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Molecular dynamics simulation of binary CaO–FeO, MgO–SiO_2, FeO–SiO_2, CaO–SiO_2 and ternary CaO–FeO–SiO_2 systems

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Abstract

Molecular dynamics models of binary CaO–FeO, MgO–SiO_2, FeO–SiO_2, CaO–SiO_2 and ternary CaO–FeO–SiO_2 systems were constructed at 1873 K using the Born–Mayer pair potentials. The potentials included the effective dipole–dipole interactions for Ca–Fe, Mg–Si, Fe–Si and Ca–Si pairs. Parameters of the dipole–dipole interactions were found by adjusting calculated Gibbs free energies of formation of binary CaO–FeO, FeO–SiO_2, MgO–SiO_2 and CaO–SiO_2 systems to experimental data.

The thermodynamic properties of CaO–FeO–SiO_2 solutions were studied by converting several iron ions into calcium ions. The Gibbs free energy increments and ratios of activity coefficients $\gamma_{CaO}/\gamma_{FeO}$ in the ternary system were calculated. Published by Elsevier Science B.V.

Keywords: Molecular dynamics; Simulation; Oxides; Ionic bonds; Born-Mayer potential; Dipole-dipole interaction; Thermodynamic properties

1. Introduction

These days, quasi-chemical, cell, and some other models in the slag chemistry incorporated into thermochemical packages, such as FACT, Thermo-Calc, and others, equipped with extensive databases provide an excellent tool for calculation of thermodynamic properties of binary and multi-component oxide systems. Success of these models in calculation of thermodynamic properties and phase diagrams is to a large extent based on the use of assessed thermodynamic parameters. Computer simulation methods, such as molecular dynamics or Monte Carlo simulation, lie in different weight category: agreement of calculated internal energy or the Gibbs free energy with experimental data within 0.1% of absolute value would be a success, and this means a discrepancy in a few kilojoules. Nevertheless, molecular dynamics and Monte Carlo methods are more universal providing structural and dynamic characteristics of molten oxides, which are so difficult to determine experimentally. More accurate thermodynamic data are expected to obtaine using "semi-empirical" molecular dynamics or Monte Carlo method. In this paper, molecular dynamics (MD) simulation of a ternary system is tested with parameters for the inter-ionic potential adjusted using experimental thermodynamic data for boundary binary systems. Particular, thermodynamic properties of the ternary CaO–FeO–SiO_2 system are calculated by the MD method with parameters

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of the Born–Mayer potentials, determined using thermodynamic data for binary CaO–FeO, FeO–SiO_2 and CaO–SiO_2 systems.

Oxide solutions in the MD simulation are considered in the approximation of pure ionic bonds, although chemical bonds in these systems have more complex ion-covalent nature. However, consideration of covalent bonds demands new simulation techniques like ab initio calculations, which combine the molecular dynamics with quantum mechanics. Up to now these methods are very time-expensive and have been applied to systems with a small number of atoms.

Computer calculations of thermodynamic properties of MeO and MeO_2 type solutes in the CaO–SiO_2 system were conducted in works [1,2] using the simple Born–Mayer pair potential, $u_{ij}(r)$, which includes Coulomb interaction between ions i and j, and core repulsion

$$u_{ij}(r) = Z_iZ_je^2/r + B_{ij}\exp(-r/R_{ij})$$

where r is the distance between ions, Z_i the ionic charge in the units of elemental charge e, B_{ij} and R_{ij} the repulsion parameters for ionic cores of pair i–j. Practically, only metallic cation–oxygen anion interactions were accounted. Parameter R_{ij} was assumed to be 29 nm for all ionic pairs. Parameters B_{ij} were determined for individual oxides using experimental structural data, and were assumed to be independent on the solution composition. Qualitatively, calculations correctly predicted the change in thermodynamic activity coefficients of MeO oxides in the CaO–SiO_2 solutions, however, quantitative agreement had not been achieved.

Results of the molecular dynamics simulation strongly depend on the parameters of the inter-ionic interactions. It could be expected that parameters of the inter-ionic potential depend on the solution composition. In this work more sophisticated Born–Mayer potential is used (Eq. (1)). It includes effective dipole–dipole interaction, which is considered to be dependent on the solution composition. The dipole–dipole interaction is introduced only as an effective interaction between cations to take into account the change in a potential with composition of the oxide system. The use of the Born–Mayer potential with dipole–dipole interaction for the CaO–FeO system gave reasonable agreement between calculated and experimental activity coefficients of FeO and CaO even at a constant interaction coefficient [3]. It will be briefly reviewed in Section 4.

In this paper, this approach is applied to calculation of thermodynamic properties of binary CaO–FeO, MgO–SiO_2, FeO–SiO_2, CaO–SiO_2 and ternary CaO–FeO–SiO_2 oxide systems.

2. Interionic potential

Interactions between ions were described by the Born–Mayer potentials

$$u_{ij}(r) = Z_iZ_je^2/r + B_{ij}\exp(-r/R_{ij}) + C_{ij}/r^6 + D_{ij}/r^8 \tag{1}$$

where C_{ij}/r^6 and D_{ij}/r^8 describe effective dipole–dipole and dipole–quadruple interactions, respectively. Coefficients C_{ij} and D_{ij} must be negative. Dipole–dipole interaction is small in comparison with the energy of ionic cores repulsion. Dipole–quadruple interaction is 5–10% of dipole–dipole interaction [4,5]. In previous works [1,2], dipole–dipole and dipole–quadruple interactions were omitted. The difference in the potential parameters for different oxides was accounted only by the repulsion parameters B_{ij}. This means that for MeO or MeO_2 oxides only the size of Me^{2+} or Me^{4+} ions was different. This is an obvious simplification. Direct chemical interaction between components of a solution is introduced here through dipole–dipole potential. Dipole–quadruple interaction in the following calculations is neglected.

