Molecular Dynamics Simulation of Ionic Melts

David K. Belashchenko* and Oleg I. Ostrovski**

*Department of Physical Chemistry, Moscow Steel and
Alloys Institute, Moscow, Russian Federation. Telephone:
+7-095-234667, Fax: +7-095-2362105
**School of Materials Science and Engineering, The
University of New South Wales, Sydney, Australia.
Telephone: +61-2-3854439, Fax:+61-2-3855956

ABSTRACT

The molecular dynamics (MD) method was employed for analysis of thermodynamic properties of molten oxides in the approximation of an ionic model. This included (i) calculation of internal energy, volume, Gibbs free energy and entropy of oxides of MeO_2 series; (ii)analysis of thermodynamic activity coefficients of MeO and MeO_2 oxides in the CaO-SiO_2 system; and (iii) calculation of titanium partitioning between Ti^{3+} and Ti^{4+} valency states in the CaO - SiO_2 melts.

Activity coefficients of MeO and MeO_2 oxides in the CaO-SiO_2 solutions were analysed in context of basicity of the CaO-SiO_2 system. It was shown that with respect to solutes of MeO series, the CaO-SiO_2 system may be regarded as a basic solution at CaO mole fraction x_{CaO} above 0.8 and as an acidic solution at $x_{CaO} < 0.8$. However, with respect to solutes of MeO_2 series such scale of basicity is not valid, the CaO-SiO_2 system may be regarded as a basic solution at $x_{CaO}>0.3$. This indicates that the scale of basicity with respect to solutes is not universal.

The MD simulation of titanium redox equilibrium with the Born-Mayer potential predicts that titanium in the wide range of CaO-SiO_2 compositions from pure SiO_2 to $2CaO \cdot SiO_2$ predominantly exists as Ti^{3+} even at oxygen partial pressure of 1 atm. Better results were obtained with the use of the Lennard-Jones potential for Ti-O pairs. The selection of the potential to describe the inter-ionic interactions in the oxide system is a crucial element of the MD simulation.

1. INTRODUCTION

The molecular dynamics (MD) is an effective method to study structure and properties of non-crystalline systems, such as liquid and amorphous metals, molten and vitreous oxides, and metallurgical slags. In some cases, experimental investigation of metallurgical melts is very difficult or even impossible due to their high melting temperature, reactivity with refractory materials and other constraints. Such constraints do not exist for the MD method which may be employed to calculate, practically, any property of a system of any composition if potentials of interaction of components of the system are known.

Thus, the choice of potentials to describe inter-atomic interactions is a crucial element in the MD method. Interactions between components of oxide systems and metallurgical slags could be presented in terms of ionic and covalent bonds. However, an accurate account of the covalent contribution involves multiparametrical three-particle potentials and is rather obscure, especially in application to complex systems such as metallurgical slags. On other hand, high degree of ionization of oxides due to high electronegativity of oxygen, makes incentive to use the pure ionic bonds approach with simple inter-ionic pair potential of the Born-Mayer type. Such approach gives reasonable results in the MD simulation even for pure silica.[1]

The Born-Mayer potential

$$u_{ij}(r) = Z_i Z_j e^2 / r + B_{ij} \exp(-r / R_{ij}) , \qquad (1)$$

where r is the distance between ions i and j; Z_i is the charge of ion i; B_{ij} and R_{ij} are repulsive parameters; was employed in MD simulation of a number of pure non-crystalline oxides.[2-7] It was shown that structure and properties of oxides strongly depend on the charge and size of a metallic ion Me^{n+}. The ion size is directly related to the B(Me-O) parameter. For ions of the same charge such as in the MeO or MeO_2 series, this is the only parameter, which provides different structure and properties of oxides along the series in the MD models. In this paper, the MD models will be examined for the MeO_2 series and for MeO and MeO_2 solutes in the CaO-SiO_2 melts. The MD simulation is also applied to rather complex redox processes, which in the present work will be considered in the application to the titanium Ti^{3+}/Ti^{4+} partitioning in the CaO-SiO_2 system.

2. COMPUTER CALCULATION OF THERMODYNAMIC PROPERTIES OF OXIDE SYSTEMS

Molecular dynamics calculation of such thermodynamic properties as energy and volume of oxide systems is a routine procedure. It is assumed in such calculations that parameters B_{ij} and R_{ij} of the potential (1) do not change with a solution composition. Relative volumes and energies can be evaluated from the corresponding properties of the solutions and pure oxides at given temperature and pressure (usually, p= 0).

