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A consideration of nonideal formation of solid solutions of silicates and alumosilicates

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Creating a database on solid solutions is of great interest, as solid solutions, characterized by a variable chemical composition, are widespread not only in natural mineral assemblages, but are often formed in a variety of technological systems. To estimate the composition of the phases of many chemical systems in wide ranges of temperatures and pressures it is necessary to know the thermodynamic properties of various solid solutions. It is important to identify the relationship of the microscopic picture of atomic interactions with macroscopic thermodynamic characteristics of the end of the series [*Navrotski*, 1992, *Avchenko*, 2009].

Contribution of ΔG^o mix for the thermodynamic properties of solid solutions consists of two parts - the enthalpy and entropy terms [*Urusov,* 1987]:

$$\Delta G^o_{mix} = \Delta H^o_{mix} - T\,\Delta S^o_{mix} \quad (1), \qquad \text{and} \quad \Delta S^o_{mix} = \Delta S^o_{id} + \Delta S_{vib}^{ex} \quad (2),$$

where ΔS^o_{id} - the entropy of mixing of ideal solutions and ΔS^o_{vib} - vibrational contribution, arises because of the nonadditivity of the specific heat capacity of solid solution.

$$\Delta S^o_{id} = -R[x\cdot \ln x + (1-x)\cdot \ln(1-x)](3).$$

Reliable values of ΔH^o_{mix} given in the literature were determined using calorimetric methods for many solid solutions of silicates and alumosilicates, while the value of ΔS^omix, defined by the classical method of low-temperature adiabatic calorimetry, until recently, was only limited by results of the study of binary solid solutions of garnets series of pyrope-grossular ($Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$) [*Hazelton and Vestrum*, 1980], disordered feldspars $NaAlSi_3O_8$-$KAlSi_3O_8$ (analbit–sanidine) [*Hazelton, et al.*, 1983] and scapolites [*Komada, et al*., 1996]. It is shown that there are positive excess heat capacity of mixing for disordered feldspars at temperatures below 300 K, which leads to excess vibrational entropy about 3 J/mol K at 298.15 K.

Creating a relaxation calorimeter (Quantum Design measuring system for the physical properties) allowed the low-temperature heat capacity measurements for the milligram quantities of the materials sample. Comparison of results of specific heat measurements of the same sample of hematite (Fe_2O_3), and performed by the classical methods showed that the error in heat capacity measurements of samples in the milligram quantities of ± 1% [*Shi, et al*., 2010].

Recently, the method of relaxation calorimetry measured the low-temperature specific heat for binary solid solutions series: pyrope-grossular [*Dachs, Geiger,* 2006], forsterite-fayalite [*Dachs, et al.*, 2007], analbit-anortite [*Benisek, et al.*, 2009], anortite-sanidine [*Benisek, et al.*, 2010], CaTs–diopside [*Benisek, et al*., 2007] and estimates are made ΔS_{vib}^{ex}.

It was shown [*Benisek and Dachs*, 2011] that the excess of the vibrational entropy (ΔS_{vib}^{ex}) for several silicate and alumosilicates solid solutions correlates with the difference of molar volumes (ΔV_i) and compressibilities (Δk_i) of the end members of solid solutions.

Empirical relationship between ΔS_{vib}^{ex}, ΔV_i and Δk_i, was calibrated for the six silicate and alumosilicates solid solutions. In this case, the sign for Δk_i is chosen to be positive if the final term with a large volume has a larger bulk modulus. Negative values arise when the final term solution with a large volume has a lower compressibility.

In the paper [*Benisek and Dachs,* 2011] obtained the equation:

$$\Delta S_{vib}^{ex} = (\Delta V_i + m\Delta k_i)\cdot f \qquad (4),$$

where $m = 0.0246$ and $f = 2.926$.

Equation (4) can be simplified by fixing the ratio f = 3 (exactly). The result is a linear dependence of ΔS_{vib}^{ex} on Δk_i:

$$\Delta S_{vib}^{ex} - 3\Delta V_i = 3m\Delta k_i. \qquad (5)$$

Using the experimentally determined thermodynamic parameters for solid solutions, given in the paper [*Benisek and Dachs*, 2011] and fixing $\Delta S_i - 3\Delta V_i = 0$ for $\Delta k_i = 0$, we find the numerical value of empirical coefficient m in equation (5) and its error: $m = 0.0228 \pm 0.003$.