3. Molecular dynamics calculation of the Gibbs free energy of an oxide solution

Initialization procedure and sensitivity analysis are presented elsewhere [1,3,6–8]. The first stage included construction of MD models of pure MeO oxides in the NpT — ensemble. These models consisted of 492 ions in a basic cube (246 ions of Me^{2+} and 246 ions of O^{2-}). Coulomb interaction was considered in the Evald–Hansen approximation [2]. The particle trajectories were calculated using Verlet algorithm. It takes usually few thousand time-steps to reach equilibrium. The amplitude of pressure fluctuations is about ±0.5 GPa but the mean pressure was rather small, less than 0.1 GPa. The mean molar volume of the system is calculated with an error of 2–3%.

Thermodynamic calculations for binary oxide systems with a simple Born–Mayer potential are described in works [1,2]. Similar calculation procedure is employed with the use of the potential (1). As an example, let us consider the MD simulation and calculation of thermodynamic properties for CaO–FeO oxides at 1873 K. Molecular dynamics models consisted of 492 ions in the basic cube with periodical boundary conditions. MD simulation started with simulation of the CaO–FeO system of a given composition. Then, some of Fe^{2+} ions were transformed into Ca^{2+} ions changing interaction parameters of the potential (1), and the equivalent amount of pure non-crystalline CaO was transformed into pure FeO. Such a process reflects the replacement of solute FeO in a binary CaO–FeO system by CaO with reference to pure non-crystalline oxides as standard states. It can be presented as a sum of two reactions: (FeO) → FeO and CaO → (CaO).

The change ΔG in the Gibbs free energy of the binary solution as a result of transformation of 1 mol of dissolved FeO into 1 mol of CaO can be described by the expression

$$\Delta G = \Delta G_{\mathrm{p}} + RT\ln\left(\frac{\gamma_{\mathrm{CaO}}}{\gamma_{\mathrm{FeO}}}\right)$$

or

$$\Delta G_{\mathrm{s}} = \Delta G - \Delta G_{\mathrm{p}} = RT\ln\left(\frac{\gamma_{\mathrm{CaO}}}{\gamma_{\mathrm{FeO}}}\right) \tag{2}$$

where $\Delta G_{\mathrm{p}} = G^0_{\mathrm{CaO}} - G^0_{\mathrm{FeO}}$ is the difference in molar Gibbs free energies of pure non-crystalline CaO and FeO; γ_{CaO} and γ_{FeO} are activity coefficients of CaO and FeO in the CaO–FeO solution.

In the MD simulation with potential (1), the transformation of dissolved FeO into CaO is implemented by the change of interaction parameters using the following formulas:

$$B_{ij} = B^0_{ij} + \lambda(B^{\mathrm{f}}_{ij} - B^0_{ij}) \qquad \text{and}$$
$$C_{ij} = C^0_{ij} + \lambda(C^{\mathrm{f}}_{ij} - C^0_{ij}) \tag{3}$$

where parameter λ varied from 0 to 1. At $\lambda = 0$, parameters B_{ij} and C_{ij} describe interactions of Fe^{2+} ions with other ions in the solution of a given composition, they are equal to initial B^0_{ij} and C^0_{ij} values. At $\lambda = 1$, parameters B_{ij} and C_{ij} describe interactions of Ca^{2+} ions, they are equal to the final B^{f}_{ij} and C^{f}_{ij} values. In the process of the variation of λ from 0 to 1, selected number of dissolved Fe^{2+} ions are transformed into Ca^{2+} ions.

The potential energy of the system can be presented as

$$U = U_0(r_1, \ldots, r_N) + \lambda U_1(r_1, r_2, \ldots, r_N) \tag{4}$$

where r_1, r_2,…, r_N are the ions coordinates, and λ the varied parameter. Then, the change in the Gibbs free energy of the system as a result of the isobaric–isothermal transfer of the system from the state with a parameter λ_1 to the state with a parameter λ_2 is described by the following expression [6,8]:

$$\Delta G = G(\lambda_2) - G(\lambda_2) = \int_{\lambda_1}^{\lambda_2}\left\langle\frac{\mathrm{d}U}{\mathrm{d}\lambda}\right\rangle\mathrm{d}\lambda = \int_{\lambda_1}^{\lambda_2}\langle U_1\rangle\mathrm{d}\lambda \tag{5}$$

for λ_1 and λ_2 not equal to zero, ΔG can be calculated by the equation

$$\Delta G = G(\lambda_2) - G(\lambda_1) = \int_{\lambda_1}^{\lambda_2}\langle\lambda U_1\rangle\mathrm{d}\ln\lambda \tag{6}$$

where $\langle\lambda U_1\rangle$ is the mean value of the energy term due to ionic core repulsion plus dipole–dipole interaction, which can be calculated in molecular dynamics "experiment". The derivative $\mathrm{d}U/\mathrm{d}\lambda$ for the pair potential (1) is equal to [3]

$$\frac{\mathrm{d}U}{\mathrm{d}\lambda} = \sum\frac{B^{\mathrm{f}}_{ij} - B^0_{ij}}{B_{ij}(\lambda)}U_{\mathrm{rep}}(ij) + \sum\frac{C^{\mathrm{f}}_{ij} - C^0_{ij}}{C_{ij}(\lambda)}U_{\mathrm{dd}}(ij) \tag{7}$$

where U_{rep} and U_{dd} are the mean values of energy terms due to ion cores repulsion and dipole–dipole interaction. The integration in (5) and (6) must be conducted along the isobaric–isothermal path, where the B_{ij} and C_{ij} values vary in a consistent way.

