 5 and 21 are 52.5 and 808 cm^{-1} , respectively, or 0.15 and 2.13 kcal./mole. If one then considers that the head originates from a single "average" state he must assign to this state a rotational energy between these limits. A value of 1.2 ± 0.5 kcal. was chosen as the additional excitation energy due to rotation of the molecule in the upper state.

The partial pressure of C_2 gas can be related to the intensity of emission, I , since I is proportional to the concentration of C_2 gas which is in turn proportional to p/T from the perfect gas law. For the reaction,



by setting

$$\Delta H_T = \Delta H_{2600^\circ K} + \Delta C_p(T - 2600), \quad (7)$$

and integrating the van't Hoff isochore, one

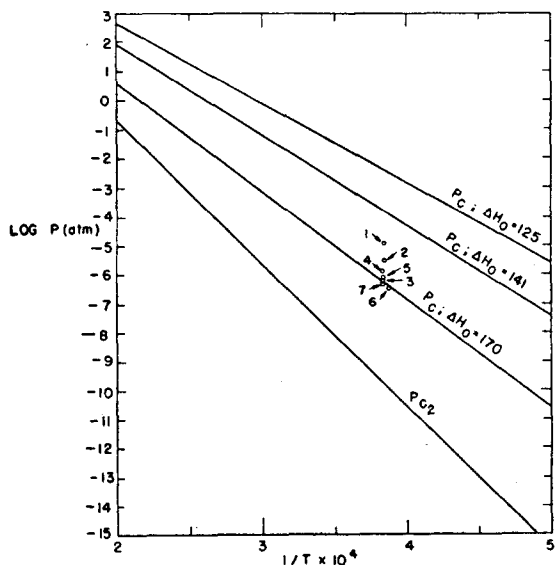


FIG. 3. Vapor pressure of graphite. The circles give the experimental vapor pressure from effusion measurements. The lowest curve gives the pressure of $C_2(g)$ in equilibrium with graphite. The upper three curves give what the pressure of $C(g)$ would be if the heat of sublimation were 125.03, 141.25, or 170.39 kcal./mole. The last is indicated as the correct one.

obtains

$$-4.576 \log p = -4.576 \log k T I = (\Delta H_{2600^\circ\text{K}})/T - 2600 \Delta C_p/T - 2.303 \Delta C_p \log T + M, \quad (8)$$

where p is the pressure exerted by the molecules of C_2 in the excited state, k is a proportionality constant, I is the intensity of the band head, and M is a constant. A plot of Σ , defined by the relation

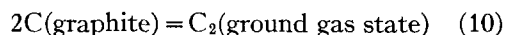
$$\begin{aligned} \Sigma = & -4.576 \log I + 2600 \Delta C_p/T \\ & + 2.303 (\Delta C_p - R) \log T \\ = & (\Delta H_{2600^\circ\text{K}})/T + M + 4.576 \log k, \end{aligned} \quad (9)$$

against $1/T$ must be a straight line of slope $\Delta H_{2600^\circ\text{K}}$ and intercept $M + 4.576 \log k$. The experimental data and the details of the calculation of Σ are given in Table I.

The ΔC_p used in the calculations was taken as -7.8 e.u. This figure was obtained by taking the difference between $5R/2 = 4.97$, the heat capacity at constant pressure of the single "average" gaseous state we are considering, and 12.8 , which is twice the heat capacity of solid graphite, as determined by extrapolating to the temperatures of the experiments the data of Worthing⁴ covering a temperature range from 1200°K to 2100°K . Although such an extrapolation may give an uncertain value, the terms involving ΔC_p do not change rapidly with temperature and do so in opposite directions, so that together they amount to only a slight correction to the intensity term.

