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# DIRECT DETERMINATION OF THE ENTHALPY OF FORMATION OF MoB IN SYNTHESIS FROM SIMPLE SUBSTANCES IN AN SHS SYSTEM

**E. G. Lavut, N. V. Chelovskaya, and O. E. Kashireninov**

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*In a calorimetric bomb equipped with an electric microfurnace for heating a sample, self-propagating high-temperature synthesis (SHS) of molybdenum boride is realized in accordance with the reaction Mo (c) + B (amorph.) = MoB (c); the enthalpy of this reaction is measured, and the standard enthalpy of formation of molybdenum boride from metal molybdenum and crystaline boron is calculated:* $\Delta_f H^0(MoB, c, \delta, \beta) = -103.9 \pm 1.2$ *kJ/mole.*

At present a sufficiently reliable value of the enthalpy of formation of MoB is lacking; apparently, the main reason for this is the difficulty in determining this quantity by traditional thermochemical methods, in particular by burning molybdenum boride in oxygen, fluorine, or chlorine because of the complex composition of the products forming in the above processes. V. M. Maslov et al. [1] have determined the thermal effect of the self-propagating synthesis of MoB from simple substances in an automatically controlled heat-conducting Calvet-type calorimeter and obtained the value $\Delta_f H_{298.15}(MoB) = -112.5 \pm 2.1$ kJ/mole. However, the authors give virtually no details of their experiment, and this makes it impossible to realistically evaluate the obtained result. The values found from studies of the equilibria of different reactions [2-5] are characterized by an extremely high error. A critical analysis of [1-5] is presented in [6], whose authors relying on the available literature data, recommend the following value of the enthalpy of formation of molybdenum boride: $\Delta_f H(MoB, c, 298.15\ K) = -105 \pm 15$ kJ/mole. Owing to the aforesaid, we thought that it would be advisible to make a new determination of the enthalpy of formation of MoB. Since, as mentioned above, use of traditional calorimetry of burning in oxygen may undoubtedly be complicated by uncertainty in the composition of the end products of the reaction in this case, it was decided to perform self-propagating high-temperature synthesis of MoB from simple substances in the calorimeter.

**Experiment.** Metallic molybdenum and amorphous boron in a finely dispersed state were used in the experiment. The main impurities (wt. %) contained in them were the following:

molybdenum: Si, 0.001; K, 0.03; Cr, 0.001; Rb, 0.001; W, 0.006; Ca, 0.001; O, 0.164;
boron: C, 0.02; Al, 0.001; Si, 0.0008; Cl, 0.008; Fe, 0.001; Cu, 0.002; O, 0.66.

The oxygen content was determined by high-temperature extraction in an inert gas flow, and the remaining impurities, by spark mass spectrometry.

A homogenized mixture of molybdenum and boron powders taken in an equimolar ratio was carefully prepared for SHS.

Preliminary studies showed that for the SHS process to proceed easily the given mixture should contain some amount of oxgygen. Under vacuum (precisely this medium was chosen to perform the SHS process in the calorimetric bomb) the required oxygen content was provided by adding molybdenum oxide (3 mg of $MoO_3$ per 2 g of mixture). Molybdenum oxide was charged into a quartz ampoule, which was then filled with a mixture of molybdenum and boron; the ampoule was evacuated to a residual pressure of $10^{-2}$ mm Hg. The enthalpy of the SHS process was determined at 298.15 K in an isothermal water bomb calorimeter provided with an electric microfurnace [7]. The temperature was measured by a copper resistance thermometer with a very small time constant [6]. The sealed ampoule containing the reagent mixture was placed in the microfurnace of the calorimetric

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Moscow State University. Institute of Structural Macrokinetics, Russian Academy of Sciences, Chernogolovka. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 65, No. 4, pp. 428-430, October, 1993.

TABLE 1. Results of Calorimentric Experiments on Determining the Enthalpy of the Self-Propagating High-Temperature Synthesis of MoB ($\Delta_r U^0 = 1012.4 \pm 5.4$ J/g of MoB)

| Parameter | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| m, g | 1.85005 | 1.84354 | 2.14042 | 2.07899 | 2.11665 | 1.79286 | 1.67030 | 1.94953 |
| $\Delta R$, Ω | 0.181196 | 0.175238 | 0.176506 | 0.173489 | 0.170925 | 0.172192 | 0.173401 | 0.174388 |
| $\varepsilon_1$, J | 119693 | 119636 | 119722 | 119662 | 119603 | 119680 | 119679 | 119738 |
| $\varepsilon_2$, J | 119678 | 119634 | 119607 | 119663 | 119596 | 119442 | 119565 | 119597 |
| $\varepsilon_{mean}$, J | 119686 | 119635 | 119664 | 119662 | 119600 | 119511 | 119622 | 119668 |
| Q, J | 21686.6 | 20964.6 | 21121.4 | 20760.0 | 20442.6 | 20578.8 | 20742.6 | 20868.7 |
| $q_{el}$, J | 19799.8 | 19116.1 | 18947.2 | 18669.2 | 18299.5 | 18767.0 | 19054.7 | 18877.8 |
| $-\Delta U$, J | 1886.8 | 1848.5 | 2174.2 | 2090.8 | 2143.1 | 1811.8 | 1687.9 | 1990.9 |
| $-\Delta_r U$, J | 1019.9 | 1002.7 | 1015.8 | 1005.7 | 1012.5 | 1010.6 | 1010.5 | 1021.2 |

