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Thermodynamic Properties of Solid Solutions of Silica in Forsterite ($Mg_2Si_{1+\gamma}O_{4+2\gamma}$)

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From solid state electrochemical measurements on Mg_2SiO_4–SiO_2 solid solutions in air at 1300 K $\leq T \leq$ 1780 K the thermodynamic (excess) functions are calculated. A pronounced nonideality is found.

Introduction

Forsterite (magnesium orthosilicate Mg_2SiO_4) belongs to the olivines. The olivine-group minerals are among the more important constituents of igneous rocks and are believed to be a dominant phase in the upper mantle of the earth. As Pluschkell and Engell found, forsterite dissolves a certain amount of silica (*1*). The thermodynamic properties of forsterite–silica solid solutions have not yet been investigated. These data are, however, necessary for the quantitative treatment of geochemical problems. Therefore, the present study was initiated so as to provide thermodynamic quantities for forsterite–silica solid solutions over the widest possible range of both concentration and temperature. The investigation was carried out using the solid galvanic cell method which has been described elsewhere (*2*). This method is based on the application of a special fluoride electrolyte as a second phase in a so-called "inert skeleton" of an appropriate silicate.

Experimental

Fine-grained powders of reagent grade MgO and SiO_2 were thermally pretreated, thoroughly mixed with a small amount of binder (oleine acid), and compressed (5×10^8 Pa) before being first sintered in air for 12 hr at 1470 K. Then the temperature was increased to 1720 K for another 96 hr. Afterward, the samples were rapidly cooled to room temperature and checked by optical microscopy and X-ray diffraction. Dense samples with about 90% of the theoretical density were obtained. The complete set of samples is listed in Table I. With the exception of sample No. 6, all samples studied contained only one single phase. Only the sample No. 6 contained a minute amount of

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TABLE I

COMPOSITION OF THE INVESTIGATED SAMPLES

Sample	x_{SiO_2}	$x_{Mg_2SiO_4}$	Formula of silica-rich forsterite ($Mg_2Si_{1+\gamma}O_{4+2\gamma}$)
1	0.012	0.988	$Mg_2Si_{1.012}O_{4.024}$
2	0.029	0.971	$Mg_2Si_{1.030}O_{4.060}$
3	0.051	0.949	$Mg_2Si_{1.054}O_{4.107}$
4	0.071	0.929	$Mg_2Si_{1.077}O_{4.153}$
5	0.095	0.905	$Mg_2Si_{1.105}O_{4.210}$
6	0.148	0.852	$Mg_2Si_{1.174}O_{4.347}$

Note. The notation $Mg_2Si_{1+\gamma}O_{4+2\gamma}$ is equivalent to the notations $2MgO \cdot (1 + \gamma)SiO_2$ or $Mg_2SiO_4 \cdot \gamma SiO_2$, respectively, with $\gamma = x_{SiO_2}/(1 - x_{SiO_2})$.

$MgSiO_3$. (Obviously, the solubility limit of SiO_2 is smaller than $x_{SiO_2} = 0.148$ at the sintering temperature.)

The solid electrolyte was prepared from a mixture of 56.5 wt% MgO, 42.2 wt% SiO_2, and 1.3 wt% MgF_2. The mixture was preheated at 1670 K for 18 hr and sintered at 1920 K for 1 hr in air. Samples of more than 90% theoretical density containing MgF_2 dispersed in Mg_2SiO_4 were obtained. As a reference electrode an equimolar mixture of Mg_2SiO_4 and MgO was used. It was prepared by thermal treatment of a mixture containing 68.4 wt% of MgO and 31.6 wt% SiO_2, first at 1670 K for 18 hr, then at 2090 K for 30 min. Pellets 8 mm in diameter and 2 mm thick were cut from the sintered products.

