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HIGH TEMPERATURE MASS SPECTROMETRIC STUDY OF MULTICOMPONENT SILICATE SYSTEMS

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Synopsis: Using high temperature mass spectrometry (Knudsen effusion method) the compositions and partial pressures of vapor over melts at 1300-1973 K have been studied in the multicomponent silicate systems containing CaO, Al_2O_3, B_2O_3, FeO, MgO, Na_2O, K_2O. Activities of the components have been determined. This makes it possible to calculate Gibbs energies in multicomponent systems by the semiempirical Kohler and Wilson methods using the data on equilibria in binary systems.

Key words: high temperature mass spectrometry, thermodynamics, multicomponent silicate systems, the Kohler and Wilson methods.

1. Introduction

Developing of modern data base for calculation of thermodynamic properties of multicomponent systems at high temperatures requires as the reliable experimental data of these systems, as well as the model approaches allowed to describe and to predict their properties. The experimental results on the vapor composition, the partial vapor pressures, the component activities , the chemical potentials and the Gibbs energy are summarized for the $CaO-Al_2O_3-SiO_2$ system and for the samples of multicomponent silicate systems containing FeO, MgO, Na_2O, K_2O, B_2O_3.

2. Experimental procedures

This study has been made by using the MS 1301 mass spectrometer, which is designed to investigate physico-chemical processes occurring during the vaporization of low volatile substances, as well as the MI 1201 mass spectrometer modified for the same aims. Vaporization has been carried out from platinum, molybdenum and tungsten effusion cells. The ratio of the areas of the effusion hole and vaporization was equaled to 1:100,400,500. The selection of the cell material from which the study has been made is accounted for by the physico-chemical characteristics of the system under consideration.The main features of the construction and the use of the different types of evaporators are described in detail in [1]. Partial pressures of components were determined by the ion comparison method (using silver, gold as standards depending on the temperature range) and by the complete isothermal evaporation method using the Hertz-Knudsen equation.

In the mass spectra the ions similar to those in the corresponding binary systems [2] were identified during the evaporation from molybdenum cell. In addition the ions $CaSiO_3^+$,$CaSiO_2^+$, $CaSiO^+$, $CaAlO^+$, $CaAl^+$, $AlSiO^+$ were observed in the mass spectra of vapor over the systems studied. The oxide activities were determined using the Belton-Fruehan equation or by the comparison method. Table 1 illustrates some of the results obtained.

Previously we discussed the application of the semiempirical Kohler method for the calculation of thermodynamic properties of the $Na_2O-B_2O_3-GeO_2$ [3] and of melt of glasses [4] based on the data for the corresponding binary systems.

Table 1 illustrates the agreement between experimental and calculated results obtained by the Kohler method for $CaO-Al_2O_3-SiO_2$ and $CaO-Al_2O-SiO_2-FeO-MgO$ melts. But the Kohler method may be considered only as a simple geometric model without any suggestions on the structure of melt. Compared with this method the Wilson method [5] is based on the concept of local composition and is taken into account the differences of interaction energies between atoms.

Table 1. The Gibbs energies of multicomponent systems studied by high temperature mass spectrometry (1)and calculated by the Kohler (2) and by the Wilson (3) methods.

Composition of the condensed phases studied, mol. fraction	T, K	The Gibbs energies, kcal/mole $-\Delta G$		
		1	2	3
SiO_2:CaO:Al_2O_3				
0.50:0.43:0.07	1933	8.3	8.4	7.4
0.50:0.31:0.19		8.5	8.8	8.4
0.50:0.25:0.25		8.2	8.9	7.9
0.33:0.33:0.33		7.5	9.1	10.6
SiO_2:CaO:MgO				
0.50:0.25:25	1833	10.3	6.2	-
SiO_2:CaO:Al_2O_3:FeO:MgO				
0.36:0.09:0.01:0.05:0.49	1933	8.0	8.3	-

The main feature of this approach is the application of the adjustable parameters for binary systems that it is necessary for calculation of the thermodynamic properties of multicomponent systems .The activity coefficient of the component in multicomponent systems may be calculated according to the following equation:

$$\ln f_i = -\ln(\sum x_i \lambda_{ij}) + 1 - \sum [x_i \lambda_{ki} / (\sum x_i \lambda_{ki} / \sum x_j \lambda_{kj})] \qquad (1)$$

where x_i- mole fraction of the i-component;

$$\lambda_{ij} = (V_j/V_i)\exp(-C_{ij}/RT) \qquad (2)$$

$$C_{ij} = \lambda_{ij} - \lambda_{ii} \qquad (3),$$

λ_{ij}, λ_{ii}-veriables characterized the interactions of the molecular pairs of i-j and i-i; V_i,V_j - the molecular volumes of i,j components. Because the glass-forming melts are the strong accosiated systems we modified equation (2) in the following way for binary systems:

$$\lambda_{ij} = (V_j/V_i) \exp[-(l_{ij} + l_{ijo}x_i)/RT] \qquad (4)$$

and consider the direct dependences of those parameters from the concentration of glassforming oxide. The values of those parameters were calculated for binary systems using the experimental data obtained by high temperature mass spectrometry summarized in [2] and were presented in table 2.

