

Molecular Dynamics Simulation of Binary CaO-FeO, MgO-SiO₂, FeO-SiO₂, CaO-SiO₂ and Ternary CaO-FeO-SiO₂ Systems

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Molecular dynamics models of binary CaO-FeO, MgO-SiO₂, FeO-SiO₂, CaO-SiO₂ and ternary CaO-FeO-SiO₂ 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-SiO₂, MgO-SiO₂ and CaO-SiO₂ systems to experimental data. The thermodynamic properties of CaO-FeO-SiO₂ solutions were studied by converting several iron ions into calcium ions. The Gibbs free energy increments and ratios of activity coefficients $\gamma_{\text{CaO}}/\gamma_{\text{FeO}}$ in the ternary system were calculated.

1 Introduction

These days, quasi-chemical, cell, and some other models in the slag chemistry incorporated into thermochemical packages such as F*A*C*T, 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 kilo-joules. 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 obtain 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-SiO₂ system are calculated by the MD method with parameters of the Born-Mayer potentials, determined using thermodynamic data for binary CaO-FeO, FeO-SiO₂ and CaO-SiO₂ 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 MeO₂ type solutes in the CaO-SiO₂ 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:

$$u_{ij}(r) = Z_i Z_j e^2/r + B_{ij} \exp(-r/R_{ij}).$$

In this expression r is a distance between ions, Z_i is the ionic charge in the units of elemental charge e , B_{ij} and R_{ij} are 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-SiO₂ 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 (equation (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 below in section 4.

In this paper, this approach is applied to calculation of thermodynamic properties of binary CaO-FeO, MgO-SiO₂, FeO-SiO₂, CaO-SiO₂ and ternary CaO-FeO-SiO₂ oxide systems.

2 Interionic Potential

Interactions between ions were described by the Born-Mayer potentials:

$$u_{ij}(r) = Z_i Z_j e^2/r + B_{ij} \exp(-r/R_{ij}) + C_{ij}/r^6 + D_{ij}/r^8 \quad (1)$$

Terms C_{ij}/r^6 and D_{ij}/r^8 describe effective dipole-dipole and dipole-quadrupole 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-quadrupole interaction is 5-10% of dipole-dipole interaction^[4,5]. In previous works,^[1,2] dipole-dipole and dipole-quadrupole 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 MeO₂ oxides only the size of Me²⁺ or Me⁴⁺ ions was different. This is an obvious simplification. Direct chemical interaction between components of a solution is introduced here through dipole-dipole potential. Dipole-quadrupole 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 Me²⁺ and 246 ions of O²⁻). Coulomb interaction was considered in the Ewald-Hansen approximation^[2]. The particle trajectories were calculated using L.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: $(\text{FeO}) \rightarrow \text{FeO}$ and $\text{CaO} \rightarrow (\text{CaO})$.

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

$$\Delta G = \Delta G_p + RT \ln (\gamma_{\text{CaO}} / \gamma_{\text{FeO}})$$

or

$$\Delta G_s = \Delta G - \Delta G_p = RT \ln (\gamma_{\text{CaO}} / \gamma_{\text{FeO}}) \quad (2)$$

where $\Delta G_p = G_{\text{CaO}}^0 - G_{\text{FeO}}^0$ 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:

$$B_{ij} = B_{ij}^0 + \lambda (B_{ij}^f - B_{ij}^0) \quad \text{and} \quad C_{ij} = C_{ij}^0 + \lambda (C_{ij}^f - C_{ij}^0) \quad (3)$$

where parameter λ is 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_{ij}^0 and C_{ij}^0 values. At $\lambda = 1$ parameters B_{ij} and C_{ij} describe interactions of Ca^{2+} ions, they are equal to the final B_{ij}^f and C_{ij}^f 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:

$$U = U_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) + \lambda U_1(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (4)$$

Here $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ are ions coordinates, and λ is 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]:

$$\Delta G = G(\lambda_2) - G(\lambda_1) = \int_{\lambda_1}^{\lambda_2} \langle U_1 \rangle d\lambda \quad (5)$$