Figure 2 gives a plot of Σ against $1/T$. The point falling out of line is the first point that was taken and it deviates from the others because the temperature changed greatly during the exposure. The line on the graph is the one obtained from a least squares reduction of Σ and $1/T$ values, giving zero weight to the first exposure. The slope of this line, 277.8 kcal./mole, is the heat at 2600°K for reaction (6). The probable error, taking equal weighting for all points except the discarded point, is calculated to be ± 1.4 kilocal.

The heat at 2600°K for the reaction



may be obtained from the above heat by sub-

tracting from it the energy of excitation of the excited gas state. As discussed previously, the rotational energy is 1.2 ± 0.5 kcal./mole, the vibrational contribution is zero, and the electronic excitation of C_2 is $19,377 \text{ cm}^{-1}$ or 55.4 kcal./mole. Thus we obtain for reaction (10),

$$\begin{aligned} \Delta H_{2600^\circ\text{K}} &= 277.8 - 1.2 - 55.4 \\ &= 221.2 \text{ kcal./mole.} \end{aligned} \quad (11)$$

To obtain the heat of the last reaction at absolute zero, one must use the heat capacities to get the change of the heat with temperature. As pointed out, the heat capacity of a gas in a single quantum state is that of a monatomic gas, $5R/2$, and its heat content change with temperature is simply $5R\Delta T/2$. For solid carbon, Wagman, Kilpatrick, Taylor, Pitzer, and Rossini⁵ give 5.814 kcal./mole as the difference of heat content between 1500° and 0°K . An integration of Worthing's heat capacity curve together with its extrapolation gave 6.597 kcal./mole as the difference in heat content of graphite at 2600°K , and 1500°K . From these two values one finds that 12.411 kcal./mole is the difference in heat content of graphite at 2600°K and 0°K . Therefore, for reaction (10)

$$\begin{aligned} \Delta H_{0^\circ\text{K}} &= \Delta H_{2600^\circ\text{K}} - 5(2600)R/2 + 2(12.411) \\ &= 233.1 \text{ kcal./mole.} \end{aligned} \quad (12)$$

A consideration of the magnitude of the possible errors in the temperature measurements indicated that if the temperature were incorrect in one direction at one end of the temperature range and in the other direction at the other end, the heat could be in error by about 15 kcal./mole. Since such a situation is not at all likely, the error in the heat attributable to the temperature is probably not over 5 kcal./mole. The uncertainties produced by the intensity measurements were about of the same order of magnitude as by the temperature measurements. Although the probable error is only ± 1.4 kilocal, the absolute uncertainty is thus set at ± 7.0 kilocal.

Since at 0°K the equilibrium gaseous state of C_2 is the ground state we have for reaction (5),

$$\Delta E_{0^\circ\text{K}} \cong \Delta H_{0^\circ\text{K}} = 233.1 \pm 7.0 \text{ kcal./mole.} \quad (13)$$

⁴ A. G. Worthing, Phys. Rev. 12, 199 (1918).

⁵ Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, J. Research Nat. Bur. Stand. 34, 143 (1945).

TABLE III. Experimental vapor pressure and heat of sublimation of graphite.

Run No.	T°K	Time (hrs)	Hole area (cm ²)	Wt. carbon collected (mg)	P (atmos.)	LogP	$\frac{\Delta F}{T}$	$\frac{\Delta E_0}{T}$	ΔE_0
1	2603	3.50	0.0884	1.971	1.153×10^{-6}	-4.938	22.60	54.49	154.85
2	2603	1.60	0.0884	0.234	3.00×10^{-6}	-5.523	25.27	62.16	161.80
3	2613	3.83	0.0884	0.132	7.08×10^{-7}	-6.150	28.14	65.03	169.92
4	2608	3.67	0.0884	0.216	1.21×10^{-6}	-5.917	27.08	63.97	166.83
5	2598	4.62	0.0319	0.073	8.97×10^{-7}	-6.047	27.67	64.56	167.73
6	2583	3.28	0.0322	0.021	3.59×10^{-7}	-6.445	29.49	66.38	171.46
7	2603	3.50	0.0325	0.033	5.25×10^{-7}	-6.280	28.74	65.63	170.83

The vapor pressure of graphite as C₂ is calculated in Table II from this value of the heat and values of the free energy function, $(\Delta F - \Delta E_0^\circ)/T$ for reaction (5). The values given by Kelley⁶ and Gordon⁷ for the free energy functions of graphite and C₂(gas), respectively, have been used in Table II. The pressure of C₂ in equilibrium with graphite at different temperatures given in the last column in Table II is plotted as the lowest curve in Fig. 3.

