Table II against the reciprocal of the dielectric constant. A smooth curve was obtained upon which the recalculated values fitted nicely. These two values have an accuracy of ±0.1 mv. The others have an accuracy of ±0.05 mv.

The mean activity coefficients for the acid in the various solutions were calculated from the experimental data by Equation (4). These values were plotted on a large graph and the rounded values at 0.002, 0.005 and 0.01 m determined. These are given in Table III. The values calculated by Equation (5) agree almost exactly with those determined from the experimental data. The greatest variation was 0.003.

TABLE III

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN ETHYLENE GLYCOL–WATER MIXTURES AT 25°

Molality	Weight per cent. ethylene glycol, % 5	15	30
0.002	0.950	0.944	0.940
.005	.925	.918	.913
.010	.898	.895	.886

Summary

1. The values of the electromotive force at 25° of cells of the type $H_2|HCl$ (m), ethylene glycol (x), water (y) |AgCl–Ag were determined for acid concentrations up to 0.01 m and for 5, 15 and 30 weight per cent. of ethylene glycol.

2. From the data obtained the standard electrode potentials for these solutions were determined.

3. It was found that the value of the ion size parameter for hydrochloric acid in the solutions studied is 4.3 Å.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, NEW YORK]

Carbon Vapor Pressure and Heat of Vaporization

BY A. L. MARSHALL AND F. J. NORTON

The values of these important physical properties, in particular, the heat of vaporization of carbon, have been in dispute in the literature for a number of years. The experimental difficulties in this high temperature field are great, and there has been a paucity of detailed direct experimental measurements. The present authors[1] have published a brief report on the heat of sublimation of carbon based on vapor pressure measurements. The recent determinations of Brewer, Giles and Jenkins[2] makes it desirable to have recorded additional complete experimental detail in the literature. In brief, the data of Brewer, *et al.*, give a value of $\Delta H_0° = 170.39$ kilocalories per mole, in excellent agreement with our value of $\Delta H_0^0 = 175.2$ kilocalories for the heat of sublimation. Further, their values for vapor pressure, obtained by an equilibrium effusion method, lie very close indeed to our experimental points, obtained from rate of evaporation of graphite rings in a vacuum.

The relation between rate of evaporation and vapor pressure, is given in the equation of Langmuir[3] derived from kinetic theory

$$m = \alpha(M/2\pi RT)^{1/2} P \qquad (1)$$

where m = rate of evaporation
α = accommodation coefficient
M = molecular weight
R = gas constant
T = absolute temperature
P = vapor pressure

Expressing P in atmospheres, m as grams per square centimeter per second evaporating, R = 83.15 × 10^6 erg deg.$^{-1}$ mole^{-1} and M = 12 for monatomic carbon, the equation becomes, using $\log_{10}$

$$\log P = \log m + {}^1/_2 \log T - 2.187 \qquad (2)$$

The factor α is taken as unity, and this is justified in the subsequent discussion. The fact that the carbon evaporates predominantly in the monatomic form is supported by these and other experiments discussed later.

Apparatus and Technique

The vapor pressure was determined from the loss in weight of rings of graphite, of measured gross surface area, heated by high frequency in a very good vacuum, varying times, at various temperatures.

The rings were turned from Acheson graphite, 2.22 cm. outside diameter, 1.11 cm. inside and of various thicknesses, from 0.21 cm. to 0.39 cm., giving 8.0 cm.^{2} to 9.85 cm.^{2} total area from which evaporation takes place. The evaporation from the interior edge of the ring is subject to a very small correction due to the fact that with straight line evaporation some atoms strike the opposite surface, but this is equivalent to only about 2% reduction in area which is negligible compared to other errors.

These rings rested upon carbon prongs, held in a carbon support. A hole in the bottom of the support served as a socket for a 60 mil. tungsten wire, sealed into the bottom of the containing vessel, a graded seal connecting hard glass to quartz.