The main concern is the error of such calculations. In the MD run, the pressure fluctuations are of ± 0.3 - 0.5

GPa. Therefore, the density is determined with an error of 2-3% and no less than 1%. The energy fluctuates in the interval of ± 20-30 kJ/g-ion, and the error of calculation of its average value is about the same. The relative volume and energy of the oxides solution determined as differences between big values, are small, and errors of their calculation may be rather high.

Nevertheless, in many cases the accuracy of the calculations appears to be quite reasonable. This may be illustrated considering, for example,the $(B_2O_3)_x(SiO_2)_{1-x}$ system. The computer simulation of this system[8] using the potential (1), gave the following results for relative volume and energy at 2000 K:

x	0.8	0.667	0.5	0.333
ΔV, cm^3/mol	-2.3	-5.3	1.0	-2.5
ΔE, kJ/mol	6.6	-8.8	-44.3	-74.5

The total energies of B_2O_3 and SiO_2 are equal to -3460.3 and -4048.7 kJ/g-ion correspondingly (relatively infinitely remote ions). It is seen that the relative energy is only about 0.4% of the energy of an ideal solution $E=xE^0_{B2O3}+(1-x)E^0_{SiO2}$. In this sense, the system is close to the ideal solution; this is in agreement with the simple eutectic form of the phase diagram of the B_2O_3-SiO_2 system. The errors are about ± 1 - 2 cm^3/mol for the volume increments and ± 20 - 30 kJ/mol for energies. The high error in the relative energy is due to the error in calculation of total energy which itself is rather low, about 0.1%. That is why it is very difficult to make calculations of relative energies more accurate.

Calculations of the Gibbs free energy and entropy of oxides are much more sophisticated in comparison with volume and energy. In this work the change in the Gibbs free energy and entropy of oxides along the homologous series Me_nO_m was examined by the following procedure.

The potential energy is presented as a sum:

$$U = U_0(\mathbf{r_1}, \mathbf{r_2}, \ldots \mathbf{r_N}) + \lambda U_1(\mathbf{r_1}, \mathbf{r_2}, \ldots \mathbf{r_N}) \qquad (2)$$

where $\mathbf{r}_i$ is the coordinate vector of i-th particle and λ is a variable parameter. Then the change in the Gibbs free energy when the system in the state with $\lambda = \lambda_1$ transfers to the state with $\lambda = \lambda_2$ is as follows[9]:

$$\delta G_\lambda = \int_{\lambda_1}^{\lambda_2} <U_1(\lambda)> d\lambda\ , \qquad (3)$$

The integration must be executed along isobaric-isothermal path. The difference in entropy of the system in two states could be calculated using data on the Gibbs free energy and internal energy.

This method was applied to examine changes in the Gibbs free energy δG and entropy of oxides in serii Me_2O, MeO, Me_2O_3, MeO_2, Me_2O_5, MeO_3, $2MeO{\cdot}SiO_2$ and others[2-7,9] using the Born-Mayer potential (1). Along the given series (say MeO) only one parameter B(Me-O) changes. In this case the equation (3) can be written in the form[9]

$$\delta G_y = \int_{y_1}^{y_2} <U(Me\text{-}O)> dy\ , \qquad (4)$$

where $y = \ln (B_{Me\text{-}O}/B_o)$, B_o is any positive value and <U(Me-O)> is the mean repulsive energy of ion cores of the Me-O pair. The energy <U(Me-O)> is calculated for different B(Me-O) in the MD experiments. The Gibbs free energy δG_y which characterises the difference in the Gibbs free energy of oxides with different parameters $B_{Me\text{-}O}$ (different Me^{2+} size) is determined by the integral (4) at constant *p* and *T*.

Let us consider results of such calculations for the MeO_2 series.[5] Parameters R_{ij}, B(Me-Me) and B(O-O) of the potential (1) were taken the same for all oxides: R_{ij} = 29 pm, B(Me-Me) = 0, B(O-O) = 1500 eV (this value was obtained from the analysis of silicates[10]). The only different parameter in the potential (1) for different oxides was B(Me-O). The following values of this parameter were considered: 850, 1250, 1729.5 (the case of SiO_2), 1848, 3500, 5000, and 8000 eV. The value of the B(Me-O) parameter is related to the Me^{4+} size; the larger is the Me^{4+} ion, the greater is the B(Me-O) value. For example, B(Me-O) ≅ 3500 corresponds to ZrO_2, and B(Me-O) ≅ 5000 corresponds to UO_2.

