Equilibrium of the Reaction between Beryllium Oxide and Carbon to Give Beryllium Carbide *
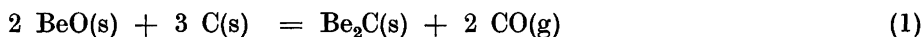
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The reduction of beryllia with carbon has been studied by measuring the carbon monoxide pressures in equilibrium with the solid phases beryllium oxide, graphite and beryllium carbide, in the temperature range 1780 to 2320°K. The measured pressures are higher than those calculated from presently accepted thermodynamic data by a factor of 1.7, corresponding to a discrepancy of 4.0 kcal in the standard free energy of the reaction around 2000°K.

Beryllia is among the most stable of all known oxides towards reduction, and because of this and other desirable properties it has attracted considerable interest in recent years as a high-temperature structural material. In some of the intended uses the oxide will be in contact with graphite at elevated temperatures, and hence the reduction with carbon is of particular interest.

The principal reactions occurring when beryllia is reduced by carbon may be written:

$$2 \text{ BeO(s)} + 3 \text{ C(s)} = \text{Be}_2\text{C(s)} + 2 \text{ CO(g)} \qquad (1)$$

$$\text{Be}_2\text{C(s)} = 2 \text{ Be(g)} + \text{C(s)} \qquad (2)$$

$$\text{BeO(s)} + \text{C(s)} = \text{Be(g)} + \text{CO(g)} \qquad (3)$$

Eqn. (3) may be derived from the two others by the relation $(3) = \frac{1}{2}((1) + (2))$. A fourth reaction in the system Be—O—C may be written

$$\text{Be}_2\text{C(s)} + \text{BeO(s)} = 3 \text{ Be(s or l)} + \text{CO(g)} \qquad (4)$$
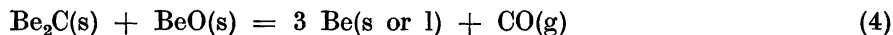
but this cannot proceed to the right in the presence of graphite and hence is not of interest for the present. Eqn. (4) with Be(g) in place of condensed metal, and eqn. (3), may occur in reverse, however, when the gaseous reaction products are cooled (see later).

The first question relates to whether or not eqns. (1) and (2) give an adequate description of the process. The presence of a dimer Be_2 in the vapour above solid beryllium was reported by Amonenko et al.,[1] but these findings could not be confirmed in the work of Nikitin and Gorokhov.[2] Theoretical considerations [3] also indicate that the molecule Be_2 will be unstable under all conditions, and it is concluded that beryllium vapour is monatomic. The products of volatilization of beryllium oxide have been studied by a number of investigators,[4-10] who all agree that the vapour consists chiefly of the species Be and O. Minor amounts of molecular species $(BeO)_x$ exist in the vapour, the trimer $(BeO)_3$ being the most abundant, but the pressures of these will be entirely insignificant in the presence of carbon. Indications of the presence of a suboxide Be_2O reported by Amonenko [1] have not been confirmed in the other investigations. The mechanism of the volatilization of beryllium carbide was investigated by Chupka et al.[11] by means of mass spectrometry; they found no evidence of any gaseous carbide of beryllium (nor of a beryllium dimer). As regards the condensed phases, only one oxygen compound and one carbon compound of beryllium have been reported. It is concluded that no species except those appearing in eqns. (1) and (2) are of importance in the reduction of beryllia with carbon, hence these equations are adequate.

The pressures of CO and Be(g) in equilibrium with the condensed phases BeO, Be_2C and C at a given temperature may be calculated from available thermodynamic data. Probably the most up-to-date compilation of thermodynamic data is represented by the JANAF tables,[12] which include all species in question. The tabulated data for condensed Be are based on calorimetric work from several sources, and those for gaseous Be on experimental vapour pressures.[13,14] The data for BeO are based on combustion calorimetry,[15] low-temperature heat capacity,[16] and a limited amount of high-temperature heat capacity [17] measurements. Recent heat capacity determinations up to $2820°K$ [18] and to $1073°K$ [19] show good agreement with the tabulated [12] values.