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[1] Marshall and Norton, THIS JOURNAL, **55**, 431 (1933).

[2] Brewer, Giles and Jenkins, *J. Chem. Phys.*, **16**, 797 (1948). This appeared also as U. S. Atomic Energy Commission Report MDDC-1575.

[3] Langmuir, *Phys. Rev.*, **2**, 329 (1913).

The containing vessel was of quartz, water cooled, as shown in Fig. 1. It was connected to the vacuum system by 3-cm. diameter tubing. At the top, 80 cm. from the sample, was an optical window. A shutter, operated through a water-cooled stopcock, kept the window free from evaporating carbon, and was opened only to take temperature readings.

A detailed drawing of the vacuum system and equipment for measurement and analysis of evolved gases is given in another paper.[4]

Temperature was measured with a disappearing filament type optical pyrometer, with neutral screens, calibrated at Nela Park by W. E. Forsythe. The pyrometer calibration was checked at the beginning and end of the experiments by means of a separately calibrated standard lamp with notched ribbon filament which was also supplied by Forsythe. This lamp was calibrated by him, and he reported the temperatures were based on the assumption of Wien's equation with C_2 taken as 1.433 cm. degrees and upon the melting point of gold taken as 1336°K. On this scale the melting point of palladium has been found to be 1829°K. For convenience in the calibration of optical pyrometers, a black body held at the melting point of palladium was used as the point of reference, Forsythe reported. Correction was made for window absorption by calibrating with and without the optical window used. Correction for emissivity of carbon at $\lambda = 0.665$ micron wave length was made, as given in "International Critical Tables." This spectral emissivity, which applies to round carbon filaments was checked for our flat surfaces by drilling small holes in a sample of the graphite which served as black body sources. The emissivity thus found checked that given above. The temperatures were found very uniform over the surface of the sample, not varying more than 15° from one spot to another.

After our experimental work had been completed, Stimson[4a] published a paper which would make small change in our temperature values. He gives as the palladium point 1552° = 1825°K. whereas Forsythe used the figure 1829°K. at the time of calibration, a difference of 4°. He also recommends $C_2 = 1.438$ cm. degrees in Planck's formula giving changes above the gold point. We used $C_2 = 1.433$ cm. degrees in Wien's equation.

For consistency we have kept the values used by Forsythe in view of the estimated uncertainties in our temperature measurement, discussed later.

The vacuum was of the order of 10^{-8} mm. The glass system was baked out at 450°, the quartz at 800°, and the raw carbon sample given a preliminary heating at 2400°K. On the first heating of the graphite it was found to give a black deposit at 2000°K. This was presumably traces of binder distilling out. After this had been eliminated, no distillation of carbon was noted at this temperature. At 2400°K., blackening of the walls started to become perceptible after an hour and a half. At 2800°K., the quartz became very much blackened in a minute from the distilling carbon.

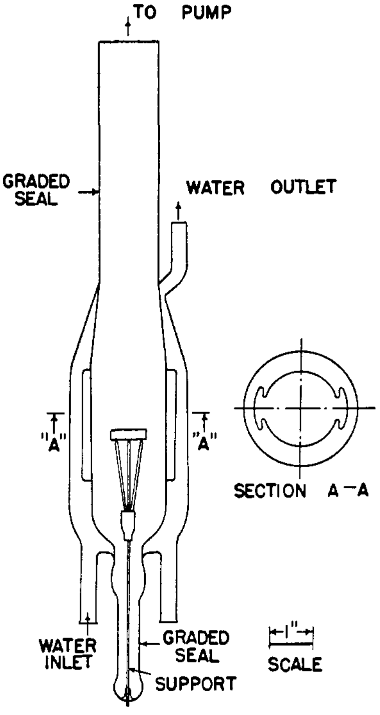

Fig. 1.—Quartz cell for vacuum evaporation of graphite.

