### Thermodynamic properties of minerals and fluids

### Yeriomin O.V. The method of calculation standard enthalpies of formation from elements for minerals of cancrinite group

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**Abstract.** The chemical elements increments for value  $\Delta_r H^0 = -14490.0 \text{ kJ/mole}$  of standard enthalpy of formation for cancrinite mineral Na<sub>6.93</sub>Ca<sub>0.545</sub>K<sub>0.01</sub>[Si<sub>6.47</sub>Al<sub>5.48</sub>Fe<sub>0.05</sub>O<sub>24</sub>](CO<sub>3</sub>)<sub>1.25</sub>·2.3H<sub>2</sub>O have been calculated by means of linear programming problems. The obtained increments are used in calculations of  $\Delta_r H^0$  values for seven minerals of cancrinite group with known properties. The mean error of calculations makes 0.53 %.

Key words: Cancrinite, standard enthalpies of formation from elements, linear programming.

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The minerals of cancrinite group represent a class of framework aluminosilicates with confined water, alkaline and alkali-earth cations (basically Na and Ca) and anions - hydrohide, carbonate, oxalate, sulfate, phosphate, chloride, etc. [Minerals, 2003].

Recently we have presented the some schemes of estimations the standard thermodynamic potentials for zeolites [Yeriomin, 2011, 2013; Yeriomin and Yurgenson, 2012]. Let's consider the application of the used methods for calculations of enthalpies of formations from elements for cancrinite group minerals.

The cancrinite from Khibino-Lovozero alkaline complex

 $Na_{6.93}^{-}Ca_{0.545}K_{0.01}[Si_{6.47}Al_{5.48}Fe_{0.05}O_{24}](CO_3)_{1.25} \cdot 2.3H_2O$  has been chosen as calibration mineral with the value of standard enthalpie  $\Delta_f H^\circ = -14490.0 \pm 16.0$  kJ/mole determined in work [Ogorodova et. al., 2009].

For reaction of the mineral formation from oxides:

we constructed the task of linear programming:

 $\mathbf{x}^* = \min\Delta_{\mathbf{f}} \mathbf{H}^{\mathbf{o}}(\mathbf{x}) \mathbf{x}, \mathbf{A} \mathbf{x} = \mathbf{b} = \operatorname{abs}(\operatorname{null}(\mathbf{A}))/2, \mathbf{x} \ge 0, \quad (2)$ 

where A - stoichiometric matrix on chemical elements of system; b - the vector of the material balance which has been written for mole quantity of reagents (1) (or one mole

of cancrinite);  $\Delta_{\mathbf{f}}\mathbf{H}^{\mathbf{o}}(\mathbf{x})$  – the standard enthalpies for components x of reactions (1), their values are taken from databases of a program complex "Selector" [Chudnenko, 2010] and works [Ogorodova et.al., 2009; Mercury et al., 2001] (tab.1.).

**Table 1.** The values of standard enthalpies of formations from elements for components x of reaction (1).

Components, x	- $\Delta_{\rm f} {\rm H}^{\rm o}, {\rm J/mole}$
Na <sub>2</sub> O	414220
CaO	635089
K <sub>2</sub> O	361500
Fe <sub>2</sub> O <sub>3</sub>	824084
$Al_2O_3$	1675725
SiO <sub>2</sub>	910735
H <sub>2</sub> O (iceI)	292746
$CO_2$	393505
$\begin{array}{l} Na_{6.93}Ca_{0.545}K_{0.01}[Si_{6.47}Al_{5.48}Fe\\ _{0.05}O_{24}](CO_3)_{1.25}\cdot 2.3H_2O \end{array}$	14490000

The solution of problem (2) with data (tab.1) represents  $\mathbf{x}^* = 1$  mole of cancrinite.

To the direct problem (2) corresponds conjugate with it dual:

$$y^*=\max by, A'y \le \Delta f H^o(x),$$
 (3)  
where ' - an index of transposing.

For nonsingular solutions  $x^*$  and  $y^*$  of problems (2) and (3) are fair equality:

$$\Delta f H^{o}(x^{*}) x^{*} = b y^{*}, \qquad (4)$$

which for reaction (1) represents the decomposition of cancrinite enthalpie value on increments of chemical elements.

Let's apply the additive scheme for estimations of standard enthalpies  $\Delta f H^{\circ}(k)$  of cancrinite group minerals - k under the formula:

$$\Delta f H^{o}(k) = Y(k) y^{*}, \qquad (5)$$

where Y (k) - stoichiometric formula of a mineral k,  $y^*$ -the dual solution of problem (3) (ra6.2).