When only parameters C_{ij} are changing, the Gibbs free energy increments are calculated by the formula

$$\Delta G = G(C_2) - G(C_1) = \sum\int_{C_1}^{C_2}\frac{U_{\mathrm{dd}}(ij)}{C_{ij}(\lambda)}\mathrm{d}C_{ij} \tag{8}$$

where $U_{\mathrm{dd}}(ij)$ is the dipole–dipole interaction energy at the given C_{ij} value.

4. The CaO–FeO system

The MD simulation of the CaO–FeO system was considered in work [3]. The reasonable agreement of calculated ratio of activity coefficients $\gamma_{CaO}/\gamma_{FeO}$ with experimental data [9,10] at 1873 K was obtained using the following parameters of the Born–Mayer potentials (1): $B_{Ca-Ca} = B_{Ca-Fe} = 0$; $B_{Ca-O} = 3283$ eV, $B_{Fe-O} = 1900$ eV, $B_{O-O} = 1500$ eV, $R_{ij} = 29$ pm for all ion pairs, $C^*_{Ca-Fe} = -43.3$ eV Å^6 $C_{Ca-Ca} = C_{Fe-Fe} = C_{Ca-O} = C_{Fe-O} = C_{O-O} = 0$. Parameter C designated as C^* was used to adjust calculated excess Gibbs free energy to experimental values. These parameters were independent of the binary solution composition. They will also be assumed to be constant for the ternary CaO–FeO–SiO$_2$ system.

The Gibbs free energy increment ΔG_p for the reaction of transformation of pure liquid FeO into non-crystalline CaO at 1873 K and zero pressure, calculated using Eq. (6) was found to be 283.6 kJ/mol. Previously the value $\Delta G_p = 282.4$ kJ/mol was obtained at 2000 K for models with 216 ions [6]. The agreement with a present work is rather good.

It should be noted that the transformation of iron ions to calcium ions and other transformations of ions were conducted at a constant ion mass (mass of the calcium cation was assumed to be equal to the mass of the iron cation). This means that only configuration term in ΔG is calculated. This fact has no effect on the calculated activity coefficients.

5. The MgO–SiO$_2$ system

Experimental data for the MgO–SiO$_2$ system at 1873 K taken from work [11] are shown in Table 1. In this table, ΔG_f is the Gibbs free energy of formation of solution from pure liquid FeO and SiO$_2$. The system shows negative deviations from ideality.

Parameters B_{ij} and R_{ij} of the potential (1) were taken from work [1,2,6]. They are as follows: $B_{Mg-Mg} = B_{Mg-Si} = 0$; $B_{Si-Si} = 2055.4$ eV; $B_{Mg-O} = 1441.4$ eV, $B_{Si-O} = 1729.5$ eV, $B_{O-O} = 1500$ eV; and $R_{ij} = 29$ pm for all ion pairs.

Then the parameter C_{Mg-Si} was introduced. The Gibbs free energies of formation of MgO–SiO$_2$ binary solutions were calculated for three cases:

1. The parameter C_{Mg-Si} was zero. In this case, calculated values depart from experimental data by 0.2–50% depending on composition.
2. Parameter C_{Mg-Si} was equal to C^{id}_{Mg-Si}. At these values of C_{Mg-Si}, solutions have zero formation energy $\Delta E_f = 0$.
3. Parameter C_{Mg-Si} was equal to C^*_{Mg-Si}, at which the ΔG_f values are equal to experimental data at 1873 K.

Parameters C^{id}_{Mg-Si} and C^*_{Mg-Si} are given in Table 1. Calculated C^{id}_{Mg-Si} values and some adjusted C^*_{Mg-Si} parameters are positive, although in reality dipole–dipole interaction energy has a negative sign. In this sense, the dipole–dipole interaction in the Born–Mayer inter-ionic potential is the effective interaction, introduced to manipulate with calculated thermodynamic properties of oxide solutions.

The C^*_{Mg-Si} parameter as a function of composition of MgO–SiO$_2$ solutions can be presented as a linear function

$$C^*_{Mg-Si} = 152.9 - 247.3(1 - X_{SiO_2}) \tag{9}$$

This provides a reasonable agreement with experimental data on the Gibbs free energies of solution formation at 1873 K.

Results of MD calculation of thermodynamic properties of magnesium silicates are given in Table 2. The term $T\,\Delta S^{ex}$ (ΔS^{ex} is the excess entropy of formation of the MgO–SiO$_2$ solution) is very

Table 1
Properties of MgO–SiO$_2$ silicates

Silicate	ΔG_f (kJ/mol) experiment [11]	ΔG_f (kJ/mol) at $C_{Mg-Si} = 0$	C^{id}_{Mg-Si}, (eV Å^6)	C^*_{Mg-Si}, (eV Å^6)
4MgO·SiO$_2$	−30.8	−22.9	105.9	−54.9
2MgO·SiO$_2$	−36.8	−36.3	147.2	−2.8
MgO·SiO$_2$	−30.1	−37.2	152.4	38.9
MgO·2SiO$_2$	−18.4	−27.0	128.5	61.8

Table 2
Calculated thermodynamic properties of $MgO–SiO_2$ silicates[a]

Silicate	V/N (cm^3/g-ion)		ΔG_f^{ex} (kJ/mol)	ΔE_f (kJ/mol)	$T\,\Delta S^{ex}$ (kJ/mol)
	$C_{Mg-Si} = C_{Mg-Si}^{id}$	$C_{Mg-Si} = C_{Mg-Si}^{*}$			
$4MgO{\cdot}SiO_2$	9.27	9.13	−23.0	−20.0	3.0
$2MgO{\cdot}SiO_2$	8.96	8.40	−26.9	−22.8	4.1
$MgO{\cdot}SiO_2$	9.76	9.40	−19.3	−20.2	−0.9
$MgO{\cdot}2SiO_2$	9.91	9.49	−8.5	−11.7	−3.2

[a] Excess Gibbs free energy, internal energy and excess entropy of formation are calculated at $C_{Mg-Si} = C_{Mg-Si}^{*}$ (experimental data are taken from work [11]). The volumes of solutions are calculated at $C_{Mg-Si} = C_{Mg-Si}^{*}$ and $C_{Mg-Si} = C_{Mg-Si}^{id}$ when $\Delta E_f = 0$.

small relatively to ΔE_f, what means that a model of the $MgO–SiO_2$ binary system is close to regular solution.

