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Abstract

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Determination of the Standard Heats of Formation of Barium Germanates

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Germanates are the closest crystal-chemical analogs of silicates and form with the latter broad series of solid solutions. For a sound search, on the basis of germanosilicates, for new materials with a specified set of physicochemical properties, it is necessary to have at one' s disposal the energy parameters of these substances, which, together with crystal-chemical data, determine the limits of miscibility in the solid phase and other physicotechnical properties of the substances.

In the literature there are a number of data on the heats of formation of silicates and titanates ([1-3]), while thermochemical investigations of germanates have not been carried out at all, with the exception of germanium dioxide ([3-6]). The present work fills the existing gap in this field of research, and at the first stage we studied the heats of formation of three barium germanates: Ba_3GeO_5, Ba_2GeO_4, and $BaGeO_3$.

As is known, germanates, like silicates, are refractory and sparingly soluble substances, which made it necessary, for carrying out the thermochemical experiment, to use highly concentrated solutions of mineral acids and elevated temperatures, provided that the internal parts of the calorimetric apparatus were reliably protected from the aggressive solvent medium by thin-layer polyethylene and Teflon. In the work a solution calorimeter with an isothermal jacket was used; the experiments were carried out at 50° in a mixture of nitric and hydrofluoric acid solutions of molar composition $1HNO_3 \cdot 1.5HF \cdot 27.7H_2O$, with a total solvent weight of ~376 g (350 ml) and sample weights of 0.3 to 0.6 g. The temperature constancy of the outer jacket of the calorimeter was maintained with an accuracy of $±$0.005°. The duration of the main period of dissolution was from 3 to 15 min. The temperature of the solvent was measured by a battery of thermistors with high values of resistance and temperature coefficient; the accuracy of temperature measurement was $±0.0002°. *After each dissolution experiment the heat capacity of the system was determined (by the electrical meth* 4.1840 *J was adopted. Calibration of the calorimeter was carried out periodically from the heat of solution of zinc ox* [8]).

To increase the rate of dissolution of the samples, about 10 wt.% soda was added

to the latter; this ensured disintegration of the pressed tablets and facilitated their complete dissolution. In all experiments the solvent was saturated with carbon dioxide. The heat of solution of soda was excluded in the subsequent thermochemical calculations; the data reported in the work refer to the heats of solution of pure substances in a solvent of molar composition $1HNO_3 \cdot 1.5HF \cdot 27.7H_2O$.

The conditions for obtaining barium germanates are described in our work ([9]). The samples used for the thermochemical investigations were distinguished by a high degree of homogeneity. Barium oxide BaO was obtained by distil-

oxygen from barium peroxide BaO_2 (reagent grade). The germanium dioxide GeO_2 used in the work was recrystallized in the quartz form. As is known, the germanates Ba_3GeO_5 and $BaGeO_3$ exhibit polymorphism ([9]); for the present work their stable low-temperature modifications were taken. Barium orthogermanate Ba_2GeO_4 crystallizes in one form, crystallochemically close to olivine orthosilicates. Taking into account the high hygroscopicity of barium oxide, as well as the appreciable chemical activity of highly basic germanates, their preparation for the thermochemical experiment was carried out in a sealed chamber with a dry atmosphere.

The dissolution of all samples was accompanied by exothermic thermal effects. Table 1 gives the heats of dissolution of five substances in cal/g (q) and kcal/mol (ΔH) for each of them.

Table 1

Compound	$-q$, cal/g	$-\Delta H$, kcal/mol	Note
BaO	414.18$±10.26	63.52±$1.60	11 experiments, reaction (1), ΔH_1
GeO_2	307.53$±2.99	32.17±$0.23	5 experiments, reaction (2), ΔH_2
$3BaO \cdot GeO_2$	286.23$±1.22	161.63±$0.68	8 experiments, reaction (3), $\Delta H_3^{(11)}$
$2BaO \cdot GeO_2$	264.80$±2.62	109.25±$1.07	5 experiments, reaction (3), $\Delta H_3^{(1)}$
$BaO \cdot GeO_2$	247.62$±0.39	63.87±$0.10	5 experiments, reaction (3), ΔH_3

As an example of calculating the heats of formation of compounds from the data on their heats of dissolution, we give, for metagermanate $BaGeO_3$, the equations of reactions with the corresponding thermal effects:

$$BaO_{(\ )} + aq_{1HNO3 \cdot 1.5HF \cdot 27.7H_2O} = Ba^{2+}(NO_3^-, F^-)_{aq} + H_2O + \Delta H_1, \quad (1)$$

$$GeO_{2(\ )} + aq_{1HNO3\cdot1.5HF\cdot27.7H_2O} = [GeF_6]^{2-}(NO_3^-, F^-)_{aq} + 2H_2O + \Delta H_2, \quad (2)$$

$$BaGeO_{3(\ )} + aq_{1HNO3\cdot1.5HF\cdot27.7H_2O} = Ba^{2+}[GeF_6]^{2-}(NO_3^-, F^-)_{aq} +$$

$$+3H_2O + \Delta H_3, \quad (3)$$

$$BaO_{(\ )} + GeO_{2(\ )} = BaGeO_{3(\ )} + \Delta H\ .$$

The heat of formation of metagermanate $BaGeO_3$ from the oxides, ΔH , is found by algebraic summation of the thermal effects of reactions (1)–(3):

$$\Delta H\ = \Delta H_1 + \Delta H_2 - \Delta H_3 = -63.52 - 32.17 + 63.87 = -31.82 \pm 0.64 \text{ kcal/mol},$$

where ΔH_1, ΔH_2, and ΔH_3 are the molar heats of dissolution of BaO, the quartz form of GeO_2, and pseudo-wollastonite $BaGeO_3$, respectively (see Table 1). In analogous fashion, the heats of formation (from the oxides) of the germanates Ba_3GeO_5 and Ba_2GeO_4 are calculated; for these, respectively, the tripled and doubled values of the heat of dissolution of barium oxide (ΔH_1) are substituted into reaction equation (1), while for reactions of type (3) the values of the heats of dissolution of the corresponding germanates (ΔH_3) are taken from Table 1.