Table 2. The values of the adjustable parameters in equation (4).

Binary system	T, K	kcal/mole			
		l_{12}	l_{120}	l_{21}	l_{210}
Na_2O-SiO_2	1300	62.0	-47.4	-115.1	126.8
K_2O-SiO_2	1300	-64.2	19.7	-110.2	107.7
Na_2O-K_2O	1300	-0.02	0.04	0.17	0.08
B_2O_3-SiO_2	1300	-3.07	9.51	-1.08	-0.79
CaO-Al_2O_3	1900	-17.5	21.1	-23.0	32.1
Al_2O_3-SiO_2	1900	-7.44	26.7	10.4	316.3
CaO-SiO_2	1900	-30.8	47.1	-36.0	55.9

The correlation between the calculated and the experimental data are shown in Tables 3,4 for the Na_2O-K_2O-SiO_2 and Na_2O-B_2O_3-SiO_2 systems.

Table 3.The Gibbs energy of Na_2O-K_2O-SiO_2 melts obtained by high temperature mass spectrometry in [6] - 1 and calculated using the Wilson method - 2.

SiO_2:K_2O:Na_2O, mol.fractions	-ΔG, kcal/mole	
	1	2
0.85:0:0.15	8.4	11.7
0.85:0.10:0.05	10.8	9.6
0.85:0.075:0.075	10.2	9.9
0.85:0.05:0.10	9.5	10.0
0.85:0.15:0	11.6	24.7

Table 4. Chemical potentials of Na_2O in the Na_2O-B_2O_3-SiO_2 system at 1273 K calculated using the Wilson method (a) and (b) obtained in [8].

Mole fractions of Na_2O	Chemical potentials of Na_2O, kcal/mole	
	(a)	(b)
0.44	50.6	56.0
0.33	56.5	60.0
0.24	63.0	65.5
0.16	71.2	73.0
0.09	83.0	80.0

Thus it was shown that using equation (4) we improved the Wilson method for the prediction of the thermodynamic properties of glassforming systems. Accounting for the mole volumes of oxides in the calculations is the advantages of the Wilson method compared with the Kohler method. It was shown that both of them can be utilized for estimations of the Gibbs energy of the silicate systems.

However these methods do not allow to consider the correlation between thermodynamic properties and structure of the condense phase as in the case of application of statistical thermodynamics approaches such as in our previous publications [2,9,10].

We illustrated the application of the general lattice theory of associated solutions for the prediction of the thermodynamic properties of the B_2O_3-GeO_2-SiO_2 and CaO-SiO_2 systems and their correlation with the structure of melts [9,10].

If we take into account the main factors which determined the relative volatility of multicomponent silicate systems, we can describe the equilibria between vapor and condensed phases as a whole. These factors are the following [11].

1. The ratio of the partial pressures of the components over pure oxides (the volatility of the pure oxides).
2. Relative contant of oxides in the condensed phase of the multicomponent system.
3. Tendency to the association of molecular forms of vapor over oxides making up the system, the differeces of electron potentials of elements forming oxides may be one of the criteria of this tendency.
4. Values of partial pressures of oxygen vapor characterizing acid-base properties of oxide melts which are the criterion of their relative volatility making it possible to assess the most probable processes of vaporization of components.

The data obtained by the high temperature mass spectrometry as regards thermodynamic properties of oxide melts, in conjunction with the values of electron potentials of elements forming oxides permitted us to find out the main regularities of their vaporization. They are as follows.

1. With the same oxide modifier one can observe the increase of volatility in a series of silicate, germanate, borate and phosphate melts.
2. Predominent in vapor over germanium and silicate melts are molecular forms which are characteristic of dissociative vaporization of oxides forming the system.
3. In vapor over borate melts containing oxides of alkaline metals, beryllium, lead, bithmuth, barium the formation of gaseous borates is most probable, their polimerization being possible too.
4. In multicomponent borosilicate and borogermanate melts with the higher content of boron oxide than oxides of alkaline metals silica metaborates of alkaline metals are the main molecular forms in vapor.

Thus the additional improvement of the Wilson method allows to describe the thermodynamic properties of multicomponent silicate systems as well as the Kohler method and the acid-base approach do for description the equilibria between melt and vapor.

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