No calorimetric determination of the heat of formation of Be_2C has been reported. The value adopted in the JANAF tables [12] is based on the data for Be vapour [13,14] in combination with the experimental data of Pollock [20] for the vapour pressure of Be over Be_2C, recalculated [21] to give $\Delta H°_f = -22.2 \pm 5$ kcal at $298°K$. No low-temperature heat capacity measurements for Be_2C have been reported, and the entropy data [12] are based on the estimated $\Delta S°_f = -2.0 \pm 1.0$ e.u. at $298°K$.[21] The values for the high-temperature heat content of Be_2C are also largely estimated.[21] Thus it appears that the data for Be_2C are the weakest link in the chain. The precision of the other relevant data should not be overrated, however. E.g., the paper by Cosgrove and Snyder [15] on the heat of formation of BeO reveals that previous investigators have overrated the precision of their own work, and this may very well be true also for the limits ± 0.1 kcal given by Cosgrove and Snyder. Summing up, this brief survey indicates that equilibrium pressures of CO calculated from the best available data might be in error by a factor of 3 or more.

Considering reaction (1) only, it would appear that the equilibrium pressure of CO over the three condensed phases BeO, C and Be_2C can be established in a furnace and very simply measured by a manometer located outside the hot part of the furnace. The dubious point in such a procedure would be the influence of the Be gas produced according to eqn. (2), since this gas on cooling will react with CO (eqn. (3) or (4) to the left) and thus may disturb the establishment of an equilibrium pressure.

Muratov and Novoselova [22,23] have reported several series of experiments on the reduction of beryllia with carbon, done according to this simple static method, with equipment previously described by Kutsev et al.[24] The CO pressures reported in their first paper [22] were between 1 and 2 powers of ten higher than those calculated from the thermodynamic data,[12] and were clearly in error since the temperature dependence of the pressures would lead to an impossible value for the entropy of reaction (1). In the second paper,[23] they explain the shortcomings of the previous work as due primarily to insufficient degassing, and they present a new set of pressure measurements with an

acceptable temperature dependence, but still a factor of 10 higher than the calculated values. In view of this discrepancy, it was deemed desirable to reinvestigate this equilibrium, using the same straightforward static pressure method, but with equipment rather different from that used by Muratov and Novoselova.

APPARATUS AND PROCEDURE

A high-vacuum furnace was used for the experiments. The heating element consists of a split graphite tube (46 mm I.D.) surrounded by graphite radiation shields and mounted in a watercooled brass vacuum chamber. The furnace chamber is connected to a 4 in. oil diffusion pump through a high-vacuum isolation valve. Power is supplied to the heating element from a low-voltage transformer backed by a voltage stabilizer. A more detailed description of this furnace will be given elsewhere.[25]

Muratov and Novoselova [23] reported difficulties in obtaining stable pressures, particularly above 1750°C, and these difficulties might be due to the transport of Be vapour from the hot to the colder zone of the furnace, leading to back-reactions as mentioned above. In order to cut down this transport of Be vapour, a reaction chamber with double walls was designed, see Fig. 1. No hole in the inner reaction chamber was provided, since experience has shown that the usual graphite qualities are sufficiently permeable to permit rapid equalization of pressure differences. A consideration of Fig. 1 will show that the gas escaping through the walls of the inner chamber will preferentially be led down the vertical tube, where condensation of its content of Be would be expected chiefly to occur. By this arrangement, transport by gaseous convection and diffusion is kept to a minimum.