**Table 2.** Chemtical elements increments (y\*, J/mole) of standard enthalpie  $\Delta_f H^o = -14490.0 \text{ kJ/mole}$  of the cancrinite mineral - Na<sub>6.93</sub>Ca<sub>0.545</sub>K<sub>0.01</sub>[Si<sub>6.47</sub>Al<sub>5.48</sub>Fe<sub>0.05</sub>O<sub>24</sub>](CO<sub>3</sub>)<sub>1.25</sub>·2.3H<sub>2</sub>O.

y* <sub>El</sub>	Са	Na	K	Al	Fe	Si	С	0	Н
	-358195	-23878	-107355	-248127	67009	-87954	257867	-419316	15986

Minerals	$\Delta_{\mathbf{f}}\mathbf{H}^{\mathbf{o}}, \mathbf{J/mole}$	Calculated on (5)
Cancrinite [Ogorodova et al., 2009]	14490000	14490000 (0.00)
$Na_{6.93}Ca_{0.545}K_{0.01}[Si_{6.47}Al_{5.48}Fe_{0.05}O_{24}](CO_3)_{1.25}\cdot 2.3H_2O$		
Cancrinite [Ogorodova et al., 2009]	15552000	15714581 (1.04)
$Na_6Ca_2[Si_6Al_6O_{24}](CO_3)_2 \cdot 2H_2O$		
Cancrinite [Liu et al., 2007]	14524070	14484089 (0.28)
$Na_{7.771}[Si_{6.004}Al_{5.956}O_{24}](CO_3)_{0.881} \cdot 3.48H_2O$		
Cancrinite [Ogorodova et al., 2009]	14691000	14686834 (0.03)
$Na_6Ca_{1.5}[Si_6Al_6O_{24}](CO_3)_{1.5} \cdot 1.1H_2O$		
Cancrisilite [Kurdakova et al., 2014]	14684000	14804207 (0.82)
$Na_{8.28}[Si_{6.07}Al_{5.93}O_{24}](CO_3)_{0.93}(OH)_{0.49}\cdot 3.64H_2O$		
Cancrisilite [Ogorodova et al., 2009]	14268000	14249157 (0.13)
Na <sub>7</sub> [Si <sub>7</sub> Al <sub>5</sub> O <sub>24</sub> ]CO <sub>3</sub> ·3H <sub>2</sub> O		
Kyanoaxalite [Olysuch et al., 2011]	14555000	14764698 (1.43)
$Na_7[Si_6Al_6O_{24}](C_2O_4)_{0.5}$ · 5H <sub>2</sub> O		
Mean error		0.53%

**Table 3.** Comparison of calculated and published data for the standard enthalpies of cancrinite group minerals. In brackets - errors (6) in percentage.

Relative errors of calculations on (5) were estimated by means of the formula:

$$\delta = 2 \left( \mathbf{x}_{i} \cdot \mathbf{x}_{j} \right) / \left( \mathbf{x}_{i} + \mathbf{x}_{j} \right), \tag{6}$$

where  $x_i$  - the calculated values and -  $x_j$  - the published data (tab.3).

The dual solution  $y^*$  (tab.1) have been presented as the bar diagram (Fig.1).



Fig. 1. The chemical elements increments of standard enthalpie of calibration cancrinite mineral.

The received values of chemical elements increments can be used for estimations of standard enthalpies of cancrinite group substances with prospective accuracy 1-3 %.

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# Shornikov S. I. Thermodynamic properties of sodium-silicate melts

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**Abstract**. Within the framework of the developed semi-empirical model, the calculations were made of thermodynamic properties of the Na<sub>2</sub>O–SiO<sub>2</sub> melts in the temperature region 900–1800 K. The calculated values of the oxide activities and the mixing energies of sodium silicate melts are compared with available experimental information.

Key words: thermodynamic properties of oxide melts, the Na\_2O–SiO\_2 system.

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Physico-chemical properties of sodium silicates, glasses and melts are of interest to the petrological and the geochemical researches and to the glass industry. In spite of numerous investigations [Shakhmatkin & Vedishcheva, 1994], the thermodynamic properties of these compounds are contradictory that was considered earlier [Shornikov, 2005]. The phase diagram presented in the fig. 1 [Zaitsev et al., 2000].