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

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

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 $dU/d\lambda$ for the pair potential (1) is equal to^[3]:

$$dU/d\lambda = \sum \frac{B_{ij}^f - B_{ij}^0}{B_{ij}(\cdot)} U_{rep}(ij) + \sum \frac{C_{ij}^f - C_{ij}^0}{C_{ij}(\cdot)} U_{dd}(ij) \quad (7)$$

Here U_{rep} and U_{dd} are 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:

$$\Delta G = G(C_2) - G(C_1) = \sum_{C_1}^{C_2} \int \frac{U_{dd}(ij)}{C_{ij}(\cdot)} dC_{ij} \quad (8)$$

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

4 The CaO - FeO system

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): $B_{Ca-Ca}=B_{Ca-Fe}=B_{Fe-Fe}=0$; $B_{Ca-O}=3283$ 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·Å⁶, $C_{Ca-Ca}=C_{Fe-Fe}=C_{Ca-O}=C_{Fe-O}=C_{O-O}=0$. 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-SiO₂ 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 equation (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-SiO₂ system

Experimental data for the MgO-SiO₂ system at 1873 K taken from work^[11] are shown in Table I. In this table, ΔG_f is the Gibbs free energy of formation of solution from pure liquid FeO and SiO₂. 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-SiO₂ 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) C_{Mg-Si} parameter was equal to C_{Mg-Si}^{id} . At these values of C_{Mg-Si} , solutions have zero formation energy $\Delta E_f = 0$, and
- (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 $C_{\text{Mg-Si}}^{\text{id}}$ and $C_{\text{Mg-Si}}^*$ are given in Table 1. Calculated $C_{\text{Mg-Si}}^{\text{id}}$ values and some adjusted $C_{\text{Mg-Si}}^*$ 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 $C_{\text{Mg-Si}}^*$ parameter as a function of composition of MgO-SiO₂ solutions can be presented as a linear function:

$$C_{\text{Mg-Si}}^* = 152.9 - 247.3 (1 - X_{\text{SiO}_2}) \quad (9)$$

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 II. The term $T\Delta S^{\text{ex}}$ (ΔS^{ex} is the excess entropy of formation of the MgO-SiO₂ solution) is very small relatively to ΔE_f , what means that a model of the MgO-SiO₂ binary system is close to regular solution.

Behavior of real molten MgO-SiO₂ solutions deviates from the model of the regular solution. This is indicated by the miscibility gap in the liquid state of the MgO-SiO₂ system^[9]. Regular solutions have a miscibility gap only when the enthalpy of their formation is positive. The enthalpy of formation of MgO-SiO₂ 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-SiO₂ 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-SiO₂ solutions is not expected to depend strongly on the Me²⁺ 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 Fe²⁺ → Ca²⁺) 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.SiO₂ is equal to -29.4 kJ/mole and standard formation entropy of this oxide is -4.83 J/mole.K^[12]. Therefore, the entropy contribution to the Gibbs free energy -TΔS, is equal to 1.44 kJ/mole 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⁻¹K⁻¹ predicted by the regular solution model.

6 The FeO-SiO₂ system

At 1873 K, the FeO-SiO₂ binary solutions are liquid in the range of $X_{\text{FeO}} \geq 0.48$. Thermodynamic properties of molten FeO-SiO₂ alloys were measured in work^[13]. The Gibbs free energy of formation of the FeO-SiO₂ solutions in from works^[13,14] and calculated excess Gibbs free energy of formation are given below:

X_{FeO}	0.9	0.8	0.667	0.5	
$\Delta G_f/RT$	-0.41	-0.50	-0.60	-0.49	
$\Delta G_f^{\text{ex}}, \text{kJ/mol}$	-1.35	0	0.56	3.20	(10)

In calculation of the excess Gibbs free energy, $\Delta G_f/RT$ for the FeO-SiO₂ solutions was assumed to be independent on temperature. Then, the excess Gibbs free energy was calculated as $\Delta G^{\text{ex}} = \Delta G - RT (X_{\text{FeO}} \ln X_{\text{FeO}} + X_{\text{SiO}_2} \ln X_{\text{SiO}_2})$. The FeO-SiO₂ 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 III.