The small size of the sample charges relative to the solvent makes it possible to regard the given solutions as dilute, and also to neglect

Table 2

Compound	$-\Delta H$, kcal/mol	$-\Delta H^0_{298}$, kcal/mol
Ba_3GeO_5 low-temperature form	61.1$±1.1\|607.4±0.34\|\|Ba{2}Ge{$	50.0$±1$5\|457.2±0.57\|\|BaGeO_{3}$
	“olivine” form	pseudo-wollastonite form

by the energy difference of the states of the water H_2O formed in reactions (1)–(3), and by the values of the heats of mixing of solutions (1) and (2). The measurements carried out at 50° are referred by us to standard conditions (temperature 25°), since the heat-capacity term of the reactions in such a narrow temperature interval does not, as a rule, exceed the experimental error.

The standard heats of formation of barium germanates were calculated using the most recent and most reliable data for the heats of formation of barium oxide

Fig. 1. Isocomponent of the heats of formation (from oxides) of barium germanates

Figure 1: Fig. 1. Isocomponent of the heats of formation (from oxides) of barium germanates

BaO and the quartz form of germanium dioxide GeO_2: -139.6 ± 0.07 and -129.08 ± 0.13 kcal/mol, respectively. Table 2 gives the values of the standard heats of formation and the heats of formation from oxides for the three barium germanates studied.

According to the method of Prof. S. A. Shchukarev ([10]), the isoatom (component) of the enthalpies of formation in a homologous series of inorganic substances, the heats of formation (from oxides) referred to one averaged gram-oxide of the component, show a monotonic change with composition. Figure 1 shows such a dependence for germanates of the $BaO–GeO_2$ system.

As can be seen from the graph, the maximum heat of formation, $-\Delta H/n$, occurs for barium orthogermanate Ba_2GeO_4, which is at the same time also the most refractory compound in this system. The monotonic dependence of the isocomponent heats of formation made it possible in this case to estimate the value of the heat of formation from oxides for barium tetragermanate $BaGe_4O_9$, $\Delta H_{ox} \simeq 35$ kcal/mol. In the tetragermanate $BaGe_4O_9$, one mole of the formula composition of germanium is in sixfold coordination ([9]), which sharply lowers the solubility of this germanate and accordingly complicates the performance of the thermochemical experiment.

Fig. 1. Isocomponent of the heats of formation (from oxides) of barium germanates

It should be noted that comparison of the obtained values of the heats of formation of barium germanates with analogous experimental values for barium silicates ([1]) shows quite satisfactory agreement (relative):

$$\frac{\Delta H_{ox}(Ba_2SiO_4)}{\Delta H_{ox}(Ba_2GeO_4)} = \frac{64.48}{50.0} = 1.29 \quad \text{and} \quad \frac{\Delta H_{ox}(BaSiO_3)}{\Delta H_{ox}(BaGeO_3)} = \frac{38.03}{31.8} = 1.2.$$

The latter, in accordance with the known regularities established by M. Kh. Karapet' yants ([11]) in series of substances of the same type, reflects the periodic dependence of the physical properties of similar compounds and serves as additional confirmation of the reliability of the obtained values of the heats of formation of barium germanates.

The close values of the heats of formation (from oxides) of germanates and barium silicates of analogous structure explain the presence of broad isomorphism in similar systems.

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REFERENCES

1. R. Barany, E. G. King, S. S. Todd, *J. Am. Chem. Soc.*, **79**, No. 14, 3639 (1957).

2. M. Kh. Karapet' yants, M. L. Karapet' yants, *Transactions of the Moscow Institute of Chemical Technology named after D. I. Mendeleev*, issue 34 (1961).

3. F. Rossini et al., *Selected Val. Thermod. Prop.*, Circ. 500 NBS, 1952.

4. W. L. Jolly, W. M. Latimer, *J. Am. Chem. Soc.*, **74**, No. 22, 5557 (1952).

5. T. Yokokawa et al., *J. Am. Chem. Soc.*, **79**, No. 13, 3365 (1957).

6. A. D. Mah, L. H. Adami, *U. S. Mines, Rep. Invest.*, No. 6034, 7 (1962); *Chem. Abstr.*, **57**, No. 9, 10590(i) (1962).

7. N. S. Newman, *J. Res. Nat. Bur. Stand.*, **62**, No. 5, 207 (1959).

8. Ibid., **66A**, No. 5, 381 (1962).

9. R. G. Grebenshchikov, N. A. Toropov, V. I. Shitova, *DAN*, **153**, No. 4, 842 (1963).

10. S. A. Shchukarev, *Scientific Notes of Leningrad University, Chemical Sciences Series*, No. 79, issue 7 (1945).

11. M. Kh. Karapet' yants, *Methods of Comparative Calculation of Physicochemical Properties*. "Nauka," 1965.

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