This investigation presents the calculation of thermodynamic properties of the Na<sub>2</sub>O-SiO<sub>2</sub> melts at temperatures from 900 to 1800 K within framework of the ideal associated solutions theory. The simplified lattice for as before the  $K_2O-SiO_2$ model. systems [Shornikov, 2013], accounts for the intermolecular interactions using the semi-phenomenological parameters. They were determined on the base of the experimental [Kozhina & Shultz, 2000; Zaitsev et al., 2000] and reference [Glushko et al., 1978–1982; Barin et al., 1993; Chase, 1998] thermodynamic data, presented in the table 1 and 2.

The initial thermodynamic data considered 13 condensed phases (7 solid and 6 liquid) and 14 gas species, these components are listed in the table 3. The same table 3 gives the calculated values of the Gibbs formation energies from elements  $(\Delta_t G^{\circ}_T)$  for the compounds and the vapor species over the Na<sub>2</sub>O-SiO<sub>2</sub> system. They were used for the calculation of the equilibrium conditions in the system at a given composition and temperature. The required equation solution for the total Gibbs energy for the system studied was found by the widely used approach, namely the Gibbs energy minimization method.





Fig. 1. The phase diagram of the Na<sub>2</sub>O–SiO<sub>2</sub> system [Zaitsev et al., 2000].

Table 1. The enthalpies $(\Delta H_T)$ and $(\Delta H_T)$	the entropies $(\Delta S_T)$	of sodium silicate	formation from	the simple oxides
[Roth & Troizsch, 1949; Yamaguchi et al., 19	983; Barin, 1995; Chase,	1998; Zaitsev et al., 20	000; Bale et al., 2002	2; Shornikov, 2005].

Compound	<i>Т</i> , К	$\Delta H_T$ , kJ/mole	$\Delta S_T$ , J / (mole·K)	Reference
Na <sub>4</sub> SiO <sub>4</sub>	800-1393	-127.13±0.76	-9.05±0.71	[Barin, 1995]
_ " _	800-1350	-127.93±0.75	-9.00±0.71	[Bale et al., 2002]
_ " _	942-1271	-127.10±0.62	$-6.90\pm0.60$	[Zaitsev et al., 2000]
_ " _	1350-2000	-172.29±0.41	-41.40±0.24	[Bale et al., 2002]
_ " _	1393-1600	$-149.86 \pm 0.75$	$-26.05\pm0.50$	[Barin, 1995]
Na <sub>6</sub> Si <sub>2</sub> O <sub>7</sub>	600-893	-112.10±0.12	-1.12±0.17	[Barin, 1995]
_ " _	800-1387	-119.90±0.57	$-1.08\pm0.53$	[Bale et al., 2002]
_ " _	1068-1285	$-110.50\pm0.58$	6.15±0.55	[Zaitsev et al., 2000]
_ " _	1273-1573	-122.75	-6.44	[Yamaguchi et al., 1983]
_ " _	1387-2000	$-159.47\pm0.38$	$-29.95\pm0.22$	[Bale et al., 2002]