Calculations were conducted in the same way as for the MgO-SiO₂ system. B_{ij} parameters of potential (1) were taken from^[1,2,6]: $B_{\text{Fe-Fe}} = B_{\text{Fe-Si}} = 0$, $B_{\text{Si-Si}} = 2055.4$ eV, $B_{\text{Fe-O}} = 1900$ eV, $B_{\text{Si-O}} = 1729.5$ eV, $B_{\text{O-O}} = 1500$ eV. At the first stage, all C_{ij} parameters were assumed to be 0. Calculated internal energies of formation for the FeO-SiO₂ solutions, ΔE_f are shown in Table IV.

Then for each solution the parameter $C_{\text{Fe-Si}} = C_{\text{Fe-Si}}^{\text{id}}$ was found, at which $\Delta E_f = 0$ (Table IV). This solution can be considered as an ideal solution. For such a solution $\Delta G_f^{\text{id}} = RT(X_{\text{FeO}} \ln X_{\text{FeO}} + X_{\text{SiO}_2} \ln X_{\text{SiO}_2})$ and the excess Gibbs free energy is 0.

Finally, $C_{\text{Fe-Si}}$ was changed from $C_{\text{Fe-Si}}^{\text{id}}$ to $C_{\text{Fe-Si}}^*$, at which Gibbs free energy increment (the excess Gibbs free energy) calculated by equation (8) is equal to the experimental value ΔG^{ex} . An example of such calculation for the FeO-SiO₂ solution with $X_{\text{FeO}}=0.9$ is shown in Table V.

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

$$\frac{U_{\text{dd}}(\text{Fe-Si})}{C_{\text{Fe-Si}}} = 0.0351 - 1.718 \cdot 10^{-5} C_{\text{Fe-Si}}$$

Thus, the excess Gibbs free energy of formation of the FeO-SiO₂ oxide with $X_{\text{FeO}}=0.9$ can be presented as:

$$\Delta G_f^{\text{ex}} = -1.35 = 2.1 \int_{262}^{C^*} (0.0351 - 1.718 \cdot 10^{-5} C) dC$$

In this equation, $\Delta G_f^{\text{ex}} = -1.35$ is the experimental value of ΔG_f^{ex} taken from (10), and the coefficient 2.1 is the number of gram-ions in 1 mole of (FeO)_{0.9}(SiO₂)_{0.1} oxide. Solving this equation we find that $C_{\text{Fe-Si}}^* = 241 \text{ eV} \cdot \text{\AA}^6$. This value is shown in Table IV. Other $C_{\text{Fe-Si}}^*$ values in Table IV were calculated in a similar way.

The following conclusions can be drawn from results of the MD calculation for FeO-SiO₂ solutions with $X_{\text{FeO}} \geq 0.5$ (Table IV):

- 1) solutions have strong negative deviations from ideality when $C_{\text{Fe-Si}} = 0$;
- 2) the excess Gibbs free energy of formation of FeO-SiO₂ solutions is around zero (the ideal solution) at $C_{\text{Fe-Si}}^{\text{id}}$ value in the interval of 239-275 eV·Å⁶;
- 3) $C_{\text{Fe-Si}}^*$ values vary in the narrow range from 239 to 258 eV·Å⁶;
- 4) the excess entropy term $T\Delta S_f^{\text{ex}}$ calculated from $\Delta G_f^{\text{ex}} = \Delta E_f - T\Delta S_f^{\text{ex}}$ is very small and can be neglected in comparison with the formation 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 $C_{\text{Fe-Si}}^*$ parameter for ferrous silicates as a function of concentration may be approximated by the equation:

$$C_{\text{Fe-Si}}^* = 390.6 - 195.1 (1 - X_{\text{SiO}_2}) \quad (11)$$

7 The CaO-SiO₂ system

At 1873 K, the homogeneous liquid CaO-SiO₂ solution stretches between 40 and 67 mol% SiO₂. 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] are shown in Table VI. This table also includes the ΔG_f data for the CaO·2SiO₂, CaO·SiO₂, 2CaO·SiO₂ and 4CaO·SiO₂ compounds assessed in work^[18] from the phase diagram. The deviations from ideality for this system are more negative than for magnesium silicates.