The reaction chamber and other graphite parts were made from high-purity graphite * which was also used for the charge. Beryllium carbide was prepared from stoichimetric amounts of graphite and beryllium metal,** ground together and heated in a graphite crucible under an argon atmosphere. The exothermic reaction was found to start at about 1050°C. The resulting, hard, yellowish carbide was mixed in a mortar with graphite and beryllium oxide ** in roughly equal amounts by weight, and the mixture charged into the inner reaction chamber. The assembly was then placed in the furnace and degassed overnight at temperatures in the range 800 to 1000°C. The vacuum in the system at the end of the degassing was around 10^{-5} torr, as measured with an ionization gauge.

After degassing, the furnace volume was isolated from the pump system, and the furnace brought to the desired temperature. In some runs, the pressure was permitted to build up as a result of the reaction, in others, carbon monoxide was admitted to the system. The carbon monoxide, of commercial quality, was found on analysis to contain 99.2 % CO. The impurities were assumed to be mainly nitrogen, and were not analysed. (O_2 and CO_2 will do no harm since both will be rapidly converted to CO in the furnace.) The gas was admitted to give pressures below or above the equilibrium value, thus approaching the equilibrium from both sides.

The pressures in the high range were read on an ordinary closed-end U-tube mercury manometer. The pressures in the lower range were read on the same manometer with a cathetometer, and alternatively with a special McLeod gauge with pressure ranges $0-0.050$, $0-0.5$ and $0-5$ torr.*** The calibration of the gauge was checked by introducing known amounts of dry air into the known volume of the furnace enclosure.

The pressures observed with this arrangement were found to be very stable after equilibrium had been established, and it was felt that the temperature determinations probably represented the main source of uncertainty. The optical pyrometer used † was

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* Graphite quality AUC from Skandinaviska Grafitindustri AB, Trollhättan, Sweden, total ash content according to the manufacturer 0.08 %.

** The Be metal and the BeO were received from the OECD High Temperature Reactor Project (DRAGON), England.

*** Type VM-ML Bauart CVC from W. C. Heraeus GMBH, Hanau, Germany.

† Cat. No. 8622-C from Leeds and Northrup Co., Philadelphia, USA.
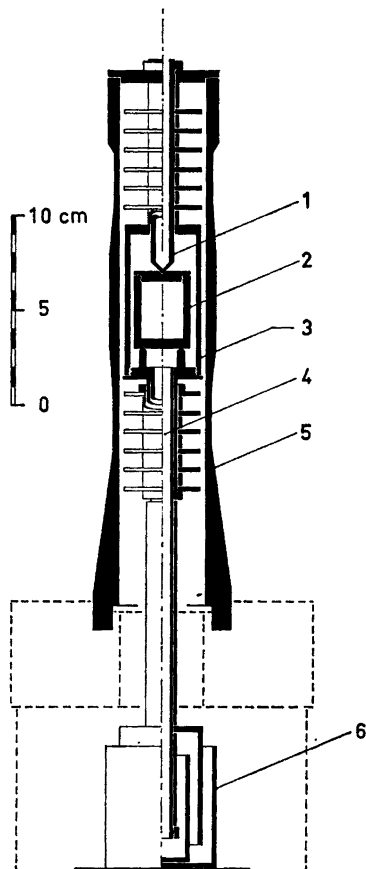
Fig. 1. Graphite reaction chamber for static pressure measurements. Double walls to diminish the transportation of Be gas from the charge. 1. Sighting tube for optical pyrometry; 2. Inner reaction chamber with charge; 3. Outer reaction chamber; 4. Gas outlet (condensor tube); 5. Furnace heating element (cylindrical radiation shields not shown); 6. Dust trap.
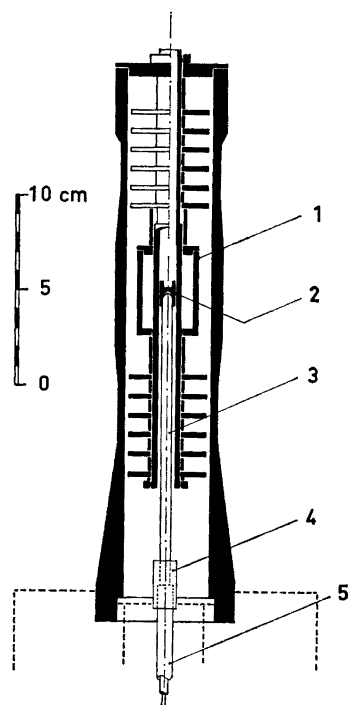
Fig. 2. Graphite reaction chamber, alternative model for simultaneous use of thermocouple and optical pyrometer. 1. Reaction chamber with charge; 2. Target for optical pyrometry; 3. Beryllia protection tube with thermocouple; 4. Graphite sleeve; 5. Alumina protection tube.