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Thermodynamic	properties o	of minerals	and fluids
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Compound	<i>Т</i> , К	$\Delta H_T$ , kJ/mole	$\Delta S_T$ , J / (mole·K)	Reference
_ " _	1423-1473	-130.54	-8.30	[Zaitsev et al., 2000]
Na <sub>2</sub> SiO <sub>3</sub>	350	-112.51±1.26	-	[Roth & Troizsch, 1949]
_ " _	800-1362	-118.17±0.34	-3.91±0.32	[Barin, 1995]
_ " _	800-1362	-117.77±0.23	$-3.44\pm0.21$	[Chase, 1998]
_ " _	800-1360	-119.20±0.42	$-5.42\pm0.40$	[Bale et al., 2002]
_ " _	953-1110	-115.40±0.60	$-2.30\pm0.60$	[Zaitsev et al., 2000]
_ " _	1273-1573	-108.62	-0.13	[Yamaguchi et al., 1983]
_ " _	1360-2000	-149.57±0.11	-27.61±0.06	[Bale et al., 2002]
_ " _	1362-1600	-120.70±0.40	-5.63±0.27	[Barin, 1995]
_ " _	1362-1600	-96.31±0.04	12.04±0.03	[Chase, 1998]
_ " _	1362-1600	-89.40	16.79	[Shornikov, 2005]
_ " _	1363-1719	-116.76±0.60	$-4.26\pm0.60$	[Zaitsev et al., 2000]
Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	800-1147	-76.27±0.26	0.27±0.28	[Barin, 1995]
_ " _	800-1141	-77.16±0.28	3.50±0.29	[Bale et al., 2002]
_ " _	973-1078	-75.66±0.72	5.70±0.70	[Zaitsev et al., 2000]
_ " _	1147-1400	-64.77±0.35	12.91±0.27	[Barin, 1995]
_ " _	1147-1600	-61.09	16.66	[Shornikov, 2005]
_ " _	1148–1719	$-80.60 \pm 1.67$	2.46±0.70	[Zaitsev et al., 2000]
_ " _	1273-1573	-83.88	0.05	[Yamaguchi et al., 1983]
_ " _	1400-2000	$-92.97 \pm 0.07$	$-7.68\pm0.04$	[Bale et al., 2002]
Na <sub>6</sub> Si <sub>8</sub> O <sub>19</sub>	973-1066	-61.99±0.13	3.97±0.13	[Bale et al., 2002]
_ " _	974-1071	-58.30±0.76	6.70±0.70	[Zaitsev et al., 2000]
_ " _	1080-1719	-66.25±0.76	2.79±0.70	[Zaitsev et al., 2000]
_ " _	1081-1600	-50.35	14.05	[Shornikov, 2005]
_ " _	1273-1573	-71.72	-0.35	[Yamaguchi et al., 1983]
_ " _	1400-2000	$-82.51\pm0.28$	-11.30±0.17	[Bale et al., 2002]

Table 2. The temperatures  $(T_m)$ , the enthalpies  $(\Delta H_m)$  and entropies  $(\Delta S_m)$  of sodium silicate melting [Botvinkin, 1955; Takahashi & Yoshio, 1970; Glushko et al., 1978–1982; Richet & Bottinga, 1986; Richet et al., 1994; Barin, 1995; Chase, 1998; Bale et al., 2002; Shornikov, 2005].

Compound	$T_m, \mathbf{K}$	$\Delta H_T$ , kJ/mole	$\Delta S_m$ , J / (mole·K)	Reference
Na <sub>2</sub> O	1405±2	36.00±4.00	25.62±2.84	[Glushko et al., 1978–1982]
_ " _	1405±1	33.94±1.50	47.70±1.50	[Barin, 1995]
_ " _	1405±1	47.70±2.00	33.95±1.42	[Chase, 1998]
Na <sub>4</sub> SiO <sub>4</sub>	1393±1	19.25±1.67	13.82±1.20	[Barin, 1995]
$Na_6Si_2O_7$	1387	_	_	[Bale et al., 2002]
Na <sub>2</sub> SiO <sub>3</sub>	1361	23.12	16.99	[Botvinkin, 1955]
_ " _	1361	35.98	26.43	[Takahashi & Yoshio, 1970]
_ " _	1362	26.00±0.50	19.09±0.38	[Richet et al., 1994]
_ " _	1362±1	19.02±1.50	25.90±1.20	[Barin, 1995]
_ " _	1362±1	25.90±2.10	19.02±1.54	[Chase, 1998]
$Na_2Si_2O_5$	1157	13.37	11.56	[Botvinkin, 1955]
_ " _	1157	15.48	13.38	[Takahashi & Yoshio, 1970]
_ " _	1147	12.57±1.38	10.96±1.20	[Richet & Bottinga, 1986]
_ " _	1147	10.34±1.50	9.01±1.31	[Barin, 1995]
Na <sub>6</sub> Si <sub>8</sub> O <sub>19</sub>	1081±10*	7.95	7.35	[Shornikov, 2005]
$SiO_2$	1996±5	9.80±0.50	4.81±0.50	[Glushko et al., 1978–1982]
_ " _	1996	9.57±0.50	4.79±0.50	[Barin et al., 1995]

\*dissociation temperature

Table 3. The Gibbs energy of formation from elements of condensed phases and vapor species over the  $Na_2O-SiO_2$  system at 1500 K, calculated in present study according to data [Glushko et al., 1978–1982; Kozhina & Shultz, 2000; Zaitsev et al., 2000].