The same general spectroscopic procedures that were used in the determination of the heat of formation of C₂(gas) can also be employed in the study of other substances such as CH, CN, and CS. The heat of formation of CH is related to the heat of sublimation of graphite through a series of reactions similar to reactions (1), (2), (3), and (4), including the heats of dissociation of CH and H₂. Since Herzberg⁸ gives values for these last two quantities, a determination of the heat of formation of CH would lead to a value for the heat of sublimation of graphite. Preliminary experiments were performed to accomplish this determination but in the presence of hydrogen the graphite tubes disintegrated so rapidly, presumably because of the formation of the relatively stable acetylene, that no reliable results were obtained.

THE VAPOR PRESSURE OF GRAPHITE AND HEAT OF FORMATION OF C(Gas)

Of the several values that Herzberg² gave as possible heats of dissociation of CO, all but three are admittedly much too low. These three are 256.18, 227.04, and 210.82 kcal./mole on the basis of the latest constants advocated by the

National Bureau of Standards.⁹ The heats for reactions (3) and (4) are given as -27.202 and -58.586 kcal./mole¹⁰, respectively, and by combining these with the possible heats of dissociation of CO one sees that one of the following three values must be the heat of sublimation of graphite: 170.39, 141.25, or 125.03 kcal./mole. By using these values with values of the free energy functions for solid graphite and gaseous monatomic carbon from Kelley⁶ and Gordon,⁷ one can calculate what the vapor pressure would be at any temperature corresponding to each of these three heats. The results of this calculation are presented in graphical form in Fig. 3. It is apparent that at low pressures the pressure of C₂(gas) is negligible in comparison with the pressure of C(gas) irrespective of which of the possible heats of sublimation is correct.

Marshall and Norton¹¹ carried out experiments on the rate of loss of weight of graphite rings heated inductively and reported that the heat of sublimation of graphite is 177 kcal./mole. Later Marshall and Johnston¹² measured the weight loss from graphite cylinders and claimed that the results indicated a very low accommodation coefficient for graphite. Since if the accommodation coefficient is very low, any vapor pressure measurement based on rates of vaporization will be too low, leading to a heat of sublimation too large; others¹ have used the argument of low accommodation coefficient to question the results of work leading to the highest value for the heat.

⁹ American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected values of hydrocarbons. Table β (part 9) conversion factors—units of molecular energy, March 31, 1945.

¹⁰ See reference 9, Table 0w, August 31, 1946 and Table 00w, June 30, 1946.

¹¹ A. L. Marshall and F. J. Norton, J. Am. Chem. Soc. 55, 431 (1933).

¹² Private Communication from H. L. Johnston; see G. Herzberg, J. Chem. Phys. 10, 306 (1942).

⁶ K. K. Kelley, U. S. Bur. Mines Bull. 383, 32 (1935).

⁷ A. R. Gordon, J. Chem. Phys. 5, 350 (1937).

⁸ G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, New York, 1939).

An equilibrium method of measuring vapor pressures and one not dependent on the measurement of rate of vaporization is one in which the material to be studied is heated in an inert vessel completely closed except for a small hole in the top. Inside the vessel equilibrium exists and the quantity of substance effusing through the hole can be calculated from the kinetic gas theory if the pressure is known. Conversely, if the quantity transported is measured, the pressure of that species inside the crucible can be calculated.