The carbon rings were lifted from the prong support by suction on a soft tube, rubber tipped. They were transferred to the balance without touching with the hands, and care was used to avoid knocking off any particles of graphite. The total weight was 0.9 to 1.8 g. The loss in weight on heating varied from 0.0020 to 0.0600 g., most values being in the latter range. They were weighed to ±0.1 mg. No change in weight was noted when the samples were left in the balance for several hours. The balance case was kept dry by beakers of concentrated sulfuric acid. No change in weight was found when a sample was removed several times with the suction tube, and none was found when the sample was put through the regular bake-out procedure. All this indicates that when the sample is taken out into the air reproducible equilibrium is rapidly established, as far as our limits of weighing go. We endeavored to give each sample as nearly the same treatment as possible. Care was taken to cool the sample to room temperature before admitting air to the system. Other work with graphite and metals showed this precaution to be very necessary.[4]

The times of heating varied from 6 minutes at

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(4) Norton and Marshall, *Trans. Am. Inst. Mining Met. Engrs.*, Institute of Metals Division, **156**, 351 (1944), "The Degassing of Metals," Technical Publication 1943. This is reprinted in Metals Technology Vol. 11, Jan. 1944. The paper is discussed and further data on graphite given by S. Dushman, "Scientific Foundations of Vacuum Technique," J. Wiley and Sons, New York, N. Y., 1949, pp. 633-637.

(4a) H. F. Stimson, *Jour. Res. Nat. Bur. Stds.*, **42**, 209-217 (1949).

2870°K. to 1050 minutes at 2357°K. This gives a hint to the limits of this method of determining carbon vapor pressure. At the high temperature, time becomes the uncertain factor, especially since a few seconds are required to come up to temperature. At the lower temperatures, rate of weight change becomes so slow that the accuracy of weighing becomes very important. In the whole temperature range, the accuracy of temperature measurement by optical pyrometry must be kept as high as possible.

The sample was heated from outside the water cooled vacuum vessel by a water cooled copper coil, with high frequency power of 1800 meter wave length (167 kilocycles). This was obtained from a self-rectifying oscillator circuit with a maximum power input of 20 kw.

Table I

Variation of Surface Temperature and Probable Error of Temperature Measurement

No.	Temp., °K.	No.	Temp., °K.	No.	Temp., °K.
1	2328	1	2510	7	2480
2	2328	2	2490	8	2510
3	2308	3	2480	9	2515
4	2323	4	2510	10	2460
5	2318	5	2480	11	2490
6	2308	6	2474	12	2500
7	2308	B. Mean error ±13°; temp., 2490 ± 5°K.			
8	2318	A. Mean error ±10°; temp., 2319 ± 3°K.			
9	2333				

An idea of the small temperature variation, at different positions on the ring, is afforded by the accompanying Table I and Fig. 2 for a test sample at two temperatures. The figures 1, 2, 3, etc., refer to the position on the ring.

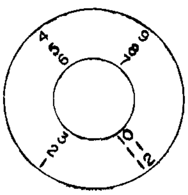

Fig. 2.—Positions of temperature measurement on graphite ring.

It seems safe to conclude that throughout the measurements, the temperature is known within ±15°K.

It was found that a solid disc heated by high frequency gave very non-uniform temperature distribution over the surface, and hence was not used.

It is exceedingly important to have very good vacuum conditions with no other gases present to react with and carry carbon away. All the loss in weight must be carbon evaporation. Furthermore, binder and tarry materials must be, and in these experiments were, completely evaporated from the sample before loss in weight measurements are made.

Brewer, *et al.*,[2] note that in their experiments there is an apparent vapor pressure decrease with time of heating at high temperature and they attribute this to traces of tar and binder being eliminated. This is undoubtedly the case and their final values after long heating are in excellent agreement with ours.