bomb; the bomb was filled with argon at a pressure of 1 atm; during the main period of the calorimetric experiment the furnace was heated prior to the start of the SHS reaction (this moment was monitored by the sharply increased resistance of the furnace heater), after which the heating was turned off. After the experiment, without discharging the bomb, two determinations were made of the energy equivalent of the calorimeter, with the purpose of monitoring the completeness of the reaction. Reaction products were identified by X-ray diffraction analysis on a DRON-3 diffractometer.

**Results.** Results of the calorimetric experiments on determining the enthalpy of interaction of amorphous boron with metallic molybdenum are summarized in Table 1. The following notation is used in Table 1: m is the mass of an equimolar mixture of molybdenum and boron, having regard for impurities; $\Delta R$ is the corrected temperature rise during the main period of the calorimetric experiment; $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_{mean}$ are the energy equivalent in the first and second determinations and its mean value; Q is the total change in the internal energy of the calorimetric system at 298.15 K; $q_{el}$ is the amount of electric energy supplied to the bomb microfurnace; $-\Delta U$ is the internal energy change during the SHS reaction in the calorimeter; $-\Delta_r U^0$ is the standard specific internal energy change in the SHS synthesis of molybdenum boride from metallic molybdenum and amorphous boron calculated by the equation $-\Delta_r U^0 = (\varepsilon_{mean}\Delta R - q_{el})m^{-1}$. The quantity $\Delta_r U^0$ found from eight experiments is equal to -1012.4 ± 5.4 J/g of MoB or -10.8.1 ± 0.6 kJ/mole of MoB. This value accounts for a correction for impurities contained in the molybdenum and boron samples, which was calculated assuming that the oxygen present in the molybdenum is combined with all metal impurities and some part of the molybdenum into higher oxides; in the case of boron we considered that metal impurities are combined into higher chlorides; silicon and some part of the boron are combined into oxides, and carbon is present in the free state. In this case, all mentioned compounds were considered as inert components.

From the data of Table 1 it is seen that all experiments give satisfactory agreement between the results on determining the first and second thermal values. This may support the complete course of the reaction of forming molybdenum boride in the bomb. However, X-ray diffraction analysis of the reaction products revealed two phases in them: $\delta$-MoB and $\beta$-MoB. No quantitative ratio between them was found since none of the phases was prepared to be used as an internal standard in X-ray diffraction analysis of phases. At the same time, from the diffractograms it is seen that the phase ratio varied from experiment to experiment by several times but despite this the scatter of the measured enthalpies of the reaction was small. This suggests that the enthalpies of formation of these phases are indistinguishable within the error of determination. This could be expected if account is taken of the fact that the structures of the phases $\delta$ and $\beta$ are close (one of them is tetragonal and the other is rhombohedral, and X-ray diffraction densities of both phases differ very slightly).

Processing of the obtained results, having regard for the above stipulations, yields a value of the molar enthalpy of formation of MoB ($\delta$, $\beta$) from metallic molybdenum and amorphous boron equal to -108.1 ± 0.6

kJ/mole. Re-calculation with allowance for the enthalpy of the transition of amorphous boron to the crystalline modification [8] leads to the following value of the enthalpy of formation of molybdenum boride from standard simple substances (by the reaction Mo (c) + B (c) = MoB (c, $\delta$, $\beta$): $\Delta_f H^0$(MoB, c, $\delta$, $\beta$, 298.15 K) = -108.1 ± 0.6 + 4.2 ± 1.0 = -103.9 ± 1.2 kJ/mole.

## REFERENCES

1. V. M. Maslov, A. S. Neganov, I. P. Porovinskaya, and A. G. Merzhanov, Fiz. Goreniya Vzryva, **14**, No. 6, 73-82 (1978).
2. P. W. Gilles and B. D. Pollock, A. E. C. Report, A. E. C. U-2894, Sept. (1953).
3. L. Brewer and H. Haraldsen, J. Electrochem. Soc., **102**, No. 7, 399-406 (1955).
4. E. Storms and B. Mueller, J. Phys. Chem., **81**, No. 4, 318-324 (1977).
5. S. Omori, Y. Hashimoto, and K. Koyama, Koon Gakkashi, 7, No. 5, 204-208 (1981).
6. V. Ya. Leonidov and N. M. Aristov (eds.), Thermodynamic Properties of Molybdenum and Tungsten Borides, Report of the High-Temperature Institute, No. 56/89, Moscow (1989).
7. E. G. Lavut and N. V. Chelovskaya, Zh. Fiz. Khim., **63**, 877 (1989).
8. V. P. Glushko and V. A. Medvedev, Thermal Constants of Substances, Moscow (1974), Deposited at VINITI, Issue 7.