Dissociation Pressure and Stability of Beryllium Carbide

By B. D. Pollock

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Equilibrium pressures for the reaction $^{1}/_{2}Be_2C(s) = Be(g) + ^{1}/_{2}C(s)$ were measured in the temperature range 1430–1669°K. by the Knudsen technique. The dissociation pressure in this temperature range is given by the equation log $P(atm.) = 7.026 \pm 0.347 - (19,720 \pm 537)/T$. The heat and free energy of formation of beryllium carbide were derived from the above equation in combination with the literature vapor pressure data for solid beryllium.

Introduction

Beryllium carbide is of potential interest in atomic power applications because of its nuclear properties; however, experimental thermodynamic data concerning it are meager. Krikorian[2] estimates heat, free energy and entropy of formation of Be_2C at 298°K. to be -13.0 ± 5 kcal., -12.4 ± 5 kcal., and -2.0 ± 1.0 entropy units, respectively, and Quirk[3] estimates -7.83 kcal. for the free energy of formation at 2400°K. However, the latter quotes, for various temperatures, estimated vapor or dissociation pressures of beryllium carbide[4] which are equal to or greater than those of pure liquid beryllium.[1,5,6] These pressures are inconsistent with a negative free energy of formation for a compound having no stable gaseous carbide species.[7] The absence of such species and the observation that beryllium carbide loses beryllium preferentially at elevated temperatures with deposition of graphite[3] indicate that the carbide dissociates according to the reaction

$$^{1}/_{2}Be_2C(s) = Be(g) + ^{1}/_{2}C(s) \qquad (1)$$
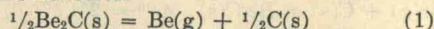
Thus a determination of the dissociation pressure as a function of temperature for this compound would yield results which could be combined with data on the vapor pressure of beryllium metal from the literature to obtain the free energy and heat of formation of the solid compound.

Experimental

Dissociation pressures were measured by the Knudsen method and the experiments were performed in the vacuum induction furnace illustrated in Fig. 1. The power source was a 6 kilowatt arc-type high frequency converter. The vacuum system was capable of maintaining residual gas pressures in the range 10^{-5}–10^{-6} mm. during the major part of each run following the initial warm-up. Knudsen cells and orifice plates were turned from National Carbon Company ATZ grade graphite. Temperatures were read with a

(1) This work was carried out as part of Contract AT-11-1-GEN-8 with the United States Atomic Energy Commission.

(2) O. H. Krikorian, "High Temperature Studies; Part II, Thermodynamic Properties of the Carbides" UCRL 2888, Apr. 1955, p. 82.

(3) J. F. Quirk, "Beryllium Carbide," *AEC-TIS Reactor Handbook*, **3**, Section 1, Ch. 1.5 (1955).

(4) Jacob Kielland and Leif Tronstad, "Det Kongelige Norske Videnskabers Selskab," Vol. VIII, No. 4, 1935, pp. 147, 150.

(5) R. B. Holden, R. Speiser and H. L. Johnston, *J. Am. Chem. Soc.*, **70**, 3897 (1948).

(6) E. A. Gulbransen and K. F. Andrew, *J. Electrochem. Soc.*, **97**, 383 (1950).

(7) W. A. Chupka, J. Berowitz, C. F. Giese and M. G. Inghram, This Journal, **62**, 611 (1958).

disappearing-filament type optical pyrometer by sighting into black-body holes in the bottom of the Knudsen cell, through a prism and optical window. The instrument, made by the Pyrometer Instrument Company of Bergenfield, New Jersey, was calibrated against a secondary standard which consisted of a tungsten ribbon lamp for which current *versus* temperature data had been obtained at the National Bureau of Standards. The window and prism correction was checked periodically. These corrections did not change significantly during the investigation. The over-all uncertainty in temperature measurements was estimated to be about 10°.

A layer of beryllium carbide was formed on the interior of the effusion cell prior to a group of experiments by heating a few pellets of metallic beryllium in the apparatus to about 1400° for a few minutes and then removing the excess metal. The carbide formed in this manner was hard, dense and adherent to the graphite. Spectroscopic examination showed only trace amounts of iron and silicon and X-ray diffraction showed Be_2C and no detectable amount of BeO. The interior of the cell was inspected visually after each run to ensure the presence of a large evaporating surface of beryllium carbide throughout each experiment. The surface area of the carbide layer was estimated to be at least 100 times the orifice area in all cases.