Experimental Results for Vapor Pressure.—Our experimental points, 25 in number, are presented in Table II. In Column 5 is the vapor pressure for each point as calculated from Equation 2. These data are plotted in Fig. 3, indicated by circles.

Table II

Experimental Data on Vapor Pressure and Heat of Vaporization of Graphite

Expt.	Loss in weight g. per sq. cm. per sec. = m	K.° temp. = T	$10000/T$	$\log_{10} P$ (P in atm.)	Heat of vaporization $\Delta H_0°$, kcal. per mole
105	$1.74 \times (10)^{-5}$	2870	3.484	−5.217	175.0
107	$1.40 \times (20)^{-5}$	2790	3.584	−5.318	171.3
100	$1.10 \times (10)^{-5}$	2790	3.584	−5.423	172.5
111a	$7.03 \times (10)^{-6}$	2810	3.559	−5.616	176.5
99	$3.46 \times (10)^{-6}$	2746	3.642	−5.928	176.3
102a	$3.48 \times (10)^{-6}$	2775	3.604	−5.921	178.1
104a	$3.19 \times (10)^{-6}$	2693	3.713	−5.968	173.3
102b	$2.61 \times (10)^{-6}$	2708	3.693	−6.053	175.4
111b	$1.10 \times (10)^{-6}$	2628	3.805	−6.436	174.8
81	$6.04 \times (10)^{-7}$	2553	3.917	−6.702	172.8
86	$3.79 \times (10)^{-7}$	2558	3.910	−6.904	175.6
94	$3.23 \times (10)^{-7}$	2546	3.928	−6.975	175.6
95	$2.87 \times (10)^{-7}$	2536	3.943	−7.027	175.4
230	$2.00 \times (10)^{-7}$	2473	4.044	−7.189	173.0
237	$1.65 \times (10)^{-7}$	2473	4.044	−7.273	173.9
252	$1.38 \times (10)^{-7}$	2473	4.044	−7.350	174.9
246	$1.05 \times (10)^{-7}$	2450	4.082	−7.471	174.5
232	$1.17 \times (10)^{-7}$	2473	4.044	−7.422	175.7
242	$9.70 \times (10)^{-8}$	2473	4.044	−7.503	176.4
83	$7.54 \times (10)^{-8}$	2420	4.132	−7.618	173.8
70	$6.94 \times (10)^{-8}$	2434	4.109	−7.653	175.4
75	$4.08 \times (10)^{-8}$	2420	4.132	−7.884	177.0
77	$3.05 \times (10)^{-6}$	2420	4.132	−8.011	178.3
97	$2.35 \times (10)^{-8}$	2357	4.241	−8.130	177.3
248	$1.65 \times (10)^{-8}$	2357	4.241	−8.284	176.6
				Av.	175.2

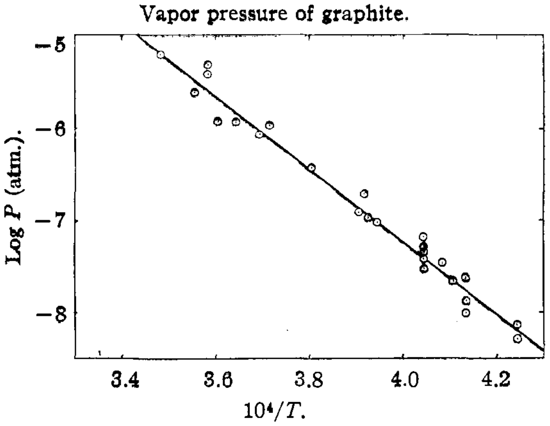

Fig. 3.—Vapor pressure of graphite. Experimental points of Table II.

Calculation of Heat of Vaporization.—It has been shown[5] that the emitter of the Swan band spectrum is the diatomic molecule of carbon. Brewer, Giles and Jenkins[2] made an experimental study up to 2963°K., of the O–O head of the C_2 Swan bands. From this the partial pressure of C_2 vapor could be determined. This pressure, P_{C_2}, they found to be a small fraction of the partial pressure of monatomic carbon P_C. In the range of our measurements, P_{C_2} was only 0.006 of P_C at our highest temperature and 0.001 at our lowest.