Condensed phases				Ga	is phase
Solid phases	$\Delta fG^{\circ}1500$ , kJ/mole	Liquid phases	$\Delta fG^{\circ}1500$ , kJ/mole	Vapor species	$\Delta fG^{\circ}1500$ , J/mole
Na <sub>2</sub> O	-211.201	Na <sub>2</sub> O	-213.636	Na	-26.838
$Na_4SiO_4$	-1422.361	Na <sub>4</sub> SiO <sub>4</sub>	-1426.797	Na <sub>2</sub>	-7.696
$Na_6Si_2O_7$	-2531.645	$Na_6Si_2O_7$	-2541.967	NaO	13.897
Na <sub>2</sub> SiO <sub>3</sub>	-1084.809	Na <sub>2</sub> SiO <sub>3</sub>	-1090.100	Na <sub>2</sub> O	-79.739

### Abstracts



**Fig. 2.** The oxide activities (*a*) and the mixing energy (*b*) in the Na<sub>2</sub>O–SiO<sub>2</sub> melts at 1173 (*a*) and 1300 (*b*) K. *Table of symbols:* The oxide activities (*a*) calculated in the present study:  $1 - a(Na_2O)$  and  $2 - a(SiO_2)$ ; the fields are according to the phase diagram [Zaitsev et al., 2000]:  $I - \beta$ -Na<sub>2</sub>O + Na<sub>4</sub>SiO<sub>4</sub>;  $II - Na_4SiO_4 + Na_6Si_2O_7$ ;  $III - Na_6Si_2O_7 + Na_2SiO_3$ ;  $IV - Na_2SiO_3 + liquid$ ; V - liquid;  $VI - SiO_2$  (tridymite) + liquid.

The mixing energy (*b*): 1, 3 – obtained by the e. m. f method at 1273 and 1300 K [Yamaguchi et al., 1983; Kozhina & Shultz, 2000]; 2, 4 – obtained by Knudsen effusion mass spectrometric method at 1293 and 1273 K [Shultz et al., 1987; Zaitsev et al., 2000]; and calculated in the present study at 1300 K, represented by line



**Fig. 3.** The activities of  $Na_2O$  (a) and  $SiO_2$  (b) in the  $Na_2O-SiO_2$  melts at 1473 K obtained by Knudsen effusion mass spectrometric method: 1 – [Shultz et al., 1987], 2 – [Rudnyi et al., 1988], 3 – [Zaitsev et al., 2000]; and calculated in the present study according to semi-empirical model, represented by lines

According to fig. 2 and 3, the calculated values of oxide activities a(i) and mixing energies ( $\Delta G$ ) of the Na<sub>2</sub>O–SiO<sub>2</sub> melts are well correspond to the experimental data [Yamaguchi et al., 1983; Rudnyi et al., 1988; Kozhina & Shultz, 2000; Zaitsev et al., 2000] and phase diagram calculated by Zaitsev et al. [Zaitsev et al., 2000]. The observed differences of data obtained by Shultz et al. [Shultz et al., 1987] from the results of other experimental studies and the present study calculations, probably, are caused by the systematic errors due to the

partial oxygen determination needed for the sodium oxide activity calculations.

Thus, within the framework of the developed semiempirical model based on the theory of ideal associated solution, the thermodynamic properties of the Na<sub>2</sub>O–SiO<sub>2</sub> melts were calculated in the temperature range of 900– 1800 K. The calculation results are corresponding to available experimental data. They also can be used as for theoretical calculations of thermodynamic properties of multicomponent melts containing this system compounds and in the practical purposes. References:

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# Shornikov S. I. Thermodynamic properties of the Na<sub>2</sub>O–GeO<sub>2</sub> melts

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**Abstracts.** Within the framework of the developed semi-empirical model, the calculations were made of thermodynamic properties of the Na<sub>2</sub>O–GeO<sub>2</sub> melts in the temperature region 900–1600 K. The results of calculations are compared with available experimental information.

Key words: thermodynamic properties of oxide melts, the  $\text{Na}_2\text{O}-\text{GeO}_2$  system.

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Physico-chemical properties of sodium germanates and melts in the Na<sub>2</sub>O–GeO<sub>2</sub> system are of interest to a theoretical calculations of low-temperature analog of the Na<sub>2</sub>O–SiO<sub>2</sub> system, which important in the petrological researches and due to their practical application in technics. The information on the compound structure and their properties, as the phase relations in the system under consideration is poor [Galakhov et al., 1985; Shakhmatkin & Vedishcheva, 1994; Shornikov, 2005], the version of the phase diagram is presented in fig. 1.



