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F. Sh. MURATOV and Corresponding Member of the Academy of Sciences of the USSR A. V. NOVOSELOVA

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Abstract

Full Text

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ON THE QUESTION OF THE EQUILIBRIUM OF THE REACTION OF REDUCTION OF BERYLLIUM OXIDE BY CARBON

In a previous work (^{1}), results were described for determining the equilibrium of the reaction:

$$BeO_{solid} + {}^3/_2C_{graph} \rightleftarrows {}^1/_2Be_2C_{solid} + CO_{gas} \quad (1)$$

in the interval 1700-1950° K by the method of Prescott (^{2,3}). It was shown that equilibrium can be reached only in the indicated interval, while at higher temperatures equilibrium is not established. Continuation of the work aimed at refining the quantitative characteristics of reaction (1) showed that in work (^{1}) certain factors affecting the measurement results had not been taken into account (for example, degassing and the mechanical strength of the specimens were insufficient).

We reproduced the experiments on determining the equilibrium in the interval 1800-2000° K. Special attention was given to preparation and thorough degassing of the specimens. For this purpose the initial components—beryllium oxide and thoroughly de-ashed wood charcoal—were calcined in a vacuum of $\sim 1 \cdot 10^{-4}$ mm Hg at a temperature of 1900-2000°. The calcination time under the indicated conditions reached 8-10 hr. Stoichiometric amounts of the components (sieved to a fineness of −200 mesh) were thoroughly mixed in a glass mill with ebonite balls for 25-30 hr. In the course of mixing, the mixture was from time to time ground in an agate mortar to prevent caking. After this the mixture was pressed into rods. In repeated experiments, pressing was carried out in a graphite press mold at a temperature of 1200° and a pressure of 15 atm/cm^2, which made it possible to obtain sufficiently strong rods. The rods were prepared immediately before the experiment. The experimental conditions have been described previously.

A static method was used to determine the equilibrium. Equilibrium was considered to have been reached if the pressure in the system remained constant for 6-8 hr. The establishment of equilibrium was checked by the sign of the pressure change. For this purpose, after equilibrium had been reached, the pressure of carbon monoxide was raised by 1-2 mm by means of dosing valves. If after this the pressure in the system continued to rise, then equilibrium had not yet been established. Conversely, if the pressure decreased to the initial value, the equilibrium was considered to have been established. Table 1 gives the course of establishment of equilibrium. The rate of establishment of equilibrium depends on the amount of reagents and the volume of the apparatus. In those cases when we took the maximum charge possible for our conditions, 3-4 g, it was difficult to detect newly formed substances in the reaction mixture, since the content of the latter was very small. Therefore we switched to work with small charges of reagents—100-150 mg. On the other hand, a small charge makes it possible to substantially reduce the error associated with additional gas evolution from the reagents.

The reduction products were subjected to chemical and X-ray phase analyses. X-ray analysis was carried out in a camera 57.4 mm in diameter using iron radiation. As was noted earlier (1), in the products

Table 1

Course of establishment of equilibrium of reaction (1) in the interval 1800-2000°K

Experiment No.	Temp., °K	1 h	2 h	3 h	5 h	8 h	10 h	12 h	15 h	18 h	20 h
1*	1808	1.48	2.24	2.69	2.81	2.85	2.88	2.95	2.93	2.94	2.93
2*	1808	1.55	2.14	2.75	2.80	2.82	2.82	2.90	2.89	2.89	2.89
3	1837	1.91	2.97	3.21	3.43	3.71	3.82	3.95	3.96	3.95	3.95
4	1837	1.75	3.15	3.78	4.20	4.62	4.69	4.66	4.66	4.66	4.66
5	1873	3.21	4.95	5.81	6.32	6.32	6.42	6.40	6.40	6.40	–
6	1873	3.51	5.25	5.75	6.50	6.60	6.61	6.58	6.61	6.61	–
7	1953	12.14	17.32	19.05	20.50	20.88	20.88	20.89	20.88	–	–
8	1953	13.01	16.93	17.02	17.40	17.42	17.42	17.42	17.42	–	–
9	2003	21.05	32.43	35.68	36.90	37.36	37.36	37.36	37.36	–	–
10	2003	22.48	35.04	38.52	39.20	39.12	39.12	39.12	39.12	–	–

* The sign of the pressure change by adding carbon monoxide at the end points was not determined.

The reduction products in the interval 1800-2000°K contained beryllium carbide and unreacted beryllium oxide and carbon.

The line diagrams of the reduction products are given in Fig. 1. Chemical analysis was carried out in experiments 7-10, i.e., in those cases where the amount of beryllium carbide formed was sufficiently appreciable. The analysis was made for the content of carbon bound in the carbide. For this purpose the reduction products were treated with a concentrated solution of caustic potash, and the methane liberated as a result of carbide hydrolysis was determined by combustion. Since the volume of the apparatus for determining equilibrium was

Fig. 1. Line diagrams of the reduction products in the interval 1800–2000°K

Figure 1: Fig. 1. Line diagrams of the reduction products in the interval 1800–2000°K

known to us, we could determine what amount of carbide should be obtained according to reaction (1). In doing this, the pressure of carbon monoxide was read off at the time when heating had been stopped and the furnace space had cooled to the thermostat temperature (+25°C). Table 2 compares the amounts of beryllium carbide found by chemical means and calculated from the pressure of carbon monoxide. It is evident from the table that the results of the two methods agree well.