This is a negligible correction, and hence, our calculation will be made assuming the evaporation of carbon to monatomic vapor only.

Using the symbols of Lewis and Randall[6] the free energy of monatomic carbon may be expressed by the equation

$$(F^\circ - E_0^\circ)/4.58T = -3/2 \log M + \log P_C - 5/2 \log T - \log g + 1.586 \quad (3)$$

where "g" is the statistical weight for the monatomic carbon vapor.[7]

The value of $g = 2j + l$, where j is the inner quantum number. For carbon, j may have the values 0, 1 and 2, for the ground states ${}^3P_0$,, ${}^3P_1$ and ${}^3P_2$. The separation of these three terms is given by Fowler and Selwyn[8] as 14.8 and 42.3 wave numbers. Hence

$$g = 1 + 3 \exp. (-h\Delta\nu_1/kT) + 5 \exp. (-h\Delta\nu_2/kT)$$

In the temperature range of our experiments, the exponentials approximate unity and $g = 9$. Equation (3) then becomes

$$(F^\circ - E_0^\circ)/4.58T = \log P_C - 5/2 \log T - 0.987 \quad (4)$$

with the vapor pressure, P_C, for monatomic carbon, expressed in atmospheres.

Values of the function $(F^\circ - E^\circ)/T$ for graphite have been tabulated.[9] For our purposes it was necessary to extrapolate this from 2100 to 4700°K.

$$F^\circ - E_0^\circ = \int_0^T C_p \, dT - T \int_0^T C_p \, d \ln T \quad (5)$$

To make an intelligent extrapolation over this wide range, the theoretical value of C_v has been computed using the Debye formula. Magnus[10] has made a similar calculation to 1100°K. in comparing his experimental values with theory

$$C_v + 1/3[2f(\beta\nu_A) + f(\beta\nu_B)] \quad (6)$$

where $\beta\nu_A = 2280$ and $\beta\nu_B = 760$. Then C_p is calculated from the formula

$$C_p - C_v = AC_p{}^2T \quad (7)$$

with $A = 4.83(10)^{-6}$.

The following Table III gives the results of these computations. It is evident that theory affords a good representation of the data of Magnus at low temperatures and of Worthing[11] up to 2000°K.

TABLE III

FREE ENERGY FUNCTION OF GRAPHITE EXTRAPOLATED TO 4800°K.

T, K°	C_v	C_p	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$-\left(\frac{F^\circ - E_0^\circ}{4.58T}\right)$
1000	5.04	5.18	2.798	0.6109
1200	5.26	5.44	3.393	0.7408
1400	5.44	5.66	3.950	0.8624
1600	5.56	5.83	4.466	0.9751
1800	5.64	5.95	4.948	1.0803
2000	5.69	6.05	5.401	1.1792
2200	5.73	6.14	5.810	1.270
2400	5.77	6.22	6.142	1.341
2600	5.80	6.31	6.521	1.423
2800	5.82	6.37	6.885	1.503
3000	5.84	6.44	7.226	1.578
3200	5.85	6.51	7.550	1.673
3400	5.86	6.57	7.865	1.717
3600	5.87	6.64	8.189	1.788
3800	5.88	6.71	8.474	1.850
4000	5.88	6.75	8.749	1.910
4200	5.89	6.84	9.014	1.968
4400	5.89	6.90	9.268	2.024
4600	5.90	6.98	9.516	2.078
4800	5.91	7.07	9.754	2.130

The calculation of C_p from C_v is uncertain due to lack of reliable data on the real coefficient of expansion of crystalline graphite as a function of temperature. Another uncertainty is the total lack of data on a possible increase of C_p above the theoretical value at high temperatures, but this deviation must be small on account of the high characteristic temperature for graphite.