The molecular dynamics models consisted of 498 ions in the basic cube. The mean values <U(Me-O)> were obtained for each model at pressure p ≅ 0. The values δG_y along the MeO_2 series were calculated using equation (4) and the configuration entropy increments were found as $\delta S_y = (\delta E_y - \delta G_y)/T$. The Gibbs free energy and entropy of oxides were calculated relatively SiO_2 assuming the Gibbs free energy and entropy of silica as a zero level. Results obtained at 2000 K are as follows.

$B_{Me\text{-}O}$, eV	850	1250	1729.5	3500	5000	8000
V/N, $cm^3{\cdot}g\text{-}ion^{-1}$	8.56	8.25	9.22	9.59	9.97	10.68
$r_{1(Me\text{-}O)}$, pm	130	149	162	200	217	237
$z_{Me\text{-}O}$	3.70	3.95	4.00	5.61	6.26	6.91
δG_y, $kJ{\cdot}g\text{-}ion^{-1}$	-679	-279	0	474	661	876
δS_y, $J{\cdot}g\text{-}ion^{-1}{\cdot}K^{-1}$	-8.5	-3.0	0	5.0	7.5	7.4

Here r_1(Me-O) is the mean Me-O distance and z(Me-O) is the mean number of oxygen atoms in the first coordination shell of a metallic ion. At B(Me-O) = 850 eV z(Me-O) = 3.7, it means that about 30% of Me^{4+} ions have trigonal coordination and 70% ions have tetrahedral coordination. The distance r_1(Me-O) and coordination number z(Me-O) increase monotonously with growth of B(Me-O). However, the oxide volume decreases when B(Me-O) increases from 850 to 1250 eV and grows with further increase in the B(Me-O) parameter. At B(Me-O) ≅ 1250 eV coordination number z(Me-O) becomes close to 4. It means that by this point, the elements of trigonal structure with z(Me-O)=3 disappear; this process is accompanied by the compression of the system.

The total energy and Gibbs free energy of MeO_2 oxides increase monotonously with the B(Me-O) value. Configuration entropy grows with increasing B(Me-O) up to B(Me-O) $\cong$ 5000 eV and remains practically unchanged with further increase in B(Me-O).

Different behaviour of structure and entropy was observed for the MeO series, where the sharp structure transformation was revealed in the interval of B(Me-O) values between 1900 (FeO) and 2550 (~CaO) eV [ref. 3].

3. THERMODYNAMICS OF MeO AND MeO_2 SOLUTES IN THE CaO-SiO_2 SYSTEM IN THE CONTEXT OF OXIDE BASICITY

The concept of basicity (acidity) plays an important role in the theory of oxide systems (slags in particulary). It is accepted that the basicity of oxides formed by metals from the same group of Periodic system (for example MeO) grows downwards along the group of Periodic system (say, from Mg to Ba), and acidity grows upwards. It is also accepted that MeO oxides are more basic than MeO_2 oxides. Similar to the neutralization reaction between acids and bases in water solutions, the reaction between basic and acidic (net-forming) oxides may be presented as $O^{2-} + O^0 = 2O^-$, where O^{2-} is a "free" oxygen ion, O^0 and O^- are "bridging" and "non-bridging" oxygen ions. Generally, it may be expected that the more is an oxide acidity, the lower is its activity coefficient in a basic solvent; and that with growth of oxide basicity its activity coefficient in an acidic solvent decreases. Such oxide system as CaO-SiO_2 is basic in the region close to CaO and acidic at high silica concentration. Therefore, there should be the range of compositions where the CaO-SiO_2 system is characterised as "neutral", and it may be expected that in this range of compositions the activity coefficients of oxides of one series (for example, MeO) will be close to one another despite the difference in their own basicities. Thus, analysis of activity coefficients of oxide solutes in the CaO-SiO_2 and other systems would be indicative in terms of basicity of these systems. In this work this analysis is performed for the activity coefficients of MeO ("basic") and MeO_2 ("acidic") oxides in the CaO-SiO_2 system.

Calculations were conducted by the MD method as described above. They include evaluation of change in the Gibbs free energy in the process of formation of CaO-SiO_2-MeO (MeO_2) solution.