Experimental

The inert effusion vessel used was equivalent to a tantalum carbide cylinder with a small hole through the upper surface. It consisted of a graphite crucible which fitted snugly inside a tantalum crucible which had been carburized on the inner surfaces. The tantalum crucible acted as the heating element in the high frequency induction furnace. The holes through the covers of the graphite and tantalum crucibles were coaxial, of the same size, and tapered in such a manner that they acted together as a single thin-edged hole. The graphite crucible was filled with Acheson graphite powder, grade No. 38, to one quarter to one half of its height. The graphite crucible was of National Carbon C-18 material and had an internal diameter of about $\frac{1}{2}$ inch and a height of about 1.2 inches with $\frac{1}{16}$ -inch walls. Two different sized holes, one about $\frac{1}{16}$ inch and one about $\frac{1}{8}$ inch, were used.

A series of thin molybdenum and tantalum spirals or cylinders surrounding the crucibles and a series of disks of the same metals supported on $\frac{1}{16}$ -inch metal pins served to decrease heat loss outward and downward from the crucibles. Heat flow out the top was decreased by having above the crucibles a series of tantalum disks each of which had a hole in the center. The size of the hole increased regularly with the distance of the disk from the top of the crucible so that an unobstructed cone was available for the escape of the carbon vapor. Above these shields was a thin platinum collector plate suspended in a water-cooled copper holder. The geometry was such that 5.09 percent of the vapor leaving the hole was collected.

The crucibles and all the molybdenum and

tantalum shielding were contained in a zircon crucible about 5.5 inch tall, 2.25 inch diameter at the bottom and about 2.5 inch diameter at the top. The zircon crucible rested on a zircon stand inside a Pyrex tube that was water cooled on the outside. The Pyrex tube was connected with a ground glass joint to the vacuum system consisting of a mechanical pump and two oil diffusion pumps in series. At the beginning of an experiment the pressure in the system was about 1 to 2×10^{-5} mm and during the heating rose to about 2 to 3×10^{-4} mm as read on a Knudsen gauge.

Energy was supplied to the crucible from a closely wound water-cooled coil of copper tubing which surrounded the jacket carrying water to cool the Pyrex tube. The coil was in series with a 20-kw spark gap converter delivering about 100 amp. at a frequency of about 16,000 cycles/sec. and with several other coils which were part of a controlling device for maintaining constant temperature in the crucible. The temperature inside the crucible was read with a calibrated optical pyrometer focused through a hole in the collector plate and on the hole in the top of the crucibles. Because of the relatively high emissivity of graphite and the small ratio of hole area to total inside area, no deviation from black-body conditions was assumed. The temperature measurements were corrected for reflection and absorption by the windows of the vacuum system.

Before a series of runs the apparatus was heated to outgas as much as possible the metallic parts and the graphite. The first four runs were made with an effusion hole about $\frac{1}{8}$ in. in diameter. In the last three runs the hole was about $\frac{1}{16}$ in. diameter. Although the first run was intended to be an outgassing one, enough data were taken to obtain a measurement. Before the first run with the smaller hole the apparatus was heated for about 1.3 hours at a temperature about 50 degrees higher than that for the succeeding runs.

The procedure was to heat fairly rapidly to the temperature of the experiment, to adjust the controlling devices and to allow vaporization to occur for several hours. The carbon was burned off the platinum plate in a micro-combustion apparatus and was determined by the weight of CO_2 which was collected. The authors are very

grateful to Mr. Charles Koch who carried out all these micro-determinations of carbon. A spectroscopic analysis of the deposit indicated that the main impurity, silicon, was less than 0.1 percent.