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-SiO₂ system were initiated by converting MgO-SiO₂ models to the CaO-SiO models. The MgO-SiO₂ models constructed with $C_{Mg-Si}=0$ were transformed into the CaO-SiO₂ models changing the parameter B_{Me-O} from 1441.4 to 3283.0 eV. As a result, the CaO-SiO₂ models were obtained with $C_{Ca-Si} = 0$.

As an example, the change in properties of the system in the process of transformation of 4MgO·SiO₂ compound to 4CaO·SiO₂ is shown in Table VII. 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 Me²⁺ and O²⁻ decreases and Gibbs free energy increment grows with increasing B_{Me-O} .

The molar Gibbs free energy of formation of $mCaO \cdot nSiO_2$ oxides was calculated as:

$$\Delta G_f(mCaO \cdot nSiO_2) = \Delta G_f(mMgO \cdot nSiO_2) + \{(2m + 3n) \delta G_\lambda(mMeO \cdot nSiO_2) - 2m \delta G_\lambda(MeO)\} / (m + n)$$

In this equation, $\delta G_\lambda(mMeO \cdot nSiO_2)$ is the Gibbs free energy increment for transformation of 1 g-ion $mMgO \cdot nSiO_2$ into 1 g-ion $mCaO \cdot nSiO_2$, and $\delta G_\lambda(MeO)$ 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-SiO₂ system at $C_{Ca-Si} = 0$ are given in Table VII. In fact, only calcium mono- and disilicate are liquid at 1873 K. The 2CaO·SiO₂ and 4CaO·SiO₂ compounds at 1873 K are considered as super-cooled liquids.

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 equation (8). Calculated C_{Ca-Si}^* parameters, at which calculated ΔG_f^{ex} values are equal to experimental data, are given in Table VIII. It is seen that C_{Ca-Si}^* parameters grow with silica concentration. The C_{Ca-Si}^* parameter as a function of the CaO-SiO₂ composition can be presented by the relationship:

$$C_{Ca-Si}^* = 160.4 - 220.7 (1 - X_{SiO_2}) \quad (12)$$

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-SiO₂ ternary system

In the molecular dynamics modelling of the ternary CaO-FeO-SiO₂ system several iron ions were transformed into the calcium ions. Such iron ions, which were subjected to trans-

formation, 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. $B_{\text{Si-Si}}$ and $B_{\text{O-O}}$ 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): $B_{\text{Ca-O}} = 3283.0$, $B_{\text{Fe-O}} = 1900.0$, $B_{\text{Si-O}} = 1729.5$. 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 $B_{\text{Me-O}}$, $C_{\text{Ca-Me}}$, $C_{\text{Fe-Me}}$ and $C_{\text{Me-Si}}$ were changing. Therefore, equation (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.