Fig. 1. Line diagrams of the reduction products in the interval 1800–2000°K

Table 2

Results of chemical analysis of the reduction products

Experiment No.	Charge* BeO+C+Be_2C, g	Found: Be_2C, g	Found: Be_2C, %	Calculated from equilibrium data: pCO at 25°, mm	Calculated from equilibrium data: V_{CO}^{**} at normal conditions, ml	Calculated from equilibrium data: Be_2C, g	Calculated from equilibrium data: Be_2C, %
7	0.0932	0.00838	8.99	14.35	12.85	0.0086	9.23
9	0.1108	0.01801	16.25	29.86	26.74	0.0179	16.16
10	0.1717	0.01877	10.23	31.97	28.63	0.0192	11.18

* For analysis, in this case, the entire ingot obtained after carrying out the reduction was taken.
** Volume of the apparatus 743.0$±$3.0 ml.

Table 3

Results of determining the equilibrium of reaction (1)

Nos.	Temp., °K	pCO exp., mm	$K_p = p$CO exp., atm $\cdot 10^{-3}$	K_p calc. by Eq. (2), atm $\cdot 10^{-3}$	$\frac{\Delta p}{p_{calc}}$, %
1	1808	2.93	3.854	3.674	+4.90

Nos.	Temp., °K	pCO exp., mm	$K_p = p\text{CO}$ exp., atm $\cdot 10^{-3}$	K_p calc. by Eq. (2), atm $\cdot 10^{-3}$	$\frac{\Delta p}{p_{\text{calc}}}$, %
2	1808	2.89	3.802	3.674	+3.48
3	1837	3.95	5.201	5.571	−6.64
4	1837	4.66	6.138	5.571	+10.18
5	1873	6.61	8.699	9.175	−5.47
6	1873	6.40	8.422	9.175	−8.94
7	1953	20.88	27.48	26.04	+5.53
8	1953	17.42	22.92	26.04	−11.98
9	2003	37.36	49.17	47.89	+2.67
10	2003	39.12	51.48	47.89	+7.50

The data obtained make it possible to find more accurate values of the thermodynamic characteristics of reaction (1) in the range 1800–2000°K (Table 3, Fig. 2). In the indicated temperature range, the dependence of the equilibrium constant on temperature has the form

$$\lg K_{p\,\text{atm}} = (9.021 \pm 0.092) - (20712 \pm 222)/T. \qquad (2)$$

It follows from equation (2) that for reaction (1)

$$\Delta H_T^0(1800\text{—}2000^\circ\text{K}) =$$

$$= 94.8 \pm 1.0 \text{ kcal/mole BeO}$$

and

$$\Delta S_T^0(1800\text{—}2000^\circ\text{K}) =$$

$$= 41.28 \pm 0.42 \text{ e.u.}$$

Fig. 2. Dependence of the equilibrium constant on temperature for reaction (1)

The dependence of the isobaric potential on temperature in the same temperature range has the form: $\Delta Z_T^0 = 94778 - 41.28\,T$. The calculation of standard quantities for reaction (1) was carried out taking account of the heat capacities of the reactants. The heat-capacity values for BeO_{tv} were taken from (4) for the interval 298–1200°K and from (5) for the interval 1200–2820°K; for C_{graph} and CO_{gas}, from (6); for $\text{Be}_2\text{C}_{\text{tv}}$, from (7) in the interval 298–1200° K. The heat capacity of Be_2C at temperatures above 1200° K was taken to be equal to $c_{p\,1200^\circ}$. Using the indicated values for reaction (1), we obtain: $\Delta H^0_{298} = 98.1$ kcal/mole, $\Delta S^0_{298} = 44.08$ e.u., and $\Delta Z^0_{298} = 85.0$ kcal/mole. Taking into account the values obtained for reaction (1), as well as the data of M. V. Smirnov and N. Ya. Chukreev (^{8}) for the reaction $Be + \frac{1}{2}CO_2 = BeO + \frac{1}{2}C$ and the data (^{6}) for the reaction $\frac{1}{2}CO_2 + \frac{1}{2}C = CO$, we obtain for the standard heat of formation of beryllium carbide the value $\Delta H^0_{298} Be_2C = -32.8$ kcal/mole, and for the standard entropy $S^0_{298} Be_2C = 4.36$ e.u.

At temperatures above 2000° K, equilibrium in reaction (1) is not established. The considerations concerning the causes of such a phenomenon, presented in work (^{1}), seem to us correct, all the more so since this is confirmed by works that have appeared recently (^{9,10}).

Moscow State University
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.