Vapor effusing from the cell was condensed on the interior of the quartz vacuum cell and no detectable deposit was found on the glass below the level of the top of the graphite cell. This observation showed that no error occurred by virtue of diffusion of beryllium through the graphite. It was found that the deposit adhered to the glass if it were less than about 3 mg., otherwise there was a tendency to flake off. Accordingly, variables were chosen so as to obtain beryllium losses of about 1 mg. After the run, the deposit was dissolved easily in a few cc. of dilute HCl and the amount of beryllium determined by a spectrophotometric method[8] with an estimated accuracy of 2–3%.

Results and Discussion

The vaporization data are summarized in Table I. The pressure of beryllium was calculated by use of the equation

$$P(atm) = 0.02254(m/at)(K)^{-1} (T/M)^{1/2} \qquad (2)$$

where (m/at) is the rate of effusion in g./cm.^{2}-second, K is the Clausing orifice correction, and T and M are the temperature in degrees Kelvin and the atomic weight of beryllium, respectively. Results of these calculations are listed in the last column of Table I and also shown in Fig. 2.

A least squares treatment of the data yielded the equation

$$\log P(atm) = (7.026 \pm 0.347) - (19{,}720 \pm 537)/T \quad (3)$$

the slope of which corresponds to a mean enthalpy

(8) M. E. Smith, "A Spectrophotometric Method for Determining Small Amounts of Beryllium in Uranium" LA-1585, August, 1953.
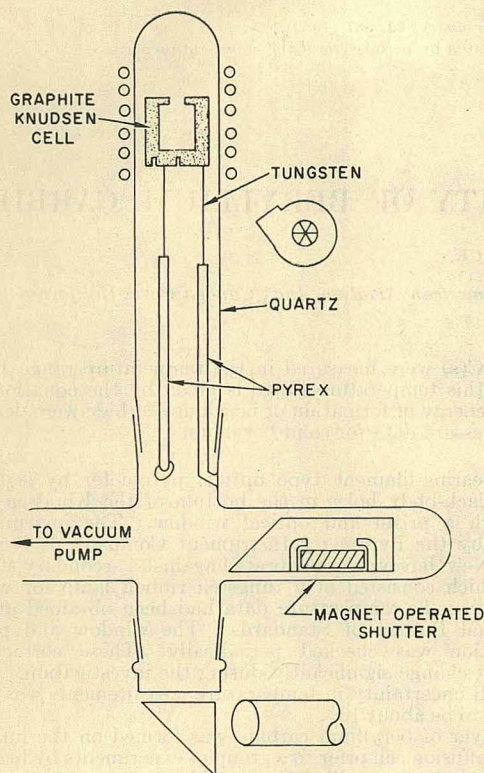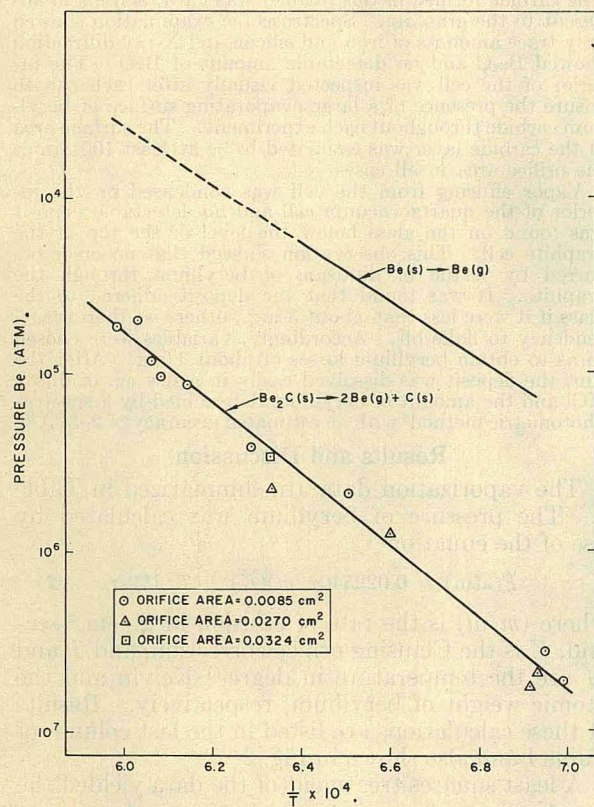
Fig. 1.

Fig. 2.—Dissociation pressure of Be_2C.