checked against two different tungsten strip lamps calibrated at the National Physical Laboratory, Teddington, England, and the resulting corrections, ranging from + 8° to + 13° in the temperature range covered, were applied to the readings. The pyrometer was sighted *via* a mirror through a silica window, and the readings were corrected for the absorbtion in the mirror (constant throughout runs) and absorbtion in the window (checked experimentally before and after each run). The sum of corrections ranged from about 30° to about 70°, depending on the absolute temperature, and the specific window used. It is seen from Fig. 1, however, that the sighting tube provided as target for the optical pyrometry is placed on top of the inner reaction chamber where the temperature may not

be representative of the bulk of the charge. This point was checked in a blank run, using a sighting tube with a small hole in the lower end permitting comparison of the temperatures in the target tube and in the (empty) reaction chamber. It was expected that the temperature in the latter would be slightly higher; on the contrary it was found that the temperature in the chamber was a few degrees lower than in the target tube, but this correction was not applied

It was also observed in the course of the experiments that the amounts of condensed products in the condensor tube subsequent to a run were less than anticipated, and that the somewhat intricate arrangement of Fig. 1 might thus not be strictly necessary. Consequently it was decided to perform some measurements with a simplified arrangement, and one which would permit the simultaneous use of a thermocouple, see Fig. 2. A 94Pt6Rh/70Pt30Rh thermocouple [26]* enclosed in beryllia insulation and protection tubes, protruded into the middle of the reaction chamber. Since beryllia is translucent and hence represents a poor target for optical pyrometry, a separate "cap" of graphite was fitted on top of the beryllia tube. The thermocouple was checked in place against the melting point of copper,** contained in a graphite crucible similar to that of Fig. 1. The observed EMF was 0.015 mV higher than the manufacturer's value for 1083°C. The thermocouple readings were corrected for this deviation on the assumption that the deviation is a linear function of the thermal EMF.

The thermocouple was used for a total of 6 h at about 1500°C, and 2 h at about 1600°C, whereupon it failed. This thermocouple should withstand 1800°C in a non-contaminating

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* Type PtRh18 from Degussa, Hanau, Germany.
** It is difficult to find a metal with a higher melting point than copper which does not form a carbide and does not dissolve significant amounts of carbon.
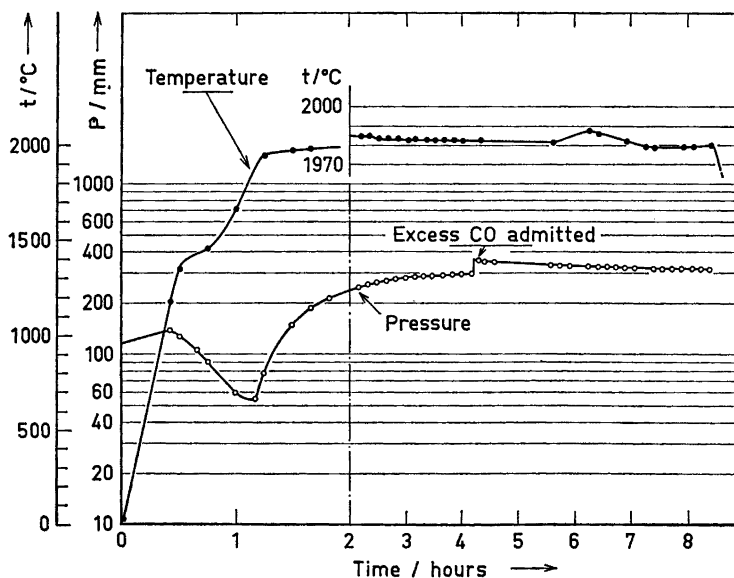