Behavior of real molten $MgO–SiO_2$ solutions deviates from the model of the regular solution. This is indicated by the miscibility gap in the liquid state of the $MgO–SiO_2$ system [9]. Regular solutions have a miscibility gap only when the enthalpy of their formation is positive. The enthalpy of formation of $MgO–SiO_2$ liquid solutions is negative, this means that at least in the area of the miscibility gap, solutions have negative excess entropy. Miscibility gaps can be seen in phase diagrams of other $MeO–SiO_2$ systems. It is quite possible that the excess entropy of these solutions is due to structural changes in silica caused by the addition of a basic MeO oxide. The excess entropy of $MeO–SiO_2$ solutions is not expected to depend strongly on the Me^{2+} size, or in other words, the excess entropy of different oxides will be approximately the same at given concentration. This means that the ion transformation (like $Fe^{2+} \rightarrow Ca^{2+}$) in the computer experiment does not affect the entropy of the solution. Moreover, the entropy term in the excess Gibbs free energy is small relatively the enthalpy. This can be seen from experimental data for crystalline silicates (data for liquid oxides are limited and scattered). For example, standard formation enthalpy of $2FeO{\cdot}SiO_2$ is equal to −29.4 kJ/mol and standard formation entropy of this oxide is −4.83 J/mol K [12]. Therefore, the entropy contribution to the Gibbs free energy $-T\,\Delta S$, is equal to 1.44 kJ/mol what is less than 1/20 of the formation enthalpy. The entropy of formation of iron orthosilicate is well below the value of 16.32 J/mol K predicted by the regular solution model.

6. The $FeO–SiO_2$ system

At 1873 K, the $FeO–SiO_2$ binary solutions are liquid in the range of $X_{FeO} \geq 0.48$. Thermodynamic properties of molten $FeO–SiO_2$ alloys were measured in work [13]. The Gibbs free energy of formation of the $FeO–SiO_2$ solutions from works [13,14] and calculated excess Gibbs free energy of formation are given below

$$\begin{array}{lcccc} X_{FeO} & 0.9 & 0.9 & 0.667 & 0.5 \\ \dfrac{\Delta G_f}{RT} & -0.41 & -0.50 & -0.60 & -0.49 \\ \Delta G_f^{ex}\ (\mathrm{kJ/mol}) & -1.35 & 0 & 0.56 & 3.20 \end{array} \tag{10}$$

In calculation of the excess Gibbs free energy, $\Delta G_f/RT$ for the $FeO–SiO_2$ solutions was assumed to be independent of temperature. Then, the excess Gibbs free energy was calculated as $\Delta G^{ex} = \Delta G - RT(X_{FeO}\ln X_{FeO} + X_{SiO_2}\ln X_{SiO_2})$. The $FeO–SiO_2$ system is close to the ideal solution.

Numbers of iron, silicon and oxygen ions in molecular dynamics models of ferrous silicates are shown in Table 3.

Table 3
Number of ions in $FeO–SiO_2$ models

Mole fraction of FeO	Number of ions			
	Fe	Si	O	Total
0.9	207	23	253	483
0.8	180	45	270	495
0.667	142	71	284	497
0.5	100	100	300	500

Table 4
Simulation of FeO–SiO$_2$ solutions at 1873 K and zero pressure[a]

X_{FeO}	L (nm)	V/N (cm^3/g-ion)	E (kJ/g-ion)	E^{id} (kJ/g-ion)	ΔE_{f} (kJ/g-ion)	$C^{\mathrm{id}}_{\mathrm{Fe-Si}}$ (eV Å^6)	$C^{*}_{\mathrm{Fe-Si}}$ (eV Å^6)	$\Delta E^{*}_{\mathrm{f}}$, (kJ/g-ion)	$(\Delta G^{*}_{\mathrm{f}})^{\mathrm{ex}}$, (kJ/g-ion)	$(T\,\Delta S^{*}_{\mathrm{ex}})^{\mathrm{ex}}$, (kJ/g-ion)
1.0	1.8960	8.34	−1830.30	−1830.30	–	–	–	–	–	–
0.9	1.9059	8.42	−2168.28	−2159.70	−18.0	262	241	−1.39	−1.35	−0.04
0.8	1.9060	8.94	−2473.54	−2459.16	−31.6	239	239	0.00	0.00	0.00
0.667	1.9468	9.10	−2835.03	−2818.50	−38.6	248	252	0.58	0.56	0.02
0.5	1.9620	9.28	−3230.80	−3213.78	−42.5	275	258	−2.73	−2.58	−0.15
0.0	1.9549	9.03	−4136.11	−4136.11	–	–	–	–	–	–

[a] Data on L, V/N, E and ΔE_{f} are calculated at $C_{\mathrm{Fe-Si}} = 0$; E^{id} is the internal energy of the ideal solution calculated at $C_{\mathrm{Fe-Si}} = C^{\mathrm{id}}_{\mathrm{Fe-Si}}$ when $G^{\mathrm{ex}}_{\mathrm{f}} = 0$.