The solid state galvanic cells employed were of the type

$$\text{Pt/O}_2\text{, MgO, Mg}_2\text{SiO}_4\|\text{Mg}_2\text{SiO}_4$$
$$\text{(I)}$$
$$(+\text{MgF}_2)\|(\text{Mg}_2\text{SiO}_4)_{\text{s.s.}}\text{, O}_2\text{/Pt,} \qquad (1)$$
$$\text{(II)}$$

where $(Mg_2SiO_4)_{s.s.}$ denotes forsterite in a homogeneous solid solution. The measurements were made in air ($p_{O_2} = 21 \times 10^3$ Pa) in the temperature range 1300–1780 K. Up to about 1350 K, quartz glass was used for the construction of the apparatus; above 1350 K alumina was used. Depending on the temperature, stable emf values were reached after about 0.5–2 hr after a change of the measuring temperature. The emf was measured with a digital vacuum tube voltmeter ($R = 10^{10}\ \Omega$).

Results and Discussion

In Table II the measured emf values for cell (1) are given. The reactions taking place in the cell (1) can be described by the following overall cell reaction

$$SiO_2(I) = SiO_2(II). \qquad (2a)$$

The measured voltage (E) reflects the difference in the silica activities on both sides of the electrolyte, $a_{SiO_2(I)}$ and $a_{SiO_2(II)}$, and can be expressed by Nernst's equation

$$E = \frac{RT}{4F} \ln \frac{a_{SiO_2(II)}}{a_{SiO_2(I)}}. \qquad (2b)$$

From our published data (*2*), standard free enthalpy values for the reaction

$$2MgO + SiO_2 = Mg_2SiO_4, \qquad (3)$$

$$\Delta G_3^0\ (\text{J/mole}) = -58{,}423 - 4.44T, \quad T(\text{K}),$$

were taken for the calculation of the activity values of SiO_2 at $p_{O_2} = 0.21 \times 10^5$ Pa in the solid solution. For cell (1),

TABLE II

EMF VALUES OF CELL (1) IN THE TEMPERATURE RANGE 1300 K ≤ T ≤ 1780 K

	emf/mV			
x_{SiO_2}	1300 K	1480 K	1600 K	1780 K
0.012	103.2	102.6	101.5	103.0
0.029	119.9	122.4	123.9	126.3
0.051	132.2	135.3	137.4	142.7
0.071	139.0	143.1	145.9	152.5
0.095	144.8	151.3	154.5	160.2
0.148	148.5	154.2	159.7	166.3

$$a_{\mathrm{SiO_2(II)}} = \exp\left(\frac{4FE - 58{,}423 - 4.44T}{RT}\right) \quad (4)$$

is obtained. From Eq. (4) the activities of SiO_2 in forsterite–silica solid solutions were obtained from the data given in Table II. Then, the activity coefficients of SiO_2, $f_{\mathrm{SiO_2}}$, in the solid solutions were calculated from

$$f_{\mathrm{SiO_2}} = \frac{a_{\mathrm{SiO_2}}}{x_{\mathrm{SiO_2}}}, \quad (5)$$

where $a_{\mathrm{SiO_2}}$ denotes $a_{\mathrm{SiO_2(II)}}$.

By one knowing the activity coefficients of SiO_2 as a function of its concentration, the values of the activity coefficient of Mg_2SiO_4 in the solid solution $f_{\mathrm{Mg_2SiO_4}}$ could be obtained by a method worked out by Darken and Gurry (*3*). For our case, the following working equation was derived

$$\ln f_{\mathrm{Mg_2SiO_4}} = -\alpha_{\mathrm{SiO_2}} x_{\mathrm{Mg_2SiO_4}} x_{\mathrm{SiO_2}} - \int_{x_{\mathrm{Mg_2SiO_4}}=1}^{x_{\mathrm{Mg_2SiO_4}}} \alpha_{\mathrm{SiO_2}} dx_{\mathrm{Mg_2SiO_4}}. \quad (6)$$

TABLE III

THE ACTIVITY COEFFICIENTS OF BOTH COMPONENTS IN THE FORSTERITE–SILICA SOLID SOLUTION IN THE TEMPERATURE RANGE 1300 K ≤ T ≤ 1780 K

$x_{\mathrm{SiO_2}}$	$f_{\mathrm{SiO_2}}$; $f_{\mathrm{Mg_2SiO_4}}$ 1300 K	1480 K	1600 K	1780 K
0.012	(a) 8.824	10.67	11.60	13.94
	(b) 1.001	1.001	1.001	1.001
0.029	(a) 6.564	8.110	9.072	10.48
	(b) 1.007	1.007	1.006	1.007
0.051	(a) 5.838	6.982	7.712	9.231
	(b) 1.012	1.013	1.013	1.013
0.071	(a) 5.288	6.339	7.013	8.471
	(b) 1.019	1.020	1.019	1.018
0.095	(a) 4.884	6.168	6.758	7.768
	(b) 1.026	1.022	1.023	1.026
0.148	(a) 3.579	4.328	5.044	5.847
	(b) 1.071	1.073	1.065	1.067

Note. (a) SiO_2; (b) Mg_2SiO_4.