Fig. 3. Pressure and (observed) temperature plotted *versus* time for run No. 4. Carbon monoxide admitted to a pressure of 116 mm before start of heating. Reverse reaction is seen to take place at temperatures above 12—1300°C. Time and temperature scales change after 2 hours. (Hump in temperature after about 3/4 hour is due to manual increase in transformer setting.)

environment, but it will carry too far to go into the possible reasons for its failure at considerably lower temperatures. As it was, however, it served as a valuable independent check on the temperature determination in the lower range.

RESULTS AND DISCUSSION

The difficulties in obtaining stable pressures at the higher temperatures [23] were not encountered in the present work. This is illustrated in Fig. 3, which shows observed pressures and temperatures as functions of time for a run at 2045°C, the highest temperature used in the present experiments. The results for the equilibrium pressures are given in Table 1, and are plotted in the usual way in Fig. 4. For comparison, the experimental results of Muratov and Novoselova [22,23] are also plotted in Fig. 4, as are the equilibrium pressures of CO and of Be calculated from the JANAF data.[12]

Table 1. Results of measurements of gas pressure in equilibrium with the solid phases
$BeO + C + Be_2C$.

t °C optical (corrected)	t °C thermo-couple	$\dfrac{10^4\ °K}{T}$	P torr	Pressure going	$\log P$ (atm)
1671		5.144	3.93	up	−2.290
1957		4.484	115.5	up	−0.818
1782		4.866	18.6	up	−1.611
2047		4.310	296	up	−0.410
2044		4.316	310	down	−0.390
1514		5.596			
	1513	5.599	0.399	up	−3.280
1513		5.599			
	1507	5.618	0.418	down	−3.260
1611		5.308			
	1603	5.330	1.52	up	−2.699
1611	—	5.308	1.56	down	−2.688

Assuming for the sake of illustration that all uncertainty in the present results stems from errors in the determination of temperature, the deviations from the straight line is within ± 8° for all points. Regarding the agreement between the thermoelectric and the optical pyrometry, it is seen from Table 1 that the deviation at first was only 1°, then increasing to 8° shortly before failure of the thermocouple. The observations are qualitatively in agreement with expectation, since contamination would be expected to give a decreasing EMF.