Calculations were conducted in the same way as for the MgO–SiO$_2$ system. B_{ij} parameters of potential (1) were taken from [1,2,6]: $B_{\mathrm{Fe-Fe}} = B_{\mathrm{Fe-Si}} = 0$, $B_{\mathrm{Si-Si}} = 2055.4\,\mathrm{eV}$, $B_{\mathrm{Fe-O}} = 1900\,\mathrm{eV}$, $B_{\mathrm{Si-O}} = 1729.5\,\mathrm{eV}$, $B_{\mathrm{O-O}} = 1500\,\mathrm{eV}$. At the first stage, all C_{ij} parameters were assumed to be 0. Calculated internal energies of formation for the FeO–SiO$_2$ solutions, ΔE_{f} are shown in Table 4.

Then for each solution the parameter $C_{\mathrm{Fe-Si}} = C^{\mathrm{id}}_{\mathrm{Fe-Si}}$ was found, at which $\Delta E_{\mathrm{f}} = 0$ (Table 4). This solution can be considered as an ideal solution. For such a solution $\Delta G^{\mathrm{id}}_{\mathrm{f}} = RT\ \ (X_{\mathrm{FeO}} \ln X_{\mathrm{FeO}} + X_{\mathrm{SiO_2}} \ln X_{\mathrm{SiO_2}})$ and the excess Gibbs free energy is 0.

Finally, $C_{\mathrm{Fe-Si}}$ was changed from $C^{\mathrm{id}}_{\mathrm{Fe-Si}}$ to $C^{*}_{\mathrm{Fe-Si}}$ at which Gibbs free energy increment (the excess Gibbs free energy) calculated by Eq. (8) is equal to the experimental value $\Delta \mathrm{G}^{\mathrm{ex}}$. An example of such calculation for the FeO–SiO$_2$ solution with $X_{\mathrm{FeO}} = 0.9$ is shown in Table 5.

Dipole–dipole interaction between iron and silicon ions (the fifth column of Table 5) as a function of $C_{\mathrm{Fe-Si}}$ parameter can be approximated by the following relationship (the last column of Table 5):

$$\frac{U_{\mathrm{dd}}(\mathrm{Fe{-}Si})}{C_{\mathrm{Fe-Si}}} = (0.0351-1.1718) \times 10^{-5} C_{\mathrm{Fe-Si}}$$

Thus, the excess Gibbs free energy of formation of the FeO–SiO$_2$ oxide with $X_{\mathrm{FeO}} = 0.9$ can be presented as

$$\Delta G^{\mathrm{ex}}_{\mathrm{f}} = -1.35 = 2.1 \int_{262}^{C^{*}} (0.0351 - 1.718 \times 10^{-5} C)\,\mathrm{d}C$$

In this equation, $\Delta G^{\mathrm{ex}}_{\mathrm{f}} = -1.35$ is the experimental value of $\Delta G^{\mathrm{ex}}_{\mathrm{f}}$ taken from (10), and the coefficient 2.1 is the number of gram-ions in 1 mol of $(\mathrm{FeO})_{0.9}$-$(\mathrm{SiO_2})_{0.1}$ oxide. Solving this equation we find that $C^{*}_{\mathrm{Fe-Si}} = 241\ \mathrm{eV\,Å^6}$. This value is shown in Table 4. Other $C^{*}_{\mathrm{Fe-Si}}$ values in Table 4 were calculated in a similar way.

The following conclusions can be drawn from results of the MD calculation for FeO–SiO$_2$ solutions with $X_{\mathrm{FeO}} \geq 0.5$ (Table 4):

1. solutions have strong negative deviations from ideality when $C_{\mathrm{Fe-Si}} = 0$;
2. the excess Gibbs free energy of formation of FeO–SiO$_2$ solutions is around zero (the ideal solution) at $C^{\mathrm{id}}_{\mathrm{Fe-Si}}$ value in the interval of 239–275 eV Å^6;
3. $C^{*}_{\mathrm{Fe-Si}}$ values vary in the narrow range from 239 to 258 eV Å^6;
4. the excess entropy term $T\,\Delta S^{\mathrm{ex}}_{\mathrm{f}}$ calculated from $\Delta G^{\mathrm{ex}}_{\mathrm{f}} = \Delta E_{\mathrm{f}} - T\,\Delta S^{\mathrm{ex}}_{\mathrm{f}}$ is very small and can be neglected in comparison with the formation

Table 5
Simulation of the FeO–SiO$_2$ solution with $X_{FeO} = 0.9$ with different $C_{\mathrm{Fe-Si}}$ parameters at 1873 K

$C_{\mathrm{Fe-Si}}$ (eV Å^6)	L (nm)[a]	p (MPa)	E (kJ/g-ion)	U_{dd} (Fe–Si) (kJ/g-ion)	U_{dd} (Fe–Si)/$C_{\mathrm{Fe-Si}}$
0	1.9059	88.6	−2168.28	–	–
100	1.9209	−11.6	−2164.74	3.30	0.0335
200	1.9299	−6.9	−2161.58	6.33	0.0316
300	1.9356	20.2	−2158.43	8.98	0.0299

[a] Where L is the length of the basic cube edge.

energy. This means that a model with zero formation energy can be considered as an ideal solution. Therefore, excess Gibbs free energy of simulated molten ferrous silicates can be calculated using only the formation energy of a system, and its excess formation entropy may be neglected;

5. the $C^*_{\mathrm{Fe-Si}}$ parameter for ferrous silicates as a function of concentration may be approximated by the equation

$$C^*_{\mathrm{Fe-Si}} = 390.6 - 195.1(1 - X_{\mathrm{SiO_2}}) \qquad (11)$$

7. The CaO–SiO$_2$ system

At 1873 K, the homogeneous liquid CaO–SiO$_2$ solution stretches between 40 and 67 mol% SiO$_2$. Thermodynamic properties of this system are discussed in [9–18]. The Gibbs free energies of formation of molten mono and disilicates measured in [15,16,19] (see [11]) are shown in Table 6. This table also includes the ΔG_f data for the CaO·2SiO$_2$, CaO·SiO$_2$, 2CaO·SiO$_2$ and 4CaO·SiO$_2$ compounds assessed in [18] from the phase diagram. The deviations from ideality for this system are more negative than for magnesium silicates.