Table 1 shows the values of molar volumes and bulk moduli for the above mentioned pairs of solid solutions. The ΔS_{vib}^{ex} values obtained experimentally by the authors, and calculated by equations 4 and 5, respectively, are presented in the last three columns.

Table 1. Molar volume (V), bulk modulus (k), the differences between the end members (ΔV_i and Δk_i), and the maximum excess vibrational entropies (ΔS_{vib}^{ex}) for the silicates and alumosilicates solid solutions

Name	V, J/bar	*k*, GPa	ΔV_i, J/bar	Δk_i, GPa	ΔS_{vib}^{ex}, J/mol·K		
					ΔS_{vib}^{ex} (exp.)	ΔS_{vib}^{ex} (eq. 4)	ΔS_{vib}^{ex} (eq. 5)
Analbit – $NaAlSi_3O_8$	10.06	52	0.85	6	2.6	2.9	2.9_9
Sanidine – $KAlSi_3O_8$	10.91	58					
Pyrope – $Mg_3Al_2Si_3O_{12}$	11.32	171	0.403	-1	1	1.1	1.1_4
Grossular – $Ca_3Al_2Si_3O_{12}$	12.53	170					
Forsterite – Mg_2SiO_4	4.365	128	0.133	-6	0	0	-0.0_4
Fayalite – Fe_2SiO_4	4.631	122					
Analbit – $NaAlSi_3O_8$	10.06	52	0.03	29	2.6	2.2	2.5_1
Anorthite – $CaAl_2Si_2O_8$	10.09	81					
Anorthite – $CaAl_2Si_2O_8$	10.09	81	0.82	-23	1	0.7	0.76_3
Sanidine – $KAlSi_3O_8$	10.91	58					
CaTs – $CaAlAlSiO_6$	6.37	127	0.25	-13	0	-0.2	-0.2_1
Diopside – $CaMgSi_2O_6$	6.62	114					

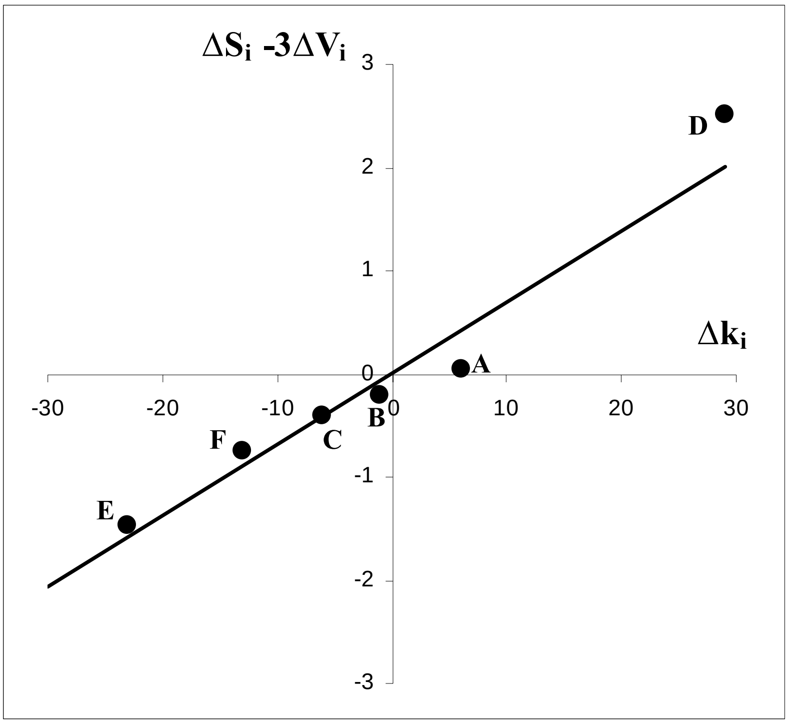

Fig. 1. The relationship of parameters of mixing of solid solutions for the pairs: A – analbite-sanidine; B – pyrope-grossular, C – forsterite-fayalite; D – disordered plagioclases; E – disordered (K,Ca)feldspars-diopside; F – CaTs-diopside

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