Results

The data are given in Table III. The accuracy of the weights given in column 5 is indicated by the results of a blank burned to test the sensitivity of the analysis which was estimated to be ± 0.004 mg. The blank registered 0.005 mg. The pressures in column 6 were calculated from the fraction of the total material transported that was collected and from the effusion equation,

$$p = z(MT)^{1/2} / 44.383a \cdot t, \quad (14)$$

where p is the pressure in atmospheres of the species of molecular weight M , z is the number of moles effusing out of the crucible in time t through a hole of area a . The values of $\Delta F/T$ in column 8 have been calculated from this pressure. The value of $(\Delta F - \Delta E_0^\circ K)/T$ for reaction (1) is the same for each of these temperatures and is -36.89 as calculated from the values of Kelley⁶ and Gordon.⁷ Column 9 gives values of $\Delta E_0^\circ K/T$ obtained by subtracting -36.89 from the values in column 8. The last column contains the value of $\Delta E_0^\circ K$ calculated from each experiment. The data are also presented as the circles in Fig. 3.

Both the table and graph indicate that the apparent vapor pressure decreases with the time of heating at high temperature. This phenomenon is probably caused by volatilization of tars remaining in the material from the binder used in the graphitization process. These tars are organic substances which if deposited on the collector plate, would register as carbon in the burning analysis. With long heating at high temperatures the tars gradually vaporize and consecutive measurements of vapor pressure show a decrease toward the true equilibrium vapor pressure of graphite. It is worth while to note that whereas this difficulty will appear in any effusion or vaporization method, because one has no way of knowing precisely the gaseous species he is observing, he may proceed with much more certainty in the tube furnace and spectroscopic experiments because there he is absolutely certain of the molecules he is ob-

TABLE IV. Sublimation points of graphite in degrees Kelvin.

Pressure(atmos.)	10 ⁻¹⁰	10 ⁻⁸	10 ⁻⁶	10 ⁻⁴	10 ⁻²
C(g)	2060	2320	2650	3090	3705
C ₂ (g)	2562	2855	3227	3715	

serving and he knows even in which particular energy states they are.

The purpose of changing the hole size in the effusion measurements was to check the magnitude of the accommodation coefficient. If the latter were very small then, irrespective of the size of the hole, all the material vaporizing should finally escape and the observed vapor pressure would be a function of the hole size. The last three runs with the smaller hole should have given apparent vapor pressures higher than the first four experiments in case the accommodation coefficient were very low. This is not the case and therefore these data indicate a relatively high accommodation coefficient.

Vapor pressures obtained by the effusion method will be correct if the accommodation coefficient is large compared to the ratio of hole area to total area inside the crucible. The agreement between the experiments with the different size holes indicates that this condition was met. The ratio of hole area to total area was 4.03×10^{-3} in the first runs and 1.46×10^{-3} in the last runs. The accommodation coefficient therefore must be greater than 4×10^{-3} , and the vapor pressures obtained are the true equilibrium vapor pressures.

In view of the facts that the vapor pressure measurements were of the equilibrium type and that the measured heat of sublimation is very nearly one of the values obtained from a consideration of the CO dissociation data, there seems to be no good reason to suppose that carbon gas left the crucible in the ⁵S state as proposed by Schmid and Gero.¹³ Shenstone¹⁴ has recently found the ⁵S state to be 33735.2 cm⁻¹ above the ground state ³P. The observation of emission from this state eliminates the possibility of its being a strongly metastable state. The fair agreement of the rates of vaporization work with this research indicates that carbon

¹³ R. Schmid and L. Gero, *Zeits. f. Physik* **99**, 281 (1936).

¹⁴ A. G. Shenstone, *Phys. Rev.* **72**, 411 (1947).

evaporates from the solid as monatomic gas in the ground electronic state.

The data obtained in the present work indicate that the heat of sublimation of graphite is about 170 kcal./mole and it is expected that the value of 170.39 ± 0.20 kcal./mole obtained from the CO spectroscopic data is more nearly correct than any other experimental value.