The following notation is introduced for components of the solution: Ca - 1, Me - 2, Si - 3, and O - 4. Let us consider, for example, the calculation for a solution of MeO in pure CaO. The models of pure CaO contained 216 or 492 ions in basic cube with periodic boundary conditions. A dilute solution of MeO in CaO was formed by replacement of a few randomly selected Ca ions by Me ions (for example Mg). As a result of formation of the dilute MeO-CaO solution only B_{14} parameter of replaced Ca ions was changed to B_{24} (in this case $Z_1 = Z_2 = 2$); this resulted in the change of the mean energy <U(Me-O)>. The energy <U(Me-O)> was calculated as a function of $y = ln\ (B_{24}/B_{14})$ in the molecular dynamics experiment; then the change in the Gibbs free energy of oxide as a result of the replacement of n molecules CaO by n molecules MeO was found using equation (4). Finally, n replaced CaO molecules formed pure CaO oxide. Pure MeO oxide was taken at the same temperature and pressure as CaO.

The total Gibbs free energy of formation of MeO-CaO solution was calculated as:

$$\Delta G = \delta G - nG_0(\mathrm{MeO}) + nG_0(\mathrm{CaO}), \quad (5)$$

where G_0(MeO) and G_0(CaO) are the Gibbs free energies of pure MeO and CaO.

Using (4), the equation (5) can be presented as

$$\Delta G = \int_{y_1}^{y_2} [\,<U(\mathrm{Me\text{-}O})> - <U^0(\mathrm{Me\text{-}O})>]\ dy\ , \quad (6)$$

where $<U^0(\mathrm{Me\text{-}O})>$ is the mean value of U(Me-O) for pure MeO oxide. The Gibbs free energy of formation of solutions of MeO and MeO_2 in the CaO - SiO_2 system are calculated by the similar procedure.

The calculated Gibbs free energy ΔG is related to the thermodynamic activity of MeO in the dilute MeO-CaO-SiO_2 solution and activity of CaO in the original (before introduction of MeO) CaO-SiO_2 solution (standard states are pure oxides):

$$\Delta G = n(RT\ ln\ a_{MeO} - RT\ ln\ a_{CaO}), \quad (7)$$

or

$$ln\ a_{MeO}/a_{CaO} = \Delta G/nRT.$$

Numbers of MeO molecules in the solution and CaO molecules which were replaced by MeO are the same, and therefore, their molar fractions x are the same. Then, $a_{MeO}/a_{CaO} = (\gamma_{MeO}x_{MeO})/(\gamma_{CaO}x_{CaO}) = \gamma_{MeO}/\gamma_{CaO}$ (activity coefficients of transformed CaO molecules and CaO in the solution are the same) and

$$ln\ \gamma_{MeO}/\gamma_{CaO} = \Delta G/nRT \quad (8)$$

The calculations were carried out for 72 models of dilute solutions of MeO and MeO_2 in the liquid CaO-SiO_2 system of five compositions with CaO/SiO_2 ratio equal to 1/0, 2/1, 1/1, 1/2 and 0/1 at temperature of 2000 K. Pure CaO and orthosilicate $2CaO \cdot SiO_2$ were undercooled at this temperature. All models, except some solutions in pure CaO, contained about 500 ions in basic cube. The MD models of binary CaO-SiO_2 system described elsewhere[10], were chosen as initial states. The following potential parameters were used for solutions[3,5,9] : $B_{11} = B_{12} = B_{22} = B_{13} = B_{23} = 0$, $B_{33} = 2055.4$ eV, $B_{14} = 3283$, $B_{34} = 1729.5$, $B_{44} = 1500$, B_{24} was varied between 800 and 8885.1 eV, and all $R_{ij} = 29$ pm. The CaO-SiO_2-MeO solutions were formed replacing randomly a few (usually four) Ca^{2+} ions by Me^{2+} ions. To form CaO-SiO_2-MeO_2 solutions, a few (usually, also four) Si^{4+} ions were replaced by Me^{4+} ions. Then the relaxation was executed by the MD method using NPT - ensemble. The average pressure was close to zero. The contributions to the potential energies of inter-ionic interactions were calculated as described above. Due to the small number of ions Me in models, fluctuations of energy U_{24} during the relaxation process were rather high, 10-15 %. Main results obtained by the MD method for the models of CaO-SiO_2-MeO (CaO/SiO_2=1/1) and SiO_2-MeO_2 solutions are shown in Table I.

