

THERMODYNAMIC MODEL OF CaO–SiO₂ GLASSES

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The CaO–SiO₂ glass forming system is a typical example of a situation when the Shakhmatkin and Vedishcheva thermodynamic model cannot explain the experimentally determined Q-units distribution. As the system components are determined as stable crystalline phases found in the equilibrium phase diagram, the reason of the model failure is the missing system component representing the Q³ structural unit. We suggested a solution to the problem by adding an artificial CaO·2SiO₂ component and we proposed a method of estimating the Gibbs energy of this component. The method is based on the linear relationship found between the reaction Gibbs energy of the formation of the system components representing the different Q_n units (n = 3, 2, 1, 0) divided by the number of non-bridging oxygen atoms in this particular component (i.e., 4-n) on one side and the n value on the other side. The method was qualified by the good coincidence of the model results with the MAS NMR experimentally determined Q-distribution. Moreover, the estimated value of Gibbs energy practically coincides with the optimised value obtained by minimising the sum of the squares of the deviations between the experimental and calculated Q-distribution with respect to the molar Gibbs energy of CaO·2SiO₂.

INTRODUCTION

Mainly, in the field of silicate glasses, the thermodynamic model of Shakhmatkin and Vedishcheva (SVTDM) has been successfully applied for the study of glass structures and properties in the past [1-9]. This model considers the glasses and melts as an ideal solution formed from salt-like products of equilibrium chemical reactions between the simple chemical entities (oxides, halogenides, chalcogenides...) and from the input (un-reacted) entities. These salt-like products (also called associates, groupings or species) have the same stoichiometry as the crystalline compounds, which exist in the equilibrium phase diagram of the considered system. The model does not use any adjustable parameters – only the molar Gibbs energies of the pure crystalline compounds, the thermodynamic temperature, and the composition of the system considered are used as the input parameters. The minimisation of the system's Gibbs energy constrained by the overall system composition has to be performed with respect to the molar amount of each system component to reach the equilibrium system composition [10]. Contemporary databases of thermodynamic properties containing the molar Gibbs energies of various species (like the FACT database [11, 12]) enable the routine construction of the Shakhmatkin and Vedishcheva models for many important multicomponent systems.

On the level of the structural groupings (e.g., Qⁿ units) the silicate glass structure is obtained as a “weighted mixture” of the structures of the system components considered in the SVTDM. However, in some cases, the stable crystalline compound corresponding to the particular structural grouping is missing. In this case, some hypothetical system component is added to the model and the molar Gibbs energy of this component is obtained by minimising the sum of the squares of the deviations between the calculated and experimental glass structure represented by the relative amounts of the different Q units [2]. However, the starting rough estimates of the unknown molar Gibbs energies are needed for such a regression treatment. The typical example is CaO–SiO₂ system, where the representative of the Q³ unit, i.e. the calcium disilicate CaO·2SiO₂ (CS₂), is not present in the equilibrium phase diagram [13]. On the other hand, the significant abundance of the Q³ unit in the CaO–SiO₂ glasses was found by MAS NMR (magic angle spinning nuclear magnetic resonance) and Raman spectroscopy [14, 15]. Schneider et al. [16] cope with this discrepancy between the experimental Q-distribution on one side and the results of the SVTDM on the other side assuming that: “the expected amount of Q⁴ silicon in the glass is organised in the silica-like domains of the molecular size, having Q³ units at their interfaces.” Nevertheless, this explanation, in fact, confirms the existence of Q³ units and it is

probably more advantageous to add some “artificial” component to explain and quantify the Q^3 abundance. Moreover, the assumption of the ideal solution behaviour also contains the regular mixing entropy, i.e., the mixing of the Q-units on the molecular/stoichiometric level. A similar situation can be found for other simple binary glass-forming systems also, e.g., MgO–SiO₂, SrO–SiO₂ [11-13].