Fig. 1. The phase diagram of the Na<sub>2</sub>O–GeO<sub>2</sub> system [Galakhov et al., 1985]. Table of symbols:  $1 - \alpha$ -Na<sub>2</sub>O + liquid;  $2 - \alpha - Na_2O + Na_4GeO_4;$  $3 - \beta - Na_2O + Na_4GeO_4;$  $4 - \gamma$ - $Na_2O + Na_4GeO_4;$  $5 - Na_4GeO_4 + liquid;$ 6 –  $Na_4GeO_4 + Na_2GeO_3;$  $7 - Na_4GeO_4 + Na_6Ge_2O_7;$ 8 - $Na_6Ge_2O_7 + Na_2GeO_3;$  $9 - Na_2GeO_3 + liquid;$ 10 - $Na_2GeO_3 + Na_4Ge_9O_{20};$  $11 - Na_4Ge_9O_{20} + liquid;$ 12 - $Na_4Ge_9O_{20} + GeO_2$ ; 13 – GeO<sub>2</sub> + liquid; 14 – liquid.

This investigation presents the calculation of thermodynamic properties of the Na<sub>2</sub>O-GeO<sub>2</sub> melts at temperatures from 900 to 1600 K within framework of the ideal associated solutions theory. The simplified lattice model. as before for the  $K_2O-SiO_2$ systems [Shornikov, 2013], accounts for the intermolecular interactions using the semi-phenomenological parameters. They were determined on the base of the experimental [Fan et al., 1993; Kozhina & Shultz, 1995; Kozhina & Shultz, 2000] and reference [Glushko et al., 1978-1982] thermodynamic data, presented in the table 1. The source thermodynamic data considered 11 condensed phases (7 solid and 4 liquid) and 14 gas species, these components are listed in the table 2.

### Abstracts

Compound	<i>Т</i> , К	$\Delta H_T$ ,	$\Delta S_T$ ,	Reference
		kJ/mole	J / (mole·K)	
Na <sub>4</sub> GeO <sub>4</sub>	1400	$-134.35\pm5.00$	_	[Fan et al., 1993]
$Na_6Ge_2O_7$	1300	-137.30±1.70	-7.31±1.31	[Kozhina & Shultz, 2000]
_ " _	1400	$-131.47 \pm 4.00$	_	[Fan et al., 1993]
_ " _	1450	-130.53±4.18	-6.24±2.72	[Kozhina & Shultz, 1995]
Na <sub>2</sub> GeO <sub>3</sub>	1300	$-129.80\pm1.70$	$-7.00\pm1.31$	[Kozhina & Shultz, 2000]
_ " _	1400	-118.36±5.00	_	[Fan et al., 1993]
_ " _	1450	-117.82±5.43	$-9.00 \pm 4.18$	[Kohsaka et al., 1978]
_ " _	1450	$-124.68 \pm 4.18$	$-6.69 \pm 2.72$	[Kozhina & Shultz, 1995]
Na <sub>2</sub> Ge <sub>4</sub> O <sub>9</sub>	1300	$-55.70\pm1.70$	4.69±1.31	[Kozhina & Shultz, 2000]
_ " _	1400	$-56.57 \pm 3.00$	_	[Fan et al., 1993]
_ " _	1450	$-55.23 \pm 4.18$	5.02±2.72	[Kozhina & Shultz, 1995]
Na <sub>4</sub> Ge <sub>9</sub> O <sub>20</sub>	1300	$-49.97 \pm 1.70$	5.35±1.31	[Kozhina & Shultz, 2000]
_ " _	1400	-51.49±3.00	-	[Fan et al., 1993]
_ " _	1450	-51.81±5.43	3.85±4.18	[Kohsaka et al., 1978]
_ " _	1450	$-50.66 \pm 4.18$	4.14±2.72	[Kozhina & Shultz, 1995]

Table 1. Enthalpies ( $\Delta H_T$ ) and entropies ( $\Delta S_T$ ) of sodium germinates formation from the simple oxides [Kohsaka et al., 1978; Fan et al., 1993; Kozhina & Shultz, 1995; Kozhina & Shultz, 2000].

Table 2. The Gibbs energy of formation from elements of condensed phases and vapor species over the Na<sub>2</sub>O– GeO<sub>2</sub> system at 1500 K, calculated in present study according to data [Glushko et al., 1978–1982; Fan et al., 1993; Kozhina & Shultz, 1995; Kozhina & Shultz, 2000].