Table I Characteristics of models of MeO-$CaO\cdot SiO_2$ and MeO_2- SiO_2 dilute solutions at 2000 K

Model	B_{24}, eV	E_{total}, kJ/g-ion	U_{24}, kJ/mol	U^0_{24}, kJ/mol	ΔG, kJ/mol	ln s[1]
		Solutions of MeO in $CaO\cdot SiO_2$				
13	800	-3180.4	839.1	838.8	63.0	3.79
14	1441.4	-3176.5	577.2	633.9	49.4	2.97
15	1900	-3175.9	523.0	561.4	35.6	2.14
16	3283	-3174.5	403.3	470.0	0	0
17	4744.1	-3172.9	334.1	419.7	-26.5	-1.59
18	8885.1	-3170.9	298.1	349.9	-67.8	-4.08
		Solutions of MeO_2 in SiO_2				
55	850	-4148.8	3162.3	3407.1	73.0	4.39
56	1250	-4139.5	2755.6	2805.8	16.4	0.99
57	1729.5	-4132.5	2458.5	0	0	0
58	3500	-4120.7	1814.1	1709.2	37.0	2.22
59	5000	-4115.5	1572.6	1492.5	70.0	4.21
60	8000	-4110.3	1303.3	1287.0	92.6	5.57

[1] The ratio s is equal to $\gamma_{MeO}/\gamma_{CaO}$ for solutions No. 13-18 and $\gamma_{MeO2}/\gamma_{SiO2}$ for solutions No. 55-60

The calculated values of $ln\ \gamma_{MeO}/\gamma_{CaO}$ for the CaO-SiO_2 solution are given in Fig.1. In the binary CaO - MeO solution where γ_{CaO}=1, activity coefficient of MeO solute increases monotonously with the growth of the parameter B_{24} (that is with the increase in the MeO basicity). For hypothetical MeO oxides with $B_{24} \leq 800$ eV the deviations from ideality are negative and very large. MgO activity coefficient (B_{24} = 1441.4 eV) is also rather small (0.157). Activity coefficient of FeO in the dilute solution of CaO (B_{24} = 1900 eV) was found to be 0.41. For solutes SrO (B_{24} = 4744.1 eV) and BaO (B_{24} = 8885.1 eV) in CaO the deviations from ideality appear to be positive. From MgO to BaO activity coefficient of MeO in CaO grows in magnitude by approximately 16 times.

In the $2CaO\cdot SiO_2$ system, the ratio $s = \gamma_{MeO}/\gamma_{CaO}$ decreases with increasing B_{24} along the MeO series by about 75 times. The difference in behaviour of MeO solutes in the pure CaO and $2CaO\cdot SiO_2$ system is principle.

The change in $ln\ s$ with composition of the CaO - SiO_2 system at different B_{24} parameters is illustrated by Fig.1. It is seen that all curves cross a concentration axis in narrow interval between ~75 and 85 mol. % CaO. In this range, activity coefficients of MeO change rather slightly with parameter B_{24}. This indicates that in the CaO - SiO_2 system with ~ 80 mol. % CaO replacement of CaO by MeO gives very small change in the Gibbs free energy and that all MeO solutes behave similar in the thermodynamic sense regardless the basicity of pure MeO oxides. Therefore, the silicate with ~80 % CaO can be regarded as a neutral oxide. At higher CaO concentration the CaO-SiO_2 system behaves as bases, and at higher SiO_2 content it demonstrates the acidic properties. This agrees with conclusion derived by Masson[12] that orthosilicates $2MeO\cdot SiO_2$ are neutral.

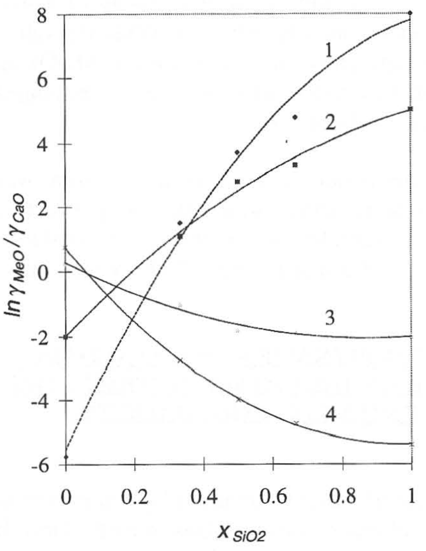

Fig.1. Ratio of activity coefficients $\gamma_{MeO}/\gamma_{CaO}$ as a function of SiO_2 molar fraction in the CaO-SiO_2 system at 2000 K for B_{24} parameters (eV): 1 - 800, 2 - 1441.4, 3 - 4744.1, 4 - 8885.1

The calculations for MeO_2 solutes in the CaO-SiO_2 system were carried out by the same procedure. Table I presents data for MeO_2 solutes in pure SiO_2. The Gibbs free energy of formation of the dilute MeO_2-SiO_2 solution is minimal at the value B_{24}= 1729.5 eV which corresponds to SiO_2. For all other compositions of the CaO-SiO_2 system the values ΔG change monotonously with B_{24} without extremal points. The peculiarity of MeO_2 solutions in pure SiO_2 may be explained by the fact that well ordered tetrahedral silica net is strongly deformed at embedding of solute ion as of larger size than Si ion (at B_{24}>1729.5 eV) as of lower size (at B_{24}< 1729.5 eV).