It was shown above for binary FeO-SiO₂, MgO-SiO₂ and CaO-SiO₂ silicates, that $C_{\text{Me-Si}}$ parameters depend on the solution composition, while for the CaO-FeO system the $C_{\text{Ca-Fe}}$ parameter may be considered as a constant. Because of this, the C_{ij} parameters in the ternary CaO-FeO-SiO₂ 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-SiO₂ oxides subjected to the MD simulation and ions numbers in the models are shown in Table IX. In the molecular dynamics experiments (NpT -ensemble) ten Fe^{2+} ions were transformed into ten Ca^{2+} ions by changing the potential parameters $B_{\text{Me-O}}$, $C_{\text{Ca-Me}}$, $C_{\text{Fe-Me}}$ and $C_{\text{Me-Si}}$. As a result of $\text{Fe}^{2+} \rightarrow \text{Ca}^{2+}$ 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 equations (2), (3), (5) and (7), like for the binary systems^[1,6]. Parameters $B_{\text{Me-O}}$, $C_{\text{Ca-Me}}$, $C_{\text{Fe-Me}}$ and $C_{\text{Me-Si}}$ changed linearly from their initial values for the Fe^{2+} -pairs to the values for the Ca^{2+} -pairs. They are shown in Table X. The derivatives $dU/d\lambda$ were calculated along the isobaric-isothermal path from $\lambda = 0.05$ to $\lambda = 0.95$ and ΔG values were evaluated using Equation (5). Finally $\gamma_{\text{CaO}}/\gamma_{\text{FeO}}$ ratios were calculated using equation (2). They are given in Table XI.

The experimental data on the CaO and FeO activity coefficients in the CaO-FeO-SiO₂ 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 XI. Calculated $\gamma_{\text{CaO}}/\gamma_{\text{FeO}}$ ratios in the ternary CaO-FeO-SiO₂ system are in a reasonable agreement with experimental data. The accuracy of calculation of the $\gamma_{\text{CaO}}/\gamma_{\text{FeO}}$ 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 $\gamma_{\text{CaO}}/\gamma_{\text{FeO}}$ ratio is 30-40%^[19,20]. Therefore, it can be concluded that calculated $\gamma_{\text{CaO}}/\gamma_{\text{FeO}}$ ratios in the ternary CaO-FeO-SiO₂ system are in a reasonable agreement with experimental data.

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-SiO₂ system is 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

$$\ln \gamma_i = -\bar{H}_i/RT, \quad (13)$$

where \bar{H}_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-SiO₂ ternary system, calculated by the MD method, was approximated by the following expression:

$$\begin{aligned} \Delta E_f = & a_1 X_1 X_2 (1-X_3) + a_2 X_1 X_2^2 (1-X_3) + a_3 X_1 X_3 (1-X_2) + a_4 X_1 X_3^2 (1-X_2) + \\ & + a_5 X_2 X_3 (1-X_1) + a_6 X_2 X_3^2 (1-X_1) + a_7 X_1 X_2 X_3 \end{aligned} \quad (14)$$

Coefficients a_i were found by the least square method using ΔE_f data for 9 boundary binary oxides and 10 compositions of the CaO-FeO-SiO₂ ternary system (5 initial compositions are shown in Table IX and another 5 compositions were obtained by transforming ten Fe-ions into Ca-ions). At 1873 K these coefficients are (kJ/mol): $a_1 = 84.882$, $a_2 = -189.468$, $a_3 = -289.211$, $a_4 = 205.869$, $a_5 = 3.0515$, $a_6 = 46.123$, $a_7 = -382.339$. ΔE_f values calculated by the MD method and using equation (14) are compared in Table XII. 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 $\bar{H}_i = d\Delta E_f / dn_i$, where n_i is the number of moles of the i -th component. Using equations (14) and (13), relative partial enthalpy and activity coefficients of CaO were calculated for 7 binary and 5 ternary compositions of liquid solutions. Calculated and experimental values of $\ln \gamma_{\text{CaO}}$ for the ternary system are shown in Table XII. 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-SiO₂, FeO-SiO₂, CaO-SiO₂ 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-SiO₂ system gives reasonable agreement between calculated and experimental $\gamma_{\text{CaO}}/\gamma_{\text{FeO}}$ 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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Table I Properties of MgO-SiO₂ silicates

Silicate	ΔG_f , kJ/mol experiment ^[11]	ΔG_f , kJ/mol at $C_{\text{Mg-Si}} = 0$	$C_{\text{Mg-Si}}^{\text{id}}$, eV. Å ⁶	$C_{\text{Mg-Si}}^*$, 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 II. Calculated thermodynamic properties of MgO-SiO₂ silicates.