Condensed phases				Gas ph	lase
Solid phases	$\Delta_f G^{\circ}_{1500},$	Liquid	$\Delta_f G^{\circ}_{1500},$	Vapor species	$\Delta_f G^{\circ}_{1500}$ ,
	kJ/mole	phases	kJ/mole		kJ/mole
Na <sub>2</sub> O	-211.201	Na <sub>2</sub> O	-213.636	Na	-26.838
Na <sub>4</sub> GeO <sub>4</sub>	-1067.082			Na <sub>2</sub>	-7.696
Na <sub>6</sub> Ge <sub>2</sub> O <sub>7</sub>	-1823.673			NaO	13.897
Na <sub>2</sub> GeO <sub>3</sub>	-736.673	Na <sub>2</sub> GeO <sub>3</sub>	-743.176	Na <sub>2</sub> O	-79.739
$Na_2Ge_4O_9$	-1680.422			$Na_2O_2$	-59.967
Na <sub>4</sub> Ge <sub>9</sub> O <sub>20</sub>	-3611.465	Na <sub>4</sub> Ge <sub>9</sub> O <sub>2</sub>	-3625.145	Ge	170.658
		0			
$GeO_2$	-290.807	$GeO_2$	-292.357	Ge <sub>2</sub>	221.010
				GeO	-155.217
				GeO <sub>2</sub>	-101.526
				$Ge_2O_2$	-295.507
				Ge <sub>3</sub> O <sub>3</sub>	-378.763
				0	154.920
				$O_2$	0.000
				O <sub>3</sub>	243.150

The same table 2 gives the calculated values of the Gibbs formation energies from elements  $(\Delta_f G^\circ_T)$  for the compounds and the vapor species over the Na<sub>2</sub>O–GeO<sub>2</sub> system. They were used for the calculation of the equilibrium conditions in the system at a given composition and temperature. The required equation solution for the total Gibbs energy for the system studied was found by the widely used approach, namely the Gibbs energy minimization method. The oxide activities a(i) and the mixing energy in the Na<sub>2</sub>O–GeO<sub>2</sub> melts ( $\Delta G$ ) are represented in fig. 2 and 3 in comparison to experimental data [Kohsaka et al., 1978; Shultz et al., 1979; Kozhina & Shultz, 1995; Kozhina & Shultz, 2000].

We may observe also on fig. 2 the calculated values of  $Na_2O$  and  $GeO_2$  activities are well correspond to the experimental data [Kohsaka et al., 1978; Kozhina & Shultz, 1995; Kozhina & Shultz, 2000]. They

showed their increasing with temperature growth. The higher values of Na<sub>2</sub>O and GeO<sub>2</sub> activities (fig. 2) and the corresponding mixing energies (fig. 3) obtained by mass spectrometric method [Shultz et al., 1979] caused by the significant nonsystematic errors in the partial pressure determinations (up to 30 %) and by the incorrect application of the Belton-Fruehan method [Belton & Fruehan, 1971] to calculate of  $a(\text{GeO}_2)$ .

Thus, within the framework of the developed semiempirical model based on the theory of ideal associated solution, the thermodynamic properties of the Na<sub>2</sub>O–GeO<sub>2</sub> melts were calculated in the temperature range of 900– 1600 K. The calculation results are corresponding to available experimental data. They also can be used as for theoretical calculations of thermodynamic properties of multicomponent melts containing this system compounds and in the practical purposes.



**Fig. 2.** The activities of Na<sub>2</sub>O (*a*) and GeO<sub>2</sub> (*b*) in the Na<sub>2</sub>O–GeO<sub>2</sub> melts: 1-3 – obtained by the e.m. f method at 1300 [Kozhina & Shultz, 1995], 1450 [Kohsaka et al., 1978] and 1543 K [Shultz et al., 1979]; 4 – obtained by Knudsen effusion mass spectrometric method at 1543 K [Shultz et al., 1979]; and calculated in the present study at the same temperatures, represented by lines of the same color.



**Fig. 3.** The mixing energy in the Na<sub>2</sub>O–GeO<sub>2</sub> melts: 1-3 - obtained by the e.m. f method at 1300 K [Kozhina & Shultz, 1995] and at 1450 K [Kohsaka et al., 1978; Kozhina & Shultz, 2000] correspondingly, 4 - obtained by Knudsen effusion mass spectrometric method at 1543 K [Shultz et al., 1979]; and calculated in the present study at the same temperatures, represented by lines of the same color.