The ratii $\gamma_{MeO2}/\gamma_{SiO2}$ as functions of composition of the CaO - SiO_2 system at various B_{24} are shown on Fig.2. In this series the ratio of activity coefficients s increases monotonously with growth of B_{24} (that is with increase of the Me^{4+} size) at CaO concentration above 30 mol. %. The acidity of MeO_2 oxides increases with decreasing B_{24} parameter. This indicates that the CaO-SiO_2 solutions are basic at concentrations above 30 mol. %CaO. The behaviour of solutes in pure SiO_2 in this sense may be regarded as anormal. It means that the CaO-SiO_2 system does not reveal the properties of a neutral solution with respect to MeO_2 solutes.

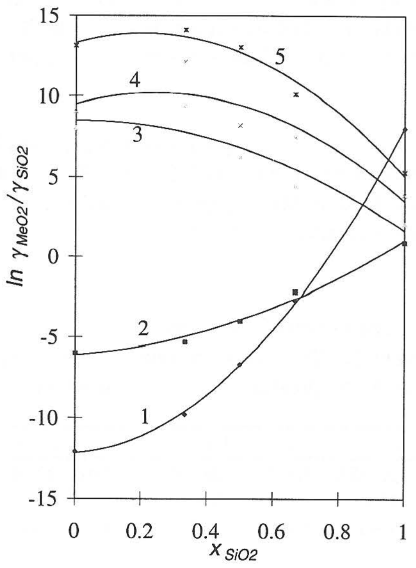

Fig.2. Ratio of activity coefficients $\gamma_{MeO}/\gamma_{SiO2}$ as a function of SiO_2 molar fraction in the CaO-SiO_2 system at 2000 K for B_{24} parameters (eV): 1 - 850, 2 - 1250, 3 - 3500, 4- 5000, 5 - 8000

It may be concluded that whether the oxide system, such as CaO-SiO_2, is basic, acidic or neutral with respect to solute element, depends upon the properties of the solute oxides. Thus, for example, the CaO-SiO_2 system with 50 mol.% CaO behaves as the acidic solution with respect to MeO solutes and as the basic system with respect to MeO_2 solutes. In this sense, the universal scale of basicity or acidity does not exist.

4. TITANIUM PARTITIONING BETWEEN Ti^{3+} AND Ti^{4+} VALENCY STATES IN THE CaO-SiO_2 SYSTEM

The MD method was used to calculate the Ti^{3+}/Ti^{4+} ratio in models of SiO_2, CaO·2SiO_2, CaO·SiO_2 and 2CaO·SiO_2. The method involves calculation of the Gibbs free energy ΔG of reaction (9) at oxygen partial pressure $p(O_2) = 1$ atm.

$$4\,Ti^{4+} + 2\,O^{2-} = 4\,Ti^{3+} + O_2\ (gas) \qquad (9)$$

Applying the Vant-Hoff equation

$$\Delta G = -RT\ ln\ K_a + RT\ ln\ \frac{p_{O_2} a^4_{Ti^{3+}}}{a^2_{O^{2-}} a^4_{Ti^{4+}}}\ , \qquad (10)$$

the equilibrium constant K_a for the reaction (9) at the given temperature can be calculated, and then, the Ti^{3+}/Ti^{4+} ratio can be determined.

Calculations were executed as follows. The Ca-Ti-Si-O system consisted of ~500 particles was placed in the basic cube with periodic boundary conditions (the length of cube edges was defined by the system density). The inter-ionic interactions were described by the Born-Mayer pair potentials (1). The simulation was conducted by the molecular dynamics method as described above. The models of SiO_2 (M1), CaO·2SiO_2 (M2), CaO·SiO_2 (M3) and 2CaO·SiO_2 (M4) created in work[10] were used as the initial states. Four randomly selected Si^{4+} ions were replaced by four Ti^{4+} ions. The less number of Ti ions would be too small because of large energy fluctuations for the interaction of Ti ions with other ions. On the other hand, the increase in the number of Ti atoms was also undesirable from view point of having the dilute solution in which the activity coefficient of titanium does not depend on the titanium concentration.