Table 6
Experimental data on the Gibbs free energy of formation of calcium silicates

Oxide	ΔG_f (kJ/mol)		
	[15]	[11,16,19]	[18]
4CaO·SiO$_2$	–	–	−42.8
2CaO·SiO$_2$	–	–	−65.8
CaO·SiO$_2$	−58.4	−41.7	−58.9
CaO·2SiO$_2$	−42.1	−30.0	−41.1

Like above, deviations from ideality will be accounted for by the effective dipole–dipole interaction of Ca–Si ions.

Molecular dynamics models for the CaO–SiO$_2$ system were initiated by converting MgO–SiO$_2$ models to the CaO–SiO models. The MgO–SiO$_2$ models constructed with $C_{\mathrm{Mg-Si}} = 0$ were transformed into the CaO–SiO$_2$ models changing the parameter $B_{\mathrm{Me-O}}$ from 1441.4 to 3283.0 eV. As a result, the CaO–SiO$_2$ models were obtained with $C_{\mathrm{Mg-Si}} = 0$.

As an example, the change in properties of the system in the process of transformation of 4MgO·SiO$_2$ compound to 4CaO·SiO$_2$ is shown in Table 7. It can be noticed that the entropy terms $T\,\delta S_\lambda$ are very small in comparison with the energy increments δE_λ. The repulsive energy between Me^{2+} and O^{2-} decreases and Gibbs free energy increment grows with increasing $B_{\mathrm{Me-O}}$.

The molar Gibbs free energy of formation of mCaO·nSiO$_2$ oxides was calculated as

$$\Delta G_f(m\mathrm{CaO}\cdot n\mathrm{SiO_2}) = \Delta G_f(\mathrm{MgO}\cdot n\mathrm{SiO_2})\{(2m+3n) + \delta G\lambda(m\mathrm{MeO}\cdot n\mathrm{SiO_2}2m\,\delta G\lambda(\mathrm{MeO}))\}/(m+n)$$

In this equation, $\delta G_\lambda(m\mathrm{MeO}\cdot n\mathrm{SiO_2})$ is the Gibbs free energy increment for transformation of 1 g-ion mMgO·nSiO$_2$ into 1 g-ion mCaO·nSiO$_2$, and δG_λ(MeO) is the Gibbs free energy increment for transformation of 1 g-ion MgO into 1 g-ion CaO. The internal energy of formation of calcium silicates was calculated in a similar way. The data obtained for the CaO–SiO$_2$ system at $C_{\mathrm{Ca-Si}} = 0$ are given in Table 7. In fact, only calcium mono- and disilicate are liquid at 1873 K. The 2CaO·SiO$_2$ and 4CaO·SiO$_2$ compounds at 1873 K are considered as super-cooled liquids.

Table 7
Computer transformation of the 4MgO·SiO$_2$ model into the 4CaO·SiO$_2$ model at 1873 K ($C_{\mathrm{Me-Si}} = 0$)

$C_{\mathrm{Me-O}}$ (eV)	L (nm)	p (MPa)	$-E_{\mathrm{total}}$ (kJ/g-ion)	$U_{\mathrm{Me-O}}$ (kJ/g-ion)	δE_λ (kJ/g-ion)	δG_λ (kJ/g-ion)	$T\,\delta S_\lambda$ (kJ/g-ion)
1441.4	1.9189	−75.3	2528.2	608.6	0	0	0
1809.72	1.9716	−57.3	2477.9	545.2	50.3	47.8	2.5
2178.04	1.9974	−28.3	2441.5	509.0	86.6	83.3	3.3
2546.36	2.0165	−30.7	2414.1	481.4	114.0	111.3	2.7
2914.68	2.0316	−29.3	2389.7	457.1	138.5	134.5	4.0
3283.0	2.0489	−99.6	2370.0	443.0	158.1	154.0	4.1

Table 8
Calculated thermodynamic properties of CaO–SiO_2 oxides at 1873 K

Oxide	ΔG_f^{ex} (kJ/mol) at $C_{Ca\text{-}Si} = 0$	ΔE_f (kJ/mol) at $C_{Ca\text{-}Si} = 0$	C^*_{Ca-Si} (eV Å^6)	ΔE_f (kJ/mol) at $C_{Ca-Si} = C^*_{Ca-Si}$	$T\,\Delta S^{ex}$ (kJ/mol) at $C_{Ca-Si} = C^*_{Ca-Si}$
4CaO·SiO_2	−43.4	29.1	~0	−29.5	5.5
2CaO·SiO_2	63.5	53.4	−18.2	−55.7	0.2
CaO·SiO_2	−67.6	53.0	67.8	−45.0	2.6
CaO·2SiO_2	52.1	46.7	84.5	−32.8	0.6

At the second step, the dipole–dipole Ca–Si interaction was included to obtain the agreement between calculated and experimental Gibbs free energies of formation of molten calcium silicates, using Eq. (8). Calculated C^*_{Ca-Si} parameters, at which calculated ΔG_f^{ex} values are equal to experimental data, are given in Table 8. It is seen that C^*_{Ca-Si} parameters grow with silica concentration. The C^*_{Ca-Si} parameter as a function of the CaO–SiO_2 composition can be presented by the relationship

$$C^*_{Ca-Si} = 160.4–220.7(1 - X_{SiO_2}) \qquad (12)$$

This expression is valid only for $X_{SiO_2} \geq 0.5$. As in magnesium silicates, the excess entropy term in the excess Gibbs free energy of formation of calcium silicates is rather small in comparison with the internal energy of formation. This result also implies that models of molten calcium silicates can be considered in approximation of regular solutions, and, therefore, hypothetical athermal silicates must be close to ideal solutions.