THEORETICAL

Method

In the equilibrium phase diagram of the binary CaO–SiO₂ system, the following silicate compounds can be found – SiO₂ (representing the Q^4 unit), 2CaO·SiO₂ (Q^0), 3CaO·2SiO₂ ($2Q^1$), CaO·SiO₂ (Q^2), and 3CaO·SiO₂ (Q^0+O^2). The 3CaO·SiO₂ compound is only stable at higher temperatures, thus, its inclusion into the model is little bit questionable. However, in the studied compositional range, the obtained equilibrium molar amounts of this component were practically negligible. On the other side, 3CaO·SiO₂ can explain some existence of the O^{2-} anions in the glass-forming melts. It can be seen that the representative of the Q^3 structural unit is missing. This unit will be introduced into the thermodynamic model by adding an artificial calcium disilicate component CaO·2SiO₂. It must be emphasised here that, at some extreme conditions (e.g., high pressure), such a compound exists, but its structure is different – it contains octahedrally coordinated silicon, etc. [17]. For the study of the glass structure, the SVTDM is evaluated at the glass transition temperature, T_g , i.e., for the temperature at which the structure of the metastable equilibrium melt is frozen. As far as the equilibrium molar amounts of the system, the components evaluated by SVTDM are not very sensitive with respect to the temperature value we used as some approximate estimate of the temperature of 1000 K. In Table 1, the molar Gibbs energies, G_m , taken from the FACT (Facility for the Analysis of Chemical Thermodynamics) database at 1000 K are summarised for the SVTDM components together with the amount of the different Q^n units represented by the individual

components. For the CS₂ component, the estimated values are reported in Table 1. The reported reaction Gibbs energies, D_rG_m , were calculated from the molar Gibbs energies by:

$$\Delta_rG_m(\alpha\text{CaO}\cdot\beta\text{SiO}_2) = G_m(\alpha\text{CaO}\cdot\beta\text{SiO}_2) - \alpha G_m(\text{CaO}) - \beta G_m(\text{SiO}_2) \quad (1)$$

In the next step, $D_rG_m(\alpha\text{CaO}\cdot b\text{SiO}_2)/NBO$ (where NBO is the number of the non-bridging oxygen atoms – Tab. 1) was plotted versus n for C₃S₂, CS and C₂S (Figure 1). The obtained linear dependence is described by the equation:

$$\frac{\Delta_rG_m}{NBO} / \text{kJ}\cdot\text{mol}^{-1} = -(31.84 \pm 0.14) - (6.25 \pm 0.10)n \quad (2)$$

Using this equation for CaO·2SiO₂ resulted in the reaction Gibbs energy $D_rG_m(\text{CaO}\cdot 2\text{SiO}_2) = -(101.22 \pm 0.89) \text{ kJ}\cdot\text{mol}^{-1}$, and the molar Gibbs energy $G_m(\text{CaO}\cdot 2\text{SiO}_2) = -(2761.18 \pm 0.89) \text{ kJ}\cdot\text{mol}^{-1}$. The obtained linear relationship can be related to the affinity of the formation of the non-bridging oxygen in the Q^n units (Q^n means $\text{SiO}_n\text{O}_{4-n}^{-(4-n)}$). The increasing number of non-bridging oxygen atoms (i.e., $4-n$) is connected to the increasing negative charge and, thus, the affinity

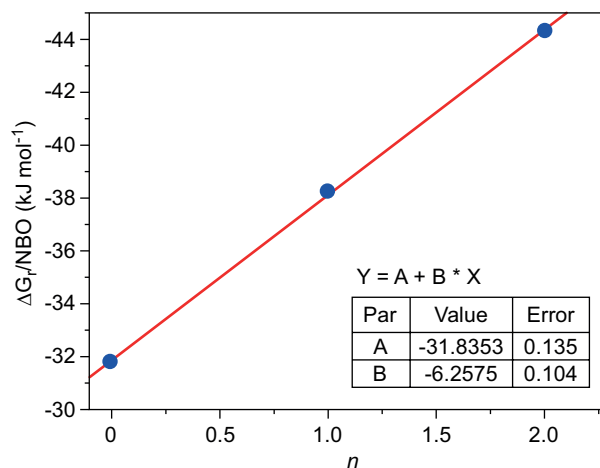


Figure 1. The reaction Gibbs energy of the Q^n formation per the non-bridging oxygen as a function of n .

Table 1. The characteristics of the CaO–SiO₂ SVTDM components (T = 1000 K).

Component	Abbrev.	Q^n	NBO	$-G_m$ (kJ·mol ⁻¹)	Δ_rG_m (kJ·mol ⁻¹)	Δ_rG_m/NBO (kJ·mol ⁻¹)
CaO	–	–	–	697.08	–	–
SiO ₂	–	Q^4	0	981.44	–	–
2CaO·SiO ₂	C ₂ S	Q^0	4	2502.70	127.10	31.775
3CaO·2SiO ₂	C ₃ S ₂	$2Q^1$	6	4283.40	229.28	38.213
CaO·SiO ₂	CS	Q^2	2	1767.10	88.58	44.290
3CaO·SiO ₂	C ₃ S	Q^0	4	3187.40	114.72	28.680
CaO·2SiO ₂	CS ₂	$2Q^3$	2	2761.18*	101.22*	50.608*

* – Estimated values.

of their formation decreases (i.e., the reaction Gibbs energy increases). A similar linear relationship can be obtained, e.g., for the Na₂O–SiO₂ system where all the Qⁿ representatives can be found in the equilibrium phase diagram.