The reaction (9) was conducted in three stages. At the stage I the charge of each of four Ti ions was gradually diminished from 4 to 3 by the formula $Z(Ti) = 4 - \lambda$, where $\lambda = 0, 0.2, 0.4, 0.6, 0.8$, and 1.0 . Simultaneously, two oxygen ions (O^*) were recharged by the formula $Z(O^*) = 2(\lambda-1)$ to keep the system electro-neutral. Thus, when $\lambda = 0$ the system presents a solution of four Ti^{4+} ions (plus eight O^{2-}) in the CaO-SiO_2 oxide; at $\lambda = 1$ the systems turns into a solution of four Ti^{3+} ions plus two neutral oxygen ions O^0, plus six O^{2-} ions in the CaO-SiO_2 oxide of the same composition. At the end of the stage I of the reaction (9) the system involves two dissolved O^0 atoms instead of gaseous oxygen molecule.

At the stage II, the interaction parameters B_{ij} in the equation (1) for all pairs with O^* were diminished down to zero. This procedure makes atoms O^* to become free and to obey the ideal gas equation $pV = nkT$. This allows to calculate the pressure $p(O^*)$.

At the stage III, two "free" O^* atoms were transferred to the gaseous phase with formation of one O_2 molecule. These three stages complete the reaction (9).

The total Gibbs free energy of the reaction (9) is the sum of the Gibbs free energies ΔG_1, ΔG_2, and ΔG_3 for stages I, II, and III correspondingly. The value ΔG_3 was found using the standard thermodynamic tables. The Gibbs free energies ΔG_1 and ΔG_2 were calculated using molecular dynamics experiments and Equation (3).

Let us introduce the following notation for components of the Ca-Ti-Si-O system: 1- Ca^{2+}, 2 - Ti, 3 - Si^{4+}, 4 - O^{2-}, 5 - O^*. The B_{ij} and R_{ij} parameters of the potential (1) were assumed to be independent on the system composition. The R_{ij} parameter was taken to be equal to 29 pm for all ion pairs; the B_{ij} parameters were: $B_{11} = B_{12} = B_{22} = B_{13} = B_{23} = 0$, $B_{33} = 2055.4$ eV, $B_{14} = 3283.0$ eV, $B_{34} = 1729.5$ eV, and $B_{44} = 1500.0$ eV. Parameters B_{24}, B_{15}, B_{25}, B_{35}, B_{45} and B_{55} were determined as follows. In the initial state with $\lambda = 0$ ions O^{2-} and O^* are identical. In the final state of the stage

I, when $\lambda = 1$, all parameters B_{i5} for pairs with neutral O^0 atoms could be taken to be equal to 1500.0 eV as for the pair O^{2-} - O^{2-}; then, $B_{15} = 3283.0 - 1783\lambda$, $B_{35}= 1729.5 - 229.5\lambda$, $B_{45}= 1500.0$, $B_{55}= 1500.0$ eV.

To determine parameter B_{24} for the potential of interaction of titanium ions with oxygen, the diffraction data on the structure of SiO_2 -TiO_2 oxides were used. The structure of SiO_2 - TiO_2 glasses was studied by the EXAFS method in work.[14] All Ti ions had the charge +4, and the Ti-O distance was found to be 189-191 pm. In our calculations, the value $r_1 (Ti^{4+} - O^{2-}) = 189$ pm was taken.

Experimental data on the structure of oxide systems containing Ti^{3+} ion were not detected. The Ti^{3+} - O^{2-} distance was evaluated from the Goldschmidt radii for Ti^{4+} and Ti^{3+}, which are equal to 64 and 69 pm respectively. Their difference is 5 pm, thus the $r_1(Ti^{3+}$ - $O^{2-})$ distance was assumed to be 189+5= 194 pm.

Then, the B_{24} parameter was found as a fitting parameter to get distances $r_1 = 189$ pm at $\lambda = 0$ and $r_1= 194$ pm at $\lambda = 1$ in the MD model of the TiO_x-SiO_2 solution. The parameter B_{24} for the pair Ti^{4+} - O^{2-} was found to be 3218.32 eV and for the pair Ti^{3+} - O^{2-} it was equal to 2720.42 eV; therefore $B_{24} = 3218.32 - 497.9\lambda$ and $B_{25}= 3218.32 - 1718.32\lambda$ $(0 \leq \lambda \leq 1)$.

The B_{ij} parameters as functions of λ were introduced arbitrary. However, this has no effect on the results of calculation, because the ΔG value does not depend on the integration path in (3), it is only important to fix the B_{ij} values at $\lambda = 0$ and $\lambda = 1$.