The free energy function as we have calculated it is compared in Fig. 4 with that of Clayton and Giauque[9] and of Kelley[12] and Gordon.[13] The latter two are in very close agreement.

If the values of Kelley and Gordon are used at our highest temperature, instead of our extrapolated function, the result is a lowering of ΔE_0° by 0.4 kcal.

From the relation of free energy to the vapor pressure comes this equation

$$\frac{\Delta F^\circ}{4.58T} = -\log p = \Delta\left(\frac{F^\circ - E_0^\circ}{4.58T}\right) + \frac{\Delta E_0^\circ}{4.58T} \quad (8)$$

Then from Equations (4) and (8), the measured values of the pressure of monatomic carbon vapor in atmospheres and the following resultant equation, values can be calculated for ΔH_0°, the heat of vaporization of carbon in kilocalories per mole. The extrapolated free energy function of Table III was used.

$$\log P_C = 5/2 \log T + 0.987 + \left(\frac{F^\circ - E_0^\circ}{4.58T}\right) - \frac{\Delta E_0^\circ}{4.58T} \quad (9)$$

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(5) Pretty, *Proc. Phys. Soc. Lond.*, **40**, 71 (1927); King and Birge, *Astrophys. J.*, **72**, 19 (1930).

(6) See Giauque, THIS JOURNAL, **52**, 4808 (1930).

(7) Fowler, "Statistical Mechanics," p. 157; Eucken, "Lehrbuch chemischen Phys.," p. 246; Schottky, "Thermodynamik," p. 262; Moelwyn-Hughes, "Physical Chem.," p. 346.

(8) Fowler and Selwyn, *Proc. Roy. Soc.* (*London*), **118**, 34 (1928).

(9) Giauque and Clayton, THIS JOURNAL, **54**, 2623 (1932).

(10) Magnus, *Ann. Physik*, **70**, 324 (1923).

(11) Worthing, *Phys. Rev.*, **1**, 199 (1918).

(12) Kelley, U. S. Bur. Mines Bull. No. 383, p. 32 (1935).

(13) Gordon, *J. Chem. Phys.*, **5**, 350 (1937).

Such values were calculated for each experimental point and are given in Col. 6 of Table II.

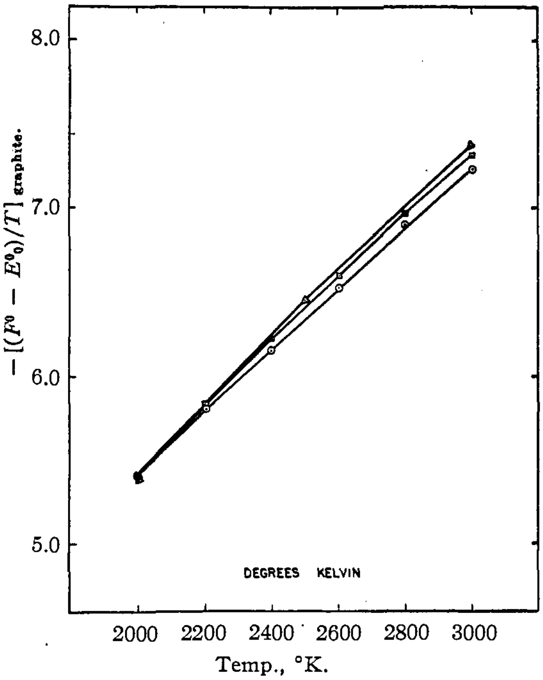

Fig. 4.—Free energy function for graphite: △, Kelley[12] and also Gordon[13]; □, Clayton and Giauque[9]; O, Marshall and Norton.[14]

The average value is 175.2 kcal. for ΔE°_0 or ΔH°_0, the heat of vaporization of graphite at absolute zero.