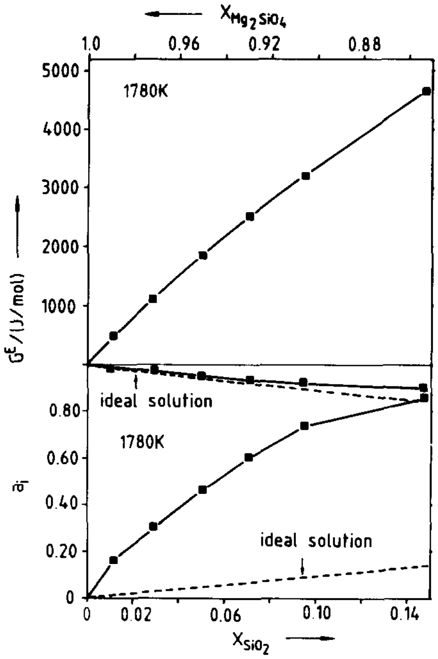

FIG. 1. Excess free enthalpy (top) and activities of the components (bottom) at T = 1780 K.

In this expression, the α function for the component SiO_2 in the solid solution is defined as

$$\alpha_{\mathrm{SiO_2}} = \frac{\ln f_{\mathrm{SiO_2}}}{x^2_{\mathrm{Mg_2SiO_4}}}. \quad (7)$$

In order to demonstrate the deviations of the solutions from ideal behavior, the excess free enthalpy was calculated:

$$G^E = RT(x_{\mathrm{SiO_2}} \ln f_{\mathrm{SiO_2}} + x_{\mathrm{Mg_2SiO_4}} \ln f_{\mathrm{Mg_2SiO_4}}). \quad (8)$$

The excess enthalpy, H^E, and the excess entropy, S^E, were also determined, using the following equations:

$$H^E = [\partial(G^E/T)/\partial(1/T)]_P \quad (9)$$

$$S^E = -\left[\frac{\partial G^E}{\partial T}\right]_P. \quad (10)$$

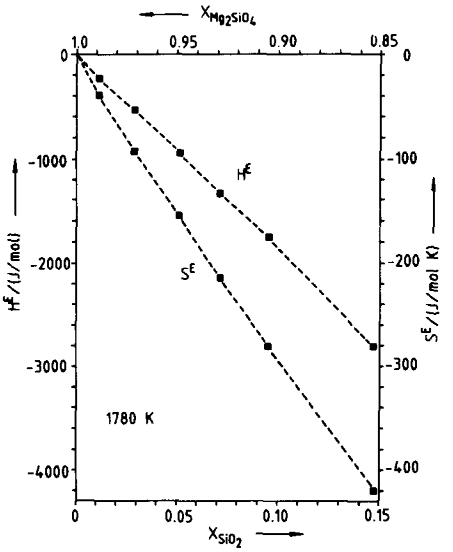

FIG. 2. Excess enthalpy H^E and excess entropy S^E at T = 1780 K.

In Table III the activity coefficients of both components of the solid solution are listed as calculated from formulas (5)–(7).

In Fig. 1 the plots of the excess free enthalpy (see Eq. (8)) and activity values vs composition of the solution are presented for 1780 K. Similar plots were obtained at the other temperatures. As results from Fig. 1, the solid solutions of silica in forsterite show positive deviations ($G^E > 0$) from Raoult's law.

In Fig. 2 the plots of both the excess enthalpy and entropy vs composition of the solution at 1780 K are shown. Because of the nonlinearity of the emf as a function of temperature, the excess enthalpy and the excess entropy depend on temperature. They possess highly negative values in the entire concentration and temperature range. Thus, the solid solution of silica in forsterite exhibits a strong nonideal behavior up to the solubility limit of silica.

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