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### Stolyarova T.A., Voronin M.V., Osadchii E.G., Brichkina E.A. Enthalpy of formation of palladium monobismuthide from elements

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**Abstract.** During the study a palladium monobismuthide thermochemical researching was carried out. The reaction of formation from elements was investigated in vacuum-blocking calorimeter. The synthesis method is described in the text. The next value of formation enthalpy was obtained:  $\Delta_f H^o_{298.15}(PdBi, cr)$ =-(57.50 ±0.87) kJ/mol.

Key words: palladium bismuthide, enthalpy, termochemistry, calorimetry.

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Binary intermetallic platinum and palladium compounds are often could be defined as specific minerals of the later stages of magmatogenic sulfide deposites riched in platinum group minerals. Native metals as well as simple binary intermetallics determine a low physical –

### Abstracts

chemical limit of the oxide and chalcogenide ore formation.

Physical-chemical analyses of mineral parageneses is a basis for understanding of ore formation geochemistry. experimental Unfortunately, there is no any thermodynamic data for many platinum group intermetallics. PdBi is one that has no, so it was chosen as the object of investigation. In nature PdBi could be found as mineral sobolevskite with hexagonal structure and may has isomorphic impurity of Te [Mineral Data Publishing 2001-2005].

Palladium monobismutide was subjected to thermochemical investigation in high-temperature vacuum-blocking calorimeter, developed in the laboratory of mineral thermodynamic of IEM RAS (Chernogolovka) [Sobolev, Vasil'ev, 1962, Fleisher, Stolyarova, 1978]. Preliminary investigations showed that PdBi synthesis from elements (platinum powder 99.99 % and powder bismuthine HP grade) in quartz glass ampoules took place at 650 °C for several minutes (5-7).

A quartz glass ampoule with weighted powder was evacuated to a pressure  $10^{-4}$  Torr, sealed and placed into a resistance furnace inside of a calorimetric bomb, which was further filled with argon gas under a pressure 10 atm.

The vessel with the calorimetric bomb was evacuated until residual pressure  $10^{-2}$  Torr. The temperature of the calorimetric isothermal cover was supported (25 ±0.02) °C automatically. Electric energy was measured with accuracy 0.02 %. Temperature changing during the experiment was fixed with a resistance thermometer consisting of ten miniature cylinder platinum sensors (total resistivity is 1098  $\Omega$  at 25 °C), located along the calorimetric bomb. The calorimeter was preliminary calibrated with electric energy in a blank experiment.

A heating time was automatically fixed (360 sec) in each experiment. Also the total time of the experiment was fixed (42 min). The accuracy of thermal calibration value is 0.05%. The reaction supposed to be complete in any case when reheating process didn't show any additional thermal effects. Results of experiments are placed to Table 1. X-ray powder diffraction analyses of the products also proved the absence of other phases except hexagonal PdBi (sobolevskite) PDF #290238 . The RMS measurements error was calculated for confidence interval 95 % [Nalimov, 1960].

As a main result the enthalpy of PdBi formation from elements was obtained:

 $\Delta_{\rm f} {\rm H}^{\rm o}_{298.15}$  (PdBi, cr)=-(57.50±0.87) kJ/mol.

Run №	Sample weight (gram)	ΔR+σ (Ohm)*	The amount of heat released during the experiment (J)			-Δ <sub>f</sub> H <sup>o</sup> <sub>298.15</sub> (kJ/mol)
			total	on the heater	during the reaction	
1	2.0829	8.0699	42936.7	42567.5	369.2	55.91
2	2.8543	8.0972	43082.0	42552.6	529.4	58.49
3	3.2189	8.1208	43171.8	42583.6	588.2	57.63
4	2.6396	8.0955	43037.3	42566.5	470.8	56.25
5	2.6872	8.0955	43037.3	42540.5	496.8	58.31
6	2.9328	8.0872	42993.2	42446.8	546.4	58.76
7	2.0286	8.0800	42851.5	42474.8	376.7	58.56
8	2.3890	8.1059	42988.8	42561.6	427.2	56.40
9	2.5920	8.1078	42998.9	42529.2	469.7	57.15
			The average			57.50

Table 1. Enthalpy of PdBi formation from elements M.M. 315.40

Note:

 $(*)\Delta R + \sigma$  – the thermometer resistance value with the correction for thermal exchange,

1-2 samples– calorimeter thermal value W= (5320.6  $\pm$ 2.0) J/ $\Omega$ 

3-6 samples W= (5316.2  $\pm 2.0$ ) J/ $\Omega$ 

7-9 samples W= (5303.4  $\pm 2.0$ ) J/ $\Omega$ 

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