THERMODYNAMIC PROPERTIES OF THE MELTS AND VAPORS OF THE $CaO-MgO-Al_2O_3-SiO_2$ SYSTEM DETERMINED BY THE MASS SPECTROMETRIC STUDY

Shornikov S.I.
Center of Isotopic Research, Karpinsky All-Russian Geological Institute (VSEGEI), Saint-Petersburg
s_shornikov@hotmail.com

Key words: *$CaO-MgO-Al_2O_3-SiO_2$ system, thermodynamic properties of melts and vapors, mass spectrometric Knudsen effusion method*

Oxide $CaO-MgO-Al_2O_3-SiO_2$ (CMAS) system is known to be very important for the physical chemistry of silicates, petrology, cosmochemistry and industry.

More than 30 compounds were found to exist in this system; the most studied are listed in the Table. The data on the evaporation processes and thermodynamic properties of individual oxides at high temperature (>1800 K) is numerous [1] comparing with those on oxide compounds and their melts.

Present work considers the regularities of the melt evaporation in CMAS system at high temperatures from 1500 to 2500 K and high vacuum of about 10^{-11} on the base of available reference data and the authors results obtained by the high temperature Knudsen effusion method; the methodical approaches for the exact determination of the thermodynamic properties of the condensed and gas phases are discussed.

As seen from the Table, the composition of the gas phase over the oxides is quite similar to that identified over the multicomponent CMAS-system melts; the percentage of the complex oxide molecules is negligible. Therefore, one can assume that the evaporation of the multicomponent melts occurs due to the reactions typical for the individual oxide evaporation.

Note that if the solid solutions regions are absent from the system, the evaporation rate of the compositions from the sub-liquidus regions of the CMAS-system is very low and the discussed composition remains constant [2, 7-9, 11, 13-15]. On the other hand, the variation of the condensed phase compositions is observed at the evaporation of the melts and solid compositions from the solid solution regions; these variations are determined by the following order of oxide evaporation - SiO_2, MgO, CaO, Al_2O_3 [2, 8-11, 15]. Obviously, the evaporation rate and the rate of the composition changes increase with temperature.

The direct observation of the variations of the evaporation rate is possible through the mass spectrometric registration of the mass spectra of vapor over the melt studied ($I(i)^+$); this approach gives us the opportunity to determine the boundaries of the phase regions ($x^*(j)$), which are necessary for the correct application of the mass spectrometric approaches for the determination of the component activities ($a(i)$) based on the Gibbs-Duhem equation

$$\ln a(i) = -\int_{x(j)=x^*(j)}^{x(j)} x(j)\, d\ln\frac{a(j)}{a(i)} = -\int_{x(j)=x^*(j)}^{x(j)} x(j)\, d\ln\frac{I(j)^+}{I(i)^+}$$

For the derived equation, as well as for a number of similar methodical approaches, it becomes possible to eliminate the systematic errors during the determination of the thermodynamic properties of the multicomponent melts – chemical potentials (activities), enthalpies, and entropies of oxides [8, 10, 11, 14, 15].

The combination of the thermodynamic data on the multicomponent melts with the information on the sub-liquidus CMAS-system regions gives the opportunity to find the temperature dependencies of the Gibbs energies of formations for the gas and condensed phase components. These dependencies can be used in the further calculations of the thermodynamic properties of the multicomponent silicate systems and to model the phase equilibriums in them using the standard calculation procedures.

Table

The vapor species over the compounds of $CaO-MgO-Al_2O_3-SiO_2$ system

System, references	Compounds (T_{fus}, K)	T, K	Vapor species
CaO [1, 2]	C (3172)	1800-2050	Ca, CaO, O, O_2
MgO [1, 2]	M (3099)	1800-2050	Mg, MgO, O, O_2
Al_2O_3 [1-3]	A (2327)	1800-2550	Al, AlO, AlO_2, Al_2, Al_2O, Al_2O_2, Al_2O_3, O, O_2
SiO_2 [4, 5]	S (1996)	1610-2100	SiO, SiO_2, Si_2O_2, O, O_2
CaO-MgO [6]			Ca, CaO, Mg, MgO, O, O_2
$CaO-Al_2O_3$ [7]	CA (1877), CA_2 (2035*), CA_6 (2148*), C_3A (1808*), C_5A_3 (1093*), $C_{12}A_7$ (1733)	1800-2050	Ca, CaO, Al, AlO, Al_2O, Al_2O_2, O, O_2, CaAlO
$CaO-SiO_2$ [8]	CS (1817), C_2S (2403), C_3S (2343*), C_3S_2 (1737*)	1700-2500	Ca, CaO, SiO, SiO_2, O, O_2, $CaSiO_3$
$MgO-Al_2O_3$ [9]	MA (2408)	1850-2250	Mg, MgO, Al, AlO, Al_2O, O, O_2, MgAlO
$MgO-SiO_2$ [10]	MS (1850*), M_2S (2163)	1873-1973	SiO, Mg
$Al_2O_3-SiO_2$ [3, 11]	AS (1307*), AS_2 (758*), A_3S_2 (2180)	1700-2550	Al, AlO, Al_2O, Al_2O_2, AlO_2, SiO, SiO_2, O, O_2, AlSiO
$CaO-MgO-Al_2O_3$ [12]	C_3MA_2 (1624*)	1960	Ca, Mg, Al, AlO
$CaO-MgO-SiO_2$ [13]	CMS (1763*), CMS_2 (1665), C_2MS_2 (1727*), C_3MS_2 (1848*)	1550-1900	Ca, Mg, SiO, SiO_2
$CaO-Al_2O_3-SiO_2$ [14]	CAS (1673*), CAS_2 (1823), C_2AS (1866), C_3AS_3 (1333*)	1800-2050	Ca, CaO, Al, AlO, Al_2O, Al_2O_2, SiO, SiO_2, AlSiO, CaAlO, $CaSiO_3$
$MgO-Al_2O_3-SiO_2$ [15]	MAS (1273*), M_2A_2S (1766*), $M_2A_2S_5$ (1738*), M_3AS_3 (1570*)	1600-2550	Mg, MgO, Al, AlO, Al_2O, SiO, SiO_2, AlSiO
$CaO-MgO-Al_2O_3-SiO_2$ [2]		1650-2000	Ca, CaO, Mg, MgO, Al, AlO, Al_2O, Al_2O_2, SiO, SiO_2, O, O_2, AlSiO, CaAlO

*) the dissociation temperature

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Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(21)'2003
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2003
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2003/informbul-1_2003/magm-10e.pdf
Published on July 15, 2003

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