RESULTS AND DISCUSSION

Using the estimated $G_m(\text{CaO} \cdot 2\text{SiO}_2)$ value, the Q-distribution was evaluated by SVTDM. The equilibrium molar amounts of the system components are plotted in Figure 2. It can be seen that the C₃S and CaO abundances are practically negligible within the studied compositional range. The obtained results are close to the experimental MAS NMR data (Figure 3, Table 2) with the standard deviation of the approximation of the relative Q-abundance $s_{\text{appr,est}} = 4.93\%$. In Table 2, some small number of cases can be found with a relatively high difference between the experimental and calculated Qⁿ relative abundance. On the other hand, the experimental values also contain some experimental errors. Schneider et al. [16] reported some examples of MAS NMR data

obtained by different authors for the CaO–SiO₂ glasses where the difference between the relative Q-abundance reaches the level of 10 %.

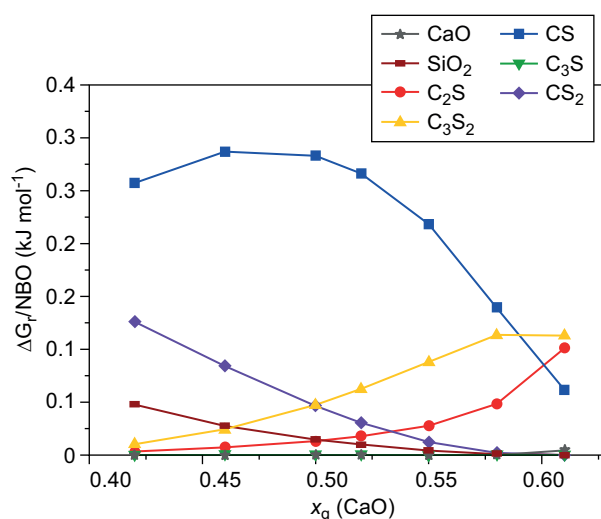


Figure 2. The equilibrium molar amounts of the system components obtained using the the estimated $G_m(\text{CS}_2)$ value.

Table 2. The Q-distribution – experimental (Exp), SVTDM without CS₂ (SV), with the estimated/optimised CS₂ Gibbs energy (Est/Opt).

I	$x_g(\text{CaO})$	Data	Q ⁰ (%)	Q ¹ (%)	Q ² (%)	Q ³ (%)	Q ⁴ (%)
1	0.42	Exp	0.00	5.00	36.50	50.20	8.30
		SV	0.38	2.67	67.64	0.00	29.31
		Est	0.58	3.46	44.33	43.43	8.20
		Opt	0.60	3.56	43.45	44.81	7.57
2	0.46	Exp	0.00	6.10	52.50	34.20	7.20
		SV	0.74	5.85	74.93	0.00	18.49
		Est	1.34	9.15	53.15	31.24	5.13
		Opt	1.39	9.39	52.14	32.32	4.76
3	0.50	Exp	0.00	16.60	64.40	19.00	0.00
		SV	1.64	13.78	76.03	0.00	8.55
		Est	2.66	19.11	56.64	18.67	2.92
		Opt	2.74	19.43	55.59	19.50	2.74
4	0.52	Exp	0.00	29.60	60.40	10.00	0.00
		SV	2.57	21.12	71.49	0.00	4.83
		Est	3.68	26.04	55.48	12.77	2.03
		Opt	3.76	26.33	54.53	13.46	1.92
5	0.55	Exp	0.00	48.20	46.00	5.80	0.00
		SV	5.19	36.90	56.43	0.00	1.49
		Est	6.12	39.18	48.47	5.30	0.93
		Opt	6.20	39.35	47.86	5.70	0.90
6	0.58	Exp	15.10	65.30	19.60	0.00	0.00
		SV	11.11	54.02	34.61	0.00	0.26
		Est	11.52	54.08	33.20	0.97	0.23
		Opt	11.56	54.09	33.05	1.08	0.23
7	0.61	Exp	20.10	65.80	14.10	0.00	0.00
		SV	26.07	58.22	15.69	0.00	0.02
		Est	26.11	58.17	15.65	0.05	0.02
		Opt	26.12	58.16	15.65	0.05	0.02