8. The CaO–FeO–SiO_2 ternary system

In the molecular dynamics modelling of the ternary CaO–FeO–SiO_2 system several iron ions were transformed into the calcium ions. Such iron ions, which were subjected to transformation, are designated as Me^{2+} ions. Thus, in the initial state Me^{2+} ions are Fe^{2+} ions and in the final state they are Ca^{2+} ions. For the ion pairs of the charge of the same sign the parameters B_{ij} can be assumed to be zero, because the ions in such pairs remote from each other to distances, at which repulsion gives rather small contribution to the energy. This assumption was adopted in this work for Ca–Ca, Fe–Fe, Ca–Fe, Ca–Si and Fe–Si pairs. $B_{Si\text{-}Si}$ and $B_{O\text{-}O}$ parameters were taken to be 2055.4 and 1500 eV correspondingly [1,2,6], although it does not have a visible effect on the results of calculation. The B_{ij} parameters for the unlike pairs were found for pure oxides in works [1,2,6] as follows (eV): $B_{Ca-O} = 3283.0$, $B_{Fe-O} = 1900.0$, $B_{Si-O} = 1729.5$. Dipole–dipole interaction was considered only for cations in pairs Ca–Fe, Ca–Me, Fe–Me, Ca–Si, Fe–Si and Me–Si. C_{ij} parameters for all other pairs were assumed to be zero. In the process of transformation of FeO to CaO only parameters $B_{Me\text{-}O}$, $C_{Ca\text{–}Me}$, $C_{Fe\text{–}Me}$ and $C_{Me\text{–}Si}$ were changing. Therefore, Eq. (7) includes only contribution from the Me–O pairs into the first sum in the RHS and contributions from Ca–Me, Fe–Me and Me–Si pairs into the second sum.

Table 9
MD models of ternary CaO–FeO–SiO_2 system at 1873 K

Model	Number of ions						Initial concentration, molar fraction		
	Ca^{2+}	Fe^{2+}	Me^{2+}	Si^{4+}	O^{2-}	Total	CaO	FeO	SiO_2
1	66	43	10	81	281	481	0.330	0.265	0.405
2	30	112	10	48	248	448	0.150	0.610	0.240
3	74	73	10	43	243	443	0.370	0.415	0.215
4	23	142	10	25	225	425	0.115	0.760	0.125
5	41	133	10	16	216	416	0.205	0.715	0.080

It was shown above for binary FeO–SiO$_2$, MgO–SiO$_2$ and CaO–SiO$_2$ silicates, that $C_{\mathrm{Me–Si}}$ parameters depend on the solution composition, while for the CaO–FeO system the $C_{\mathrm{Ca–Fe}}$ parameter may be considered as a constant. Because of this, the C_{ij} parameters in the ternary CaO–FeO–SiO$_2$ silicates were assumed to be independent of the CaO/FeO ratio and were calculated from the data for the binary systems with the same silica concentration as in the ternary solution.

Compositions of CaO–FeO–SiO$_2$ oxides subjected to the MD simulation and ions numbers in the models are shown in Table 9. In the molecular dynamics experiments (*NpT* — ensemble) 10 Fe^{2+} ions were transformed into 10 Ca^{2+} ions by changing the potential parameters $B_{\mathrm{Me–O}}$, $C_{\mathrm{Ca–Me}}$, $C_{\mathrm{Fe–Me}}$ and $C_{\mathrm{Me–Si}}$. As a result of Fe^{2+} → Ca^{2+} transformation, the concentration of a ternary oxide slightly changed, and this was taken into account by averaging concentrations between initial and final compositions.

The calculations were conducted using Eqs. (2), (3), (5) and (7), like for the binary systems [1,6]. Parameters $B_{\mathrm{Me–O}}$, $C_{\mathrm{Ca–Me}}$, $C_{\mathrm{Fe–Me}}$ and $C_{\mathrm{Me–Si}}$ changed linearly from their initial values for the Fe^{2+}-pairs to the values for the Ca^{2+}-pairs. They are shown in Table 10. The derivatives $\mathrm{d}U/\mathrm{d}\lambda$ were calculated along the isobaric–isothermal path from $\lambda = 0.05$ to 0.95 and ΔG values were evaluated using Eq. (5). Finally $\gamma_{\mathrm{CaO}}/\gamma_{\mathrm{FeO}}$ ratios were calculated using Eq. (2). They are given in Table 11.

The experimental data on the CaO and FeO activity coefficients in the CaO–FeO–SiO$_2$ system [9,20] were recalculated from the standard state pure solid CaO to pure liquid CaO as in work [3]. Such data are shown in Table 11. Calculated $\gamma_{\mathrm{CaO}}/\gamma_{\mathrm{FeO}}$ ratios in the ternary CaO–FeO–SiO$_2$ system are in a reasonable agreement with experimental data. The accuracy of calculation of the $\gamma_{\mathrm{CaO}}/\gamma_{\mathrm{FeO}}$ ratio is 15–30%. This is estimated from the errors of 1–2 kJ/mol in the MD calculation of the Gibbs free energy increments. The accuracy of experimental data for the $\gamma_{\mathrm{CaO}}/\gamma_{\mathrm{FeO}}$ ratio is 30–40% [19,20]. Therefore, it can be concluded that calculated $\gamma_{\mathrm{CaO}}/\gamma_{\mathrm{FeO}}$ ratios in the ternary CaO–FeO–SiO$_2$ system are in a reasonable agreement with experimental data.