Accommodation Coefficient.—The factor α in Equation (1) is the accommodation coefficient, and represents the ratio of the rate at which atoms actually condense on the surface to the rate at which they strike the surface. It is, in general, equal to unity. This is particularly so for atoms of the same kind condensing on its own surface, since the forces tending to hold it on the surface once it hits, are so much greater than those causing evaporation. This is so, *a fortiori*, for materials of low vapor pressure, that is, with low tendency to escape from the surface.

Langmuir[3] has shown that for a metal atom condensing on its own surface, $\alpha = 1$. This value for α is supported by measurements on the vapor pressure of copper and iron[15] and measurements on high boiling organic liquids[15] by various vaporization techniques show $\alpha = 1$.

On liquid and solid mercury Knudsen[16] and Volmer and Estermann[17] measured $\alpha = 1$.

Values other than unity are extremely rare. For very dissimilar materials as hydrogen on tungsten, the coefficient may be different from 1 but never by orders of magnitude. Further, with increase in temperature, α rapidly approaches unity.

In the case of carbon, the main argument that the coefficient is unity lies in the very good agreement between the actual values of vapor pressure we have found by the Langmuir equation with $\alpha = 1$, and the values obtained by Brewer, Giles and Jenkins[2] who used an equilibrium effusion method.

Spectroscopic Correlations.—The controversy on this subject which has been going on for some years in the literature will not be discussed in detail. The basis for the spectroscopic method relies on an energy balance of the processes.

$$\begin{aligned} CO &= O + C(\text{gas}) \\ O &= 1/2O_2 \\ C(\text{solid}) + 1/2O_2 &= CO \end{aligned}$$

A knowledge of the energy change in each reaction enables the heat of vaporization to be calculated for the over-all reaction

$$C(\text{solid}) = C(\text{gas})$$

The main source of uncertainty in this thermodynamic cycle is the heat of dissociation of carbon monoxide.

Gaydon[18] lists with detailed references to papers the following values for D(CO) the energy of dissociation of CO in electron volts determined by spectroscopic methods, and each "put forward by the authors with apparent conviction," as Gaydon says.

Table IV

D(CO) e.v.	Date
10.5	1934
9.85	1934
8.43	1935
8.43	1935
6.921	1936
10.0	1936
9.144	1937
8.8	1939
9.6	1941
9.1	1943
10.1	1943
11.111	1945

It is evident that great care is needed in the interpretation of spectroscopic data applied to molecular dissociation. In a detailed review he concludes the evidence favors D(CO) = 11.11 e.v., leading to ΔH°_0 for carbon = 170.6 ± 0.2 kcal. Brewer, *et al.*,[2] agree with this and on spectroscopic and experimental grounds arrive at $\Delta H^\circ_0 = 170.39$ kcal./mole. Papers by Gero and Valatin[19] find as the best spectroscopic value of $\Delta H^\circ_0 = 169.735$.

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(14) Marshall, Dornte and Norton, This Journal, **59**, 1161 (1937).

(15) Verhoek and Marshall, *ibid.*, **61**, 2737 (1939).

(16) Knudsen, *Ann. Physik*, **29**, 179 (1909).

(17) Volmer and Estermann, *Z. Physik*, **7**, 1 (1921).

(18) Gaydon, "Dissociation Energies," John Wiley and Sons, New York, N. Y., 1947, p. 169–187; also see his "Spectroscopy and Combustion Theory," Chapman & Hall, London, 1948, pp. 188–192.

(19) Gero and Valatin, *J. Chem. Phys.*, **16**, 1011, 1014, 1018 (1948).

Springall[20] gives, from an N_2–CN cycle, a value of 171.6 for ΔH_{298} for graphite.