In the next step, the estimated value of $G_m(\text{CaO}\cdot 2\text{SiO}_2)$ was optimised by minimising the sum of the squares of the deviations between the experimental and calculated relative amounts of the Q-units:

$$S[G_m(\text{CaO}\cdot 2\text{SiO}_2)] = \sum_{i=1}^M \sum_{j=0}^4 (Q_{i,clc}^j - Q_{i,exp}^j)^2 = \min. \quad (3)$$

where $M = 7$ (the number of the glass compositions) and $Q_{i,clc/exp}^j$ is the calculated/experimental relative amount of the Q^j structural unit in the i -th glass. In such a way, the optimised value of $G_m(\text{CaO}\cdot 2\text{SiO}_2) = -2762.20 \text{ kJ}\cdot\text{mol}^{-1}$ was obtained. This value coincides with the estimated value 2761.18 within its standard deviation (0.89). The standard deviation of the approximation obtained for the optimised $G_m(\text{CaO}\cdot 2\text{SiO}_2)$ value, $s_{\text{apr,opt}} = 4.90 \%$, is practically identical with the value obtained for the estimated G_m value.

The Q-distributions (i.e., the ^{29}Si MAS NMR experimental [14], the SVTDM obtained without the CS_2 component, and obtained with the CS_2 component using the estimated/optimised molar Gibbs energy of CS_2) are summarised in Table 2. In Figure 3, only the

Q^2 and Q^3 distributions are graphically compared. It can be concluded that the results obtained with the estimated and optimised $G_m(\text{CS}_2)$ values are practically identical. This can be considered as some validation of the method proposed for estimating the molar Gibbs energies. Therefore, it can be concluded that the proposed method gives the G_m estimate of high quality. Nevertheless, further study of the application of the proposed method to other glass forming systems is needed.

CONCLUSION

The proposed method of estimating the molar Gibbs energy of the artificial components added to the SVTDM model in the case when some Q-structural unit is not found in the equilibrium phase diagram was validated by the comparison with the results obtained by minimising the sum of the squares of the deviations between the calculated and experimental Q-distribution. In the future, more extensive testing of the proposed method is needed in the systems where the same problem, i.e., the missing Q-unit representative, was found. On the other hand, it can be suggested that the successful application of the proposed method is based on the fact that the main contribution to the molar Gibbs energy comes from the bond energy of the silicon with bridging and non-bridging oxygen atoms, while the entropic contribution connected to the structure/symmetry of the different groupings is not as substantial.

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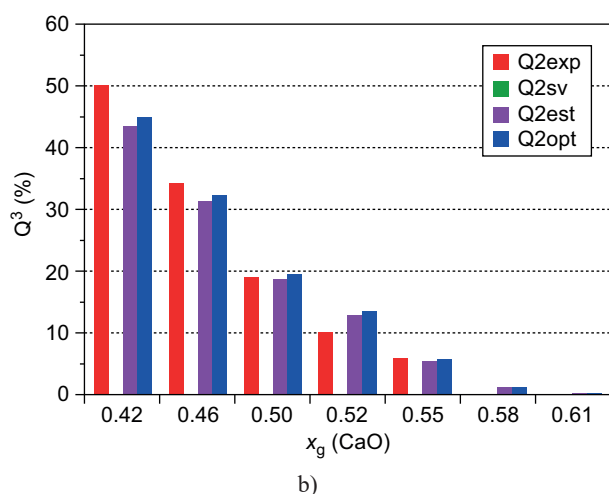
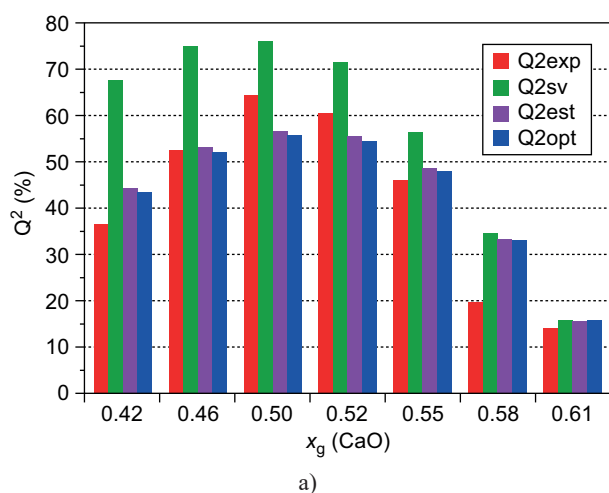


Figure 3. The Q^2 & Q^3 distribution - from the left: experimental (exp), without CS_2 (sv), G_m estimated (est), G_m optimised (opt).

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