Calculations based upon values of $(\Delta F - \Delta E_0^\circ \text{K})/T$ calculated from data of Kelley⁶ and Gordon⁷ and upon the heats of formation of gaseous C and C₂ indicate that at 4640°K one atmosphere of C(g) would be in equilibrium with solid graphite; at 5390°K the pressure of C₂(g) above solid graphite would be one atmosphere; and that at 4630°K the combined pressure of C(g) and C₂(g) would be one atmosphere in equilibrium with solid graphite. These temperatures are not necessarily realizable sublimation points because the melting point of graphite may be lower. There is no reliable determination of the melting point, but if it does lie lower than the temperatures given, then the true boiling points of liquid carbon will be higher. Table IV gives the temperatures in degrees Kelvin at which the indicated species reach the indicated partial pressures in equilibrium with graphite. These temperatures have been calculated in the same manner as that used for the above sublimation points. The ratio of the partial pressure of C₂(g) to the partial pressure of C(g) in equilibrium with graphite increases regularly with increasing temperature and is given approximately by the following values: $10^{-4.94}$ at 2000°K, $10^{-3.65}$ at 2500°K, $10^{-2.81}$ at 3000°K, $10^{-2.22}$ at 3500°K, $10^{-1.79}$ at 4000°K, and $10^{-1.47}$ at 4500°K.

Correlation With Other Work

As noted above, Johnston¹² has reported that preliminary measurements have indicated that the accommodation coefficient of carbon gas on graphite might be very low. We are not familiar with all the details of this work, but Simpson¹⁵ has recently performed experiments of a similar type and has concluded that they indicate that the accommodation coefficient is very close to

unity. Comparison of our equilibrium vapor pressure data with the data of Marshall and Norton¹¹ obtained by measurement of the rate of evaporation of graphite indicates that the accommodation coefficient is not less than 0.3. Experimental uncertainties do not allow us to fix it any closer to unity. Therefore, one may summarize by stating that the accommodation coefficient of carbon gas on graphite at high temperatures is close to unity and can be given a rough value of about 0.3.

The only other recent experiments on the vapor pressure of graphite are those of Basset¹⁶ and of Ribaud and Begue.¹⁷ Their results have been interpreted by others¹ as supporting a much higher vapor pressure than the present work indicates. The work by Basset was performed on graphite rods of fair purity which he heated to high temperatures in high pressures of argon. His outgassing procedure was performed at a lower temperature than the experiments and probably, therefore, was not sufficient to dispose of the residual tars. His temperature readings, furthermore, were taken with an optical pyrometer which could conceivably give temperature indications far too low because of smoke or particles in the argon. Ribaud and Begue tried to obtain the temperature of sublimation of graphite at several pressures of argon by observing the maximum temperatures of a graphite crucible packed in lampblack, when they increased the high frequency power supplied inductively to the crucible. Such an experiment need not necessarily give a true sublimation point because if insufficient power were available, it would give only the temperature at which the rate of heat loss from the crucible by conduction, convection, radiation, and evaporation is equal to the power input. In addition, their experiments are subject to the same criticism as are those of Basset.

These possible errors are in such a direction that if they exist the observed temperatures would be too low, or the observed vapor pressures would be too high. It is in this direction that the work of these others differs from the results of the present work.

¹⁵ O. C. Simpson and R. J. Thorn, private communication of work to be published soon.

¹⁶ J. Basset, *Brennstoff-Chemie* **23**, 127 (1942).

¹⁷ G. Ribaud and J. Begue, *Comptes Rendus* **221**, 73 (1945).

