CHEMISTRY

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1960

SovietRxiv

Abstract

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CHEMISTRY

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DETERMINATION OF THE ENTHALPY AND HEAT CAPACITY OF BERYLLIUM OXIDE IN THE TEMPERATURE RANGE 1200-2820° K

(Presented by Academician A. N. Frumkin, 19 XII 1959)

The enthalpy and heat capacity of beryllium oxide were measured by Magnus and Danz ([1]) in the temperature range 374-1175° K. (The results of Magnus and Danz were used in Kelley' s tables ([2]), who estimates their accuracy at 3%.) The present article gives the results of an experimental determination of the heat content and heat capacity of beryllium oxide in the solid phase in the temperature range 1200-2820° K—up to the melting temperature. These measurements were carried out by the method of mixing using a massive calorimeter with an isothermal jacket. The sample was heated in a high-temperature vacuum furnace; its temperature was measured by means of an ÉOP-51M standard optical pyrometer with an accuracy from 0.05 to 0.2%.

The beryllium oxide samples were pressed from crystalline powder. The samples were given the shape of an ampoule made in the form of a truncated cone. For binding, a small amount of glucose (up to 0.1%) was added to the sample; it burned out during firing. The samples were fired at a temperature of 1400° C (preliminary firing) and at a temperature of 1800° C (final firing). The BeO samples contained, in insignificant amounts (not exceeding a few hundredths of a percent), impurities of a number of metals (Al, Ni, Cu, Zn, Hg, Fe, Ti, etc.). After firing, the samples contained 99.9% BeO. The approximate weight of the samples was 35 g. As the material for making the ampoules we chose molybdenum and tungsten. According to Johnson' s data ([3]), the BeO—Mo and BeO—W systems in vacuum do not react up to temperatures of 2200-2300° K. We did not observe interaction even at higher temperatures.

The determination of the enthalpy of beryllium oxide in the temperature range 1200-2400° K was carried out in molybdenum ampoules made of sheet metal 0.2 mm thick. Tantalum proved unsuitable as a material for ampoules (at temperatures around 2300° K, a BeO sample enclosed in a tantalum ampoule became covered with a gray coating, whose X-ray diffraction analysis showed the formation of compounds of beryllium oxide with tantalum). In the temperature range

2400–2820° K, tungsten ampoules were used. A drawback of tungsten ampoules is their brittleness, as well as their considerable weight (the large heat content of the ampoule increases the error of the experiment). Tungsten ampoules were also used to determine the heat of transition from the solid phase to the liquid; in this connection they had a special design ensuring complete tightness of the inner cavity of the ampoule. The heat content of the molybdenum and tungsten ampoules was determined by dropping empty ampoules.

Table 1 gives the experimental values of the heat content of beryllium oxide obtained at the Kharkov State Institute of Measures and Measuring Instruments (KhGIMI). The error in measuring the enthalpy is 0.25% in the range 1100–2000° K and 0.5% in the range above 2000° K. From the experimental data obtained, by the least-

Table 1

Run No.	T, °K	$H_T - H_{298.16}$, cal/mol	Run No.	T, °K	$H_T - H_{298.16}$, cal/mol	Run No.	T, °K	$H_T - H_{298.16}$, cal/mol
1	1142	8646	21	1813	17060	41	2278	23782
2	1169	9030	22	1838	17340	42	2310	24000
3	1208	9408	23	1864	17740	43	2329	24270
4	1242	9855	24	1889	18060	44	2334	24152
5	1276	10230	25	1915	18455	45	2408	25400
6	1286	10280	26	1925	18766	46	2432	25600
7	1336	10990	27	2002	19702	47	2475	26263
8	1344	11156	28	2035	19916	48	2526	27680
9	1358	11311	29	2054	20305	49	2566	28100
10	1418	12031	30	2065	20380	50	2637	28330
11	1443	12332	31	2084	20811	51	2646	28600
12	1471	12645	32	2102	21020	52	2672	28900
13	1475	12707	33	2119	21345	53	2697	29930
14	1511	13160	34	2126	21189	54	2820	40833
15	1522	13290	35	2142	21520	55	2822	40883
16	1595	14232	36	2155	21774	56	2840	46917
17	1646	14716	37	2164	22039			
18	1681	15308	38	2182	22065			
19	1684	15333	39	2297	22955			
20	1703	15562	40	2262	23100			

Note. Runs Nos. 1 through 44 were carried out in molybdenum ampoules; Nos. 45 through 53 in tungsten ampoules; in runs Nos. 54—56 partial melting of the specimen occurred.

The coefficients of the interpolation equation were found by the method of least squares. The equations for enthalpy and heat capacity have the following form:

$$H_T - H_{298.16} = 9.471T + 1.045 \cdot 10^{-3}T^2 - 3540 \text{ cal/mol},$$

$$c_p = 9.471 + 2.090 \cdot 10^{-3}T \text{ cal/mol} \cdot \text{deg} \quad (1200\text{—}2820^\circ\text{K}).$$

The root-mean-square error in determining the numerical values of the coefficients of the above equation is 0.4%, and for experiments with tungsten ampoules, 1.1%.

The data on the enthalpy of BeO at high temperatures presented in this work were obtained for the first time. In this connection, comparison of the KhGIMIP data with those of other authors can be made only at temperatures of 1200° K. The heat-content values calculated from the KhGIMIP equation, with an accuracy up to 1%, agree with the results of Rodigina and Gomel' skii ([4]), obtained at the Sverdlovsk Branch of VNIIM, and also with the data published by Kelly.

In the course of the work on determining the enthalpy, data on the melting temperature of BeO were obtained. According to our measurements, the melting temperature of beryllium oxide proved to be $2820 \pm 9^\circ$ K.

The value of the melting temperature of beryllium oxide obtained by Ya. I. Ol' shanskii ([5]) is $2843 \pm 30^\circ$ K, while that given by M. P. Slavinskii ([6]) is $2793 \pm 30^\circ$ K.

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Received
17 X 1959

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