Table 10
Parameters $B_{\mathrm{Me–O}}$ (eV), $C_{\mathrm{Ca–Me}}$, $C_{\mathrm{Fe–Me}}$, and $C_{\mathrm{Me–Si}}$ (eV Å^6) for different λ values for the model #2 (Table 9) of the CaO–FeO–SiO$_2$ system

λ	$B_{\mathrm{me–O}}$	$C_{\mathrm{Ca–Me}}$	$C_{\mathrm{Fe–Me}}$	$C_{\mathrm{Me–Si}}$
0	1900.00	−43.3	0	242.3
0.2	2176.60	−34.64	−8.66	192.4
0.4	2453.20	−25.98	−17.32	142.5
0.6	2729.80	−17.32	−25.98	92.5
0.8	3006.40	−8.66	−34.64	42.6
1.0	3283.00	0	−43.3	−7.3

Table 11
Activity coefficients $\gamma_{\mathrm{CaO}}/\gamma_{\mathrm{FeO}}$ ratio in the ternary CaO–FeO–SiO$_2$ solutions

Model	$\gamma_{\mathrm{CaO}}/\gamma_{\mathrm{FeO}}$	
	Calculated	Experiment [9,20]
1	0.0036	0.0020
2	0.0111	0.0090
3	0.0467	0.0261
4	0.0160	0.0245
5	0.0640	0.0770

The excess entropy term in the Gibbs free energy increment calculated by (2) is relatively small what implies that models of the ternary CaO–FeO–SiO$_2$ system are close to regular solutions. In the approximation of a regular solution activity coefficient γ_i of a component i can be calculated by the formula

$$\ln \gamma_i = \frac{\Delta H_i}{RT} \tag{13}$$

where ΔH_i is a relative partial molar enthalpy. To find the relative partial enthalpy of a component i, the integral internal energy of formation of the CaO–FeO–SiO$_2$ ternary system, calculated by the MD method, was approximated by the following expression:

$$\begin{aligned}\Delta E_{\mathrm{f}} = {} & a_1X_1X_2(1-X_3) + a_2X_1X_2^2(1-X_3) \\ & + a_3X_1X_3(1-X_2) + a_4X_1X_3^2(1-X_2) \\ & + a_5X_2X_3(1-X_1) + a_6X_2X_3^2(1-X_1) \\ & + a_7X_1X_2X_3\end{aligned} \tag{14}$$

where coefficients a_i were found by the least square method using ΔE_{f} data for nine boundary binary oxides and 10 compositions of the CaO–FeO–SiO$_2$ ternary system (five initial compositions are shown in Table 9 and another five compositions were obtained by transforming 10 Fe-ions into Ca-ions). At 1873 K these coefficients are (kJ/mol): $a_1 = 84.882$, $a_2 = -189.468$, $a_3 = ! - 289.211$, $a_4 = 205.869$, $a_5 =$

Table 12
Activity coefficients γ_{CaO} (the standard state is the super-cooled liquid CaO) in the CaO–FeO–SiO_2 system

Model	X_{CaO}	X_{FeO}	X_{SiO_2}	ΔE_f (kJ/mol)		ln γ_{CaO}, calculated using (14)	ln γ_{CaO}, experiment [9,20]
				MD caculation	Formula (14)		
2	0.150	0.610	0.240	−10.3	−12.1	−4.74	−4.85
3	0.370	0.415	0.215	−25.8	−22.5	−1.89	−2.99
4	0.115	0.760	0.125	−7.2	−8.9	−4.13	−4.10
5	0.205	0.715	0.080	−15.1	−12.3	−1.97	−2.42

3.0515, $a_6 = 46.123$, $a_7 = -382.339$. ΔE_f values calculated by the MD method and using Eq. (14) are compared in Table 12. The agreement between them is reasonable. The standard deviation in the correlation of ΔE_f values found by these two methods for 19 binary and ternary solutions is equal to 2.61 kJ/mol, what is close to the error of MD calculation.

The partial relative enthalpy of a component i is equal to the derivative $\Delta H_i = \mathrm{d}\,\Delta E_f/\mathrm{d}n_i$, where n_i is the number of moles of the ith component. Using Eqs. (14) and (13), relative partial enthalpy and activity coefficients of CaO were calculated for seven binary and five ternary compositions of liquid solutions. Calculated and experimental values of ln γ_{CaO} for the ternary system are shown in Table 12. In four models out of five (models 1–3 and 5), the calculated activity coefficients of CaO are higher than the experimental ones. This consistent discrepancy can be attributed to the use of the regular solutions approximation.

9. Conclusions

Results of molecular dynamics calculations of thermodynamic properties of oxide solutions depend strongly on the ionic potentials. Introduction of effective dipole–dipole interaction between cations for binary CaO–FeO, MgO–SiO_2, FeO–SiO_2, CaO–SiO_2 systems allows to get thermodynamic properties of solutions close to experimental data. The use of C_{ij} parameters of the effective dipole–dipole interaction obtained from experimental data for binary system in the MD modelling of the ternary CaO–FeO–SiO_2 system gives reasonable agreement between calculated and experimental $\gamma_{CaO}/\gamma_{FeO}$ ratio.

Results of MD calculation show that models of the systems studied above are close to regular solutions, and therefore, athermal systems are almost ideal solutions.

The MD method presented in this paper gives reasonable results on thermodynamic properties of ternary oxide systems. It also provides data on structure of oxide solutions and can be used for calculation of dynamic properties.

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