THE HEATS OF DISSOCIATION OF C₂ AND CO

The values for the heats of formation of C(g) and C₂(g) are related to the heat of dissociation of C₂ through the equations

$$2C(\text{graphite}) = C_2(g), \quad (5)$$

$$C_2(g) = 2C(g), \quad (15)$$

$$2C(\text{graphite}) = 2C(g). \quad (1)$$

Here, the sum of the first two equations yields the last, and the sum of the heats for the first two must be the heat of the last. That is, the sum of the heat of dissociation of C₂ and the heat of formation of C₂(g) must be twice the heat of formation of C(g). The heat of dissociation of C₂ is not known but Herzberg¹⁸ has pointed out that vibrational levels in the ground state have been observed as high as $v=11$. This vibrational level has an energy above the C₂ ground state of about 16,441 cm⁻¹ or about 47.00 kcal./mole. The heat of dissociation of the C₂ molecule must be greater than this energy. By adding to the 47.00 kcal./mole the heat of formation of C₂(g), 233.1 kcal., one obtains 280.1 kcal. as the lower limit for twice the heat of formation of C(g). This value eliminates 125.03 as the heat of formation of C(g) and makes 141.25 very improbable since at $v=11$ the vibrational spacing is still large and it does not seem reasonable that the spacing would go to zero after this vibrational level. This evidence indicates, in conformity with the vapor pressure measurements, that the heat of formation of C(g) is 170.39 kcal./mole.

This discussion is based on the assumption that C₂ in the ³Π-ground state dissociates to atoms in the normal state. This seems like a safe assumption since very few cases are known in which the ground state of a molecule does not dissociate to normal atoms. Furthermore, since the correlation rules between atomic and molecular states do not permit a ³Π-state to dissociate into any S state, the ground state of C₂ cannot be dissociating into carbon atoms in the ⁵S state.

By taking this heat of formation of C(g) and the heat of formation of C₂(g) one can calculate

¹⁸ G. Herzberg, *Phys. Rev.* **70**, 762 (1946). N. L. Singh, *Ind. J. Phys.* **19**, 167 (1945) would reduce the highest observed level in the Swan system to $v=9$, which reduces lower limit of heat of sublimation slightly.

the heat of dissociation of C₂ to be 340.78 – 233.1 = 107.7 kcal./mole or 4.7 volts. Three recent estimates of this value have been made. A Birge-Sponer¹⁹ linear extrapolation of the vibrational energy level spacings based upon only a few levels gives about 6.8 volts as the heat of dissociation. Herzberg¹⁸ claimed that this value is about 3.6 volts. Gaydon²⁰ has stated that it would not be difficult to make a graphical extrapolation to about five volts. The present results indicate that the Birge-Sponer extrapolation gives too large a value, probably because only a few vibrational levels can be used, and that Gaydon's estimate is nearly correct.

Having the heat of formation of C(gas), one may use the thermochemical cycle represented in Eqs. (1), (2), (3), and (4) to choose the correct value for the heat of dissociation of CO. This procedure gives 11.109 ev as the energy of dissociation of CO corresponding to a heat of sublimation of carbon of about 170 kcal./mole.

The Birge-Sponer extrapolation of the vibrational levels of the ground state for this molecule gives 11.2 ev for *D*_{CO}. This extrapolation is based upon a large number of levels and gives very close agreement with the experimental value determined in this work. Gaydon²⁰ very recently has discussed at some length the problem of the energy of dissociation of CO. He has discussed the Birge-Sponer extrapolations, the predissociations in CO, the rule of non-crossing of potential energy curves, the photo-dissociation of CO, electron impact experiments, the dissociation energy of CO⁺, the dissociation energies of CN and C₂N₂, and theoretical considerations of the bond energies of some organic molecules. He concludes that none of these data is definitely contradictory to a heat of dissociation of 11.11 ev for CO, and that several of them strongly indicate this value to be correct. Thus his conclusions are in agreement with the results of the present work. The present experiments show also that Gaydon is probably correct in his contention that the Birge-Sponer method of extrapolating the vibrational energy level spacings can be quite useful in helping one fix the dissociation energies of many diatomic molecules.

¹⁹ R. T. Birge and H. Sponer, *Phys. Rev.* **28**, 259 (1926).

²⁰ A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, Ltd., London, 1947).