One characteristic of the spectroscopic method is that, when correctly applied, it can restrict to certain discrete magnitudes the derived thermodynamic quantities. For definite, allowed values of D(CO), the heat of dissociation of CO, there is fixed the ΔH_0° for the heat of vaporization of carbon. This is illustrated by the following Table V from Gaydon.[18]

TABLE V

Spectroscopic state of dissociation products Carbon	Oxygen	D(CO), e. v.	ΔH_0° kcal., for carbon
^{3}P	^{3}P	11.11	170.6
^{1}D	^{3}P	9.847	141.7
^{3}P	^{1}D	9.144	125.2
^{1}S	^{3}P	8.427	108.7
^{1}D	^{1}D	7.880	...
^{3}P	^{1}S	6.921	74.1
^{5}S	^{3}P	6.7	...

As Long and Norrish[21] point out, in order to use spectroscopic data for thermodynamic calcutions, it is also necessary to be certain whether the evaporating carbon atoms come off the graphite in the ground (^{3}P) state or with the lowest tetravalent (^{5}S) electronic configuration.

In Fig. 5 are plotted our data for the vapor pressure of carbon, together with the experimental points of Brewer, Giles and Jenkins, and their determination of P_{C_2} the partial pressure of diatomic carbon. As mentioned before they find this P_{C_2} is under one-half of one per cent. of the total carbon vapor pressure. There are also drawn their curves calculated for ΔH_0° values of 170, 141 and 125 kcal. They point out that the uppermost of their experimental points were the first taken, and that on repeated firing of the graphite sample the values tend toward a constant final low value. Their final values fall very directly on our curve. It is also evident from Fig. 5 that only the ΔH_0° curve for 170 kcal. fits the observed points.

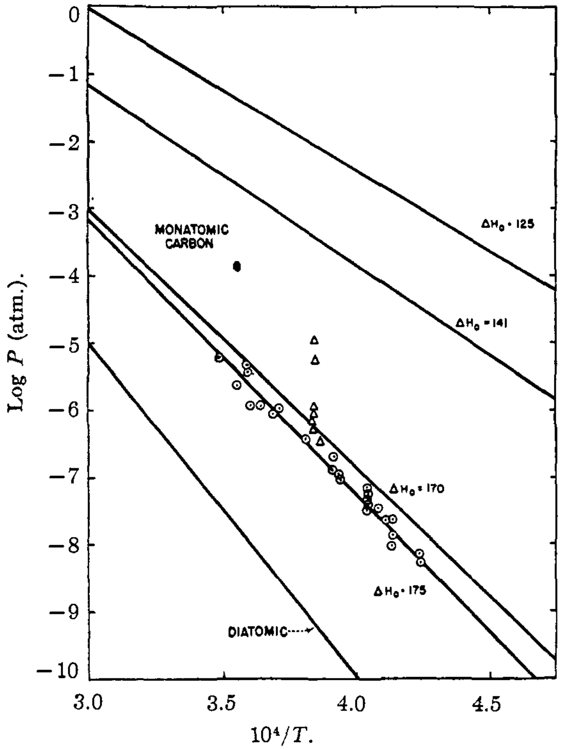

Fig. 5.—Heat of vaporization of carbon related to vapor pressure measurements: △, data of Brewer, Giles and Jenkins[2]; O, data of Marshall and Norton.

Summary

Vapor pressures were computed from the measured sublimation rates by use of the Langmuir equation with the accommodation coefficient set equal to unity. Agreement of the vapor pressures so derived with those published by Brewer, Giles and Jenkins,[2] who used an effusion method, justifies this choice of accommodation coefficient.

From these data, the heat of evaporation of carbon was calculated and a value of $\Delta H_0^\circ = 175.2$ kcal. per mole found. This is in agreement with recent experimental determinations and with the spectroscopic theoretical value of 170 kcal.

SCHENECTADY 5, NEW YORK RECEIVED MAY 4, 1949

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[20] Springall, *Trans. Faraday Soc.*, **43**, 177-184 (1947).

[21] Long and Norrish, *Proc. Roy. Soc.* (*London*), **A187**, 337-355 (1946).