TABLE I

Expt. no.	Temp., °K.	Time, sec.	Wt. loss Be, mg.	Orifice area, cm.²	Claus- ing factor	P (atm.)
2	1669	4680	1.60	0.0085	0.69	1.79×10^{-5}
1	1659	4260	1.50	.0085	.69	1.83×10^{-5}
4	1647	4500	0.94	.0085	.69	1.08×10^{-5}
3	1643	6120	1.00	.0085	.69	8.5×10^{-6}
13	1628	4980	0.83	.0085	.69	8.6×10^{-6}
11	1590	6720	0.50	.0085	.69	3.80×10^{-6}
16	1580	9660	2.80	.0324	.81	3.3×10^{-6}
12	1578	4200	0.45	.0270	.65	2.18×10^{-6}
7	1536	10,800	.45	.0085	.69	2.08×10^{-6}
6	1515	12,600	.95	.0270	.65	1.25×10^{-6}
8	1446	27,600	.29	.0270	.65	1.72×10^{-7}
14	1442	26,900	.33	.0270	.65	2.00×10^{-7}
10	1434	25,000	.14	.0085	.69	2.72×10^{-7}
9	1430	23,450	.09	.0085	.69	1.86×10^{-7}

and condensed phases must be known and the existence of equilibrium between the solid and vapor during the experiment must be shown. Chupka, Berkowitz, Giese and Inghram showed in a mass spectrometric study that Be(g) is the only important gaseous species above Be_2C at approximately 1900°K.[7] This was confirmed by an experiment performed at 1580°K. in this Laboratory in which the gross weight loss of a Knudsen cell was found to be equal to the amount of beryllium in the sublimate. Solid solubility in beryllium carbide is assumed to be negligible. The existence of equilibrium is shown by the non-dependence of measured pressures on orifice area. Thus, equation 3 may be used for thermodynamic calculations.

The standard free energy of formation of beryllium carbide may be obtained by combining the data for reaction 1 with data for the vapor pressure of beryllium by the usual thermodynamic treatment

$$2Br(g) + C(s) = Be_2C(s) \quad \Delta F^0 = 2(4.576T) \log P \quad (4)$$
$$2Be(s) = 2Be(g) \quad \Delta F^0 = 2(4.576T) \log P^0 \quad (5)$$
$$2Be(s) + C(s) = Be_2C(s) \quad \Delta F^0 =$$
$$9.152T(\log P - \log P^0) \quad (6)$$
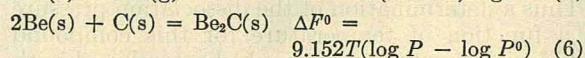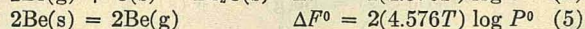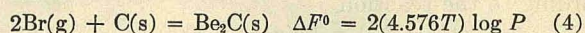
The vapor pressure of solid beryllium is[5]

$$\log P^0 \text{(atm.)} = 6.186 + 1.454 \times 10^{-4} T - \frac{16,734 \, (\pm 80)}{T}$$
$$(7)$$

If equations 3 and 7 are substituted in (6) one obtains for the free energy of formation of Be_2C

$$\Delta F^0(f) = (7.688 \pm 3.176)T -$$
$$1.331 \times 10^{-3} T^2 - 27,328 \, (\pm 500) \quad (8)$$

The heat of formation may be obtained from the expression

$$\frac{\partial (\Delta F^0/T)}{\partial T} = \frac{-\Delta H^0}{T^2}$$

which gives

$$\Delta H^0(f) = 1.331 \times 10^{-3} T^2 - 27,328 \, (\pm 5000)$$

The entropy of formation may be obtained from the expression

$$\Delta H^0 = \Delta F^0 + T \Delta S^0$$

At 1500°K., the approximate mid-point of the experimental temperature range, these equations give −18.8 kcal. for $\Delta F^0(f)$, −24.3 kcal. for $\Delta H^0(f)$ and

change of 90.2 ± 2.5 kcal. for reaction 1 in the temperature range 1430–1669°K.

For the data to be used for calculation of thermodynamic quantities, the identity of the gaseous

-3.7 e.u. for ΔS^0(f). For reactions in which reactants and products are solids entropy changes are usually small, *i.e.*, 1–2 e.u. per gram atom of constituents. Thus the value found above indicates that the magnitude and temperature dependence of the pressures measured in this investigation are consistent.

To obtain values of $\Delta F^0{}_{298}$ and $\Delta H^0{}_{298}$ in the absence of high temperature heat capacity data it is assumed that ΔC_p for reaction 6 is zero and the approximate expression

$$\Delta F(T) = \Delta H_{298} - T(\Delta S_{298})$$

will be used together with Krikorian's estimate of $\Delta S^0{}_{298}$(f). These assumptions lead to a value of -21.8 ± 5.0 kcal. for $\Delta H^0{}_{298}$, and -21.2 ± 5.0 for $\Delta F^0{}_{298}$.