It is assumed that the measured pressures do not represent the equilibrium carbon monoxide pressures, but rather the total equilibrium pressures
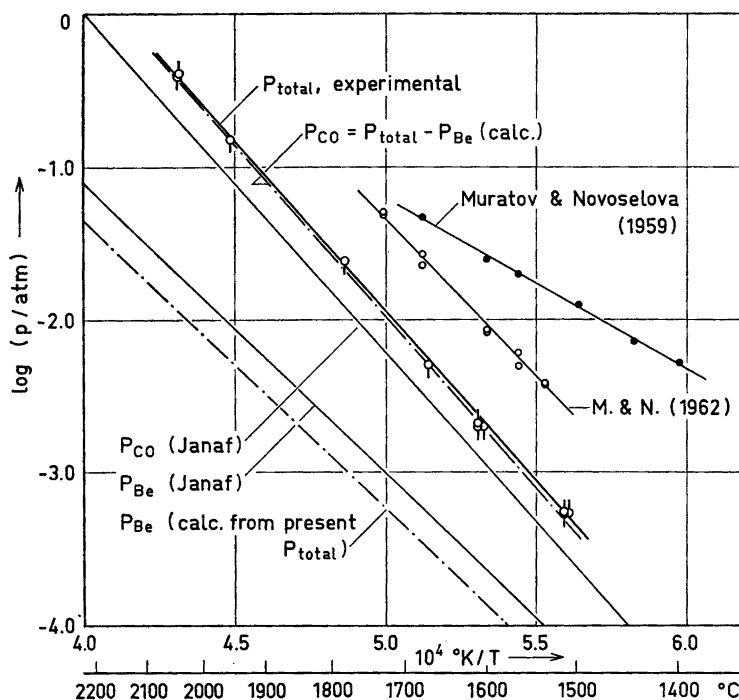
Fig. 4. Open circles: Experimental values for the total equilibrium pressures over the phases BeO + C + Be₂C. Tails on the circles indicate direction of approach towards constant pressure (tadpole notation). Included in the drawing are also the curve for the Be(g) pressure calculated from the present experimental results in conjunction with thermodynamic data for BeO, C and CO from the JANAF tables,[12] and the equilibrium CO pressure calculated from the experimental pressures by subtracting this Be pressure; furthermore are included the Be pressure calculated from the JANAF[12] values for Be₂C, and the experimental values obtained by Muratov and Novoselova.[22,23]

(P_{CO} + P_{Be}). This assumption has not been verified experimentally, but it seems plausible from a detailed consideration of the processes as they would be expected to occur, particularly in the setup shown in Fig. 1. The corrections for the partial pressure of Be is small, however, amounting to only 1/10 (or less) of the total pressure. A discrepancy between the presently observed pressures and the CO pressures calculated from the JANAF[12] data is evident. It is reasonable from the survey of the thermodynamic data given above to assume that the difference stems mainly from the data for Be₂C. Regarded in this way, the present observations indicate that Be₂C is more stable than previously assumed. A self-consistent treatment of the present observations would consist in correcting the measured total pressure by subtracting the partial pressure of Be over Be₂C, calculated from the same data. This latter Be pressure is also shown in Fig. 4, as well as the curve for the equilibrium pressures of CO arrived at in this way.

The value of the CO pressure at 2000°K leads to a standard free energy change of reaction (1), $\Delta G°_{(1)\,2000} = 36.3$ kcal, as compared to the JANAF value of 40.3 kcal. The experimental value is considered to be fairly reliable, accepting a temperature error of $\pm\,10°$ gives an uncertainty of $\pm\,0.9$ kcal.

The heat of reaction calculated from the slope, on the other hand, will be markedly unrealible in spite of all efforts to the contrary. Assuming again limits of error $\pm\,10°$, the heat of reaction (1) at 2000°K is calculated to $\Delta H°_{(1)\,2000} = 205 \pm 5$ kcal, which is to be compared with the JANAF value 203.8 kcal.

Ascribing all of the discrepancy to the data for Be_2C, the experimental values quoted here indicate that the entropy of formation of Be_2C from the elements should be 2.6 ($\pm\,2.5$) e.u. less negative than given in the tables,[12] or at 1500°K (referring to solid Be), $\Delta S°_{f,1500} = -0.5 \pm 2.5$ e.u. for Be_2C. The JANAF value for the same quantity, -3.1 e.u., falls on the borderline of the quoted limits of error and seems to be somewhat too negative also when comparing with the corresponding value for SiC (one of the few carbides where reliable heat capacity data are available), viz., -1.7 e.u. at 1500°K. The present experiments do not warrant any further refinement of the data for Be_2C, in particular since the data [12] for Be (metal) and for BeO are also subject to some uncertainty.

The main result, however, is that the equilibrium carbon monoxide pressure of reaction (1) has been determined, as this was also the goal of the investigation. The results may be expressed by the equation

$$\log P_{CO} = 9.22 - \frac{22400}{T} \pm 0.05 \qquad\qquad (1800-2300°K)$$

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