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

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

Table III Number of ions in FeO-SiO₂ 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 IV Simulation of FeO-SiO₂ solutions at 1873 K and zero pressure (data on L , V/N , E and ΔE_f are calculated at $C_{\text{Fe-Si}} = 0$; E^{id} is the internal energy of the ideal solution calculated at $C_{\text{Fe-Si}} = C_{\text{Fe-Si}}^{\text{id}}$ when $G_f^{\text{ex}} = 0$)

X_{FeO}	L , nm	V/N , cm ³ /g-ion	E , kJ/g-ion	E^{id} , kJ/g-ion	ΔE_f , kJ/g-ion	$C_{\text{Fe-Si}}^{\text{id}}$, eV·Å ⁶	$C_{\text{Fe-Si}}^*$, eV·Å ⁶	ΔE_f^* , kJ/g-ion	$(\Delta G_f^*)^{\text{ex}}$, kJ/g-ion	$(T\Delta S_{\text{ex}}^*)^{\text{ex}}$, 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	-	-	-	-	-	-

Table V Simulation of the FeO-SiO₂ solution with $X_{\text{FeO}}=0.9$ with different $C_{\text{Fe-Si}}$ parameters at 1873 K (L is the length of the basic cube edge)

$C_{\text{Fe-Si}}$, eV·Å ⁶	L , nm	p , MPa	E , kJ/g-ion	U_{dd} (Fe-Si), kJ/g-ion	$\frac{U_{\text{dd}}(\text{Fe-Si})}{C_{\text{Fe-Si}}}$
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

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

Oxide	ΔG_f , kJ/mol		
	[15]	[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

Table VII Computer transformation of the 4MgO-SiO₂ model into the 4CaO-SiO₂ model at 1873 K ($C_{\text{Me-Si}} = 0$)

$C_{\text{Me-O}}$, eV	L , nm	p , MPa	$-E_{\text{total}}$, kJ/g-ion	$U_{\text{Me-O}}$, 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 VIII Calculated thermodynamic properties of CaO-SiO₂ oxides at 1873 K

Oxide	$\Delta G_{\text{f}}^{\text{ex}}$, kJ/mol at $C_{\text{Ca-Si}} = 0$	ΔE_{f} , kJ/mol at $C_{\text{Ca-Si}} = 0$	$C_{\text{Ca-Si}}^*$, eV·Å ⁶	ΔE_{f} , kJ/mol at $C_{\text{Ca-Si}} = C_{\text{Ca-Si}}^*$	$T\Delta S^{\text{ex}}$, kJ/mol at $C_{\text{Ca-Si}} = C_{\text{Ca-Si}}^*$
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

Table IX MD Models of ternary CaO-FeO-SiO₂ 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

Table X Parameters $B_{\text{Me-O}}$ (eV), $C_{\text{Ca-Me}}$, $C_{\text{Fe-Me}}$, and $C_{\text{Me-Si}}$ (eV·Å⁶) for different λ values for the model #2 (Table IX) of the CaO-FeO-SiO₂ system

λ	$B_{\text{Me-O}}$	$C_{\text{Ca-Me}}$	$C_{\text{Fe-Me}}$	$C_{\text{Me-Si}}$
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 XI Activity coefficients $\gamma_{\text{CaO}}/\gamma_{\text{FeO}}$ ratio in the ternary CaO-FeO-SiO₂ solutions

Model	$\gamma_{\text{CaO}}/\gamma_{\text{FeO}}$	
	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

Table XII Activity coefficients γ_{CaO} (the standard state is the super-cooled liquid CaO) in the CaO-FeO-SiO₂ system

Model	X_{CaO}	X_{FeO}	X_{SiO_2}	ΔE_f , kJ/mol		$\ln\gamma_{\text{CaO}}$ Calculated using (14)	$\ln\gamma_{\text{CaO}}$ Experiment [9,20]
				MD Calcula- tion	Formula (14)		
1	0.330	0.265	0.405	-32.0	-30.4	-4.33	-5.63
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