Finally, all parameters of pair potentials (1) are specified, and the derivative of the potential energy, U, with respect to variable λ, $dU/d\lambda$, for the stage I may be found as follows:

$$dU/d\lambda = -\frac{1}{Z_2}[E_{12} + 2E_{22} + E_{23} + E_{24} + E_{25}]Coul + \\ + \frac{2}{Z_5}[E_{15} + E_{25} + E_{35} + E_{45} + 2E_{55}]Coul + \\ + \sum \frac{B_{ij}(\lambda = 1) - B_{ij}(\lambda = 0)}{B_{ij}(\lambda)} U_{rep}(ij) \quad (11)$$

The first two sums in equation (11) include Coulomb interactions for different pairs, the last sum contains the terms which describe the ion cores repulsion ($U_{rep}(ij)$ is the repulsion energy of ions i and j). This sum at the stage I includes only terms for 24, 15, 25, and 35 pairs. Calculated derivatives $dU/d\lambda$ for the CaO - SiO_2 system of different compositions with λ=0; 0.2; 0.4; 0.6; 0.8; and 0.95, were used in equation (3) to find ΔG_1 values.

An example of calculation for solution of TiO_x in $2CaO{\cdot}SiO_2$ at 1823 K is shown in Table II. The Gibbs free energy for the I stage also contains the contribution due to the transfer of 4 electrons from two O^{2-} ions to four Ti^{4+} ions. This contribution is equal to 186.48 eV (= $-4I_3 + 2Q$, where I_3 is an ionization potential of Ti^{3+} and Q is an affinity of O atom to 2 electrons). The total energy ΔG_{10} of the reaction at the stage I is equal to ΔG_1-86.48 eV. The values of ΔG_{10} for models M1 - M4 are shown in the Table III. The statistical scattering of these data is not too high, about 2.6 eV.

At the stage II all B_{i5} parameters were steadily diminished to zero in accordance with formula $B_{i5} = 1500(1 - \lambda)$. Calculated values of ΔG_2 are given in Table III. They are in rather narrow interval of 1.9 - 2.1 eV.

Table II The model of the dilute TiO_x- $2CaO{\cdot}SiO_2$ solution at different Ti^{3+}/Ti^{4+} ratio (different λ); l is a length of a basic cube, p - pressure, r_{24} - Ti - O^{2-} distance

λ	0	0.2	0.4	0.6	0.8	0.95
l, A	20.375	20.326	20.384	20.350	20.410	20.390
p, Mpa	-38	103	-47	56	4	-10
r_{24}, A	1.88	1.90	1.91	1.93	1.94	1.97
$U_{rep}(ij)$, eV						
ij = 24	77.192	71.689	65.964	60.565	54.407	48.979
15	7.872	5.490	3.128	1.811	0.907	0.309
25	3.877	1.805	1.200	0.300	0.003	0.001
35	0.004	0.004	0.003	0.005	0.016	0.015
E_{coul}, eV						
12	8877.96	8454.36	8016.42	7604.40	7099.12	6792.60
22	173.52	155.14	138.64	124.69	112.34	101.90
23	8399.64	8015.26	7554.02	7139.23	6702.93	6408.00
24	-18126.4	-17308.3	-16359.6	-15368.8	-14535.0	-13697.4
15	-2270.05	-1816.79	-1348.76	-897.01	-447.38	-111.14
25	-164.08	-120.79	-84.80	-50.31	-20.30	-5.01
35	-2082.16	-1666.84	-1248.57	-831.00	-411.80	-103.50
45	4410.07	3528.94	2648.33	1756.85	873.35	219.16
55	6.96	4.47	2.45	1.13	0.31	0.02
$dU_{rep}/d\lambda$	-18.3	-15.9	-13.9	-12.0	-10.5	-9.2
$dE_{Coul}/d\lambda$	258.8	254.0	200.0	173.3	192.6	106.8
$dU/d\lambda$	240.5	238.1	186.2	161.3	182.1	97.6

Table III The Gibbs free energy of reaction (9) and equilibrium Ti^{3+}/Ti^{4+} ratio for CaO - SiO_2 - TiO_x models at 1823 K and different oxygen pressures (atm) calculated with the Born-Mayer potential

Model	ΔG_{10} eV	ΔG_2 eV	ΔG_3 kJ	ΔG kJ	ln Ti^{3+}/Ti^{4+}		
					$p(O_2)=$ 1	$p(O_2)=$ 10^{-4}	$p(O_2)=$ 10^{-9}
M1-1	-2.9	-1.88	-387.1	-850	14.0	16.3	19.2
M1-2	-1.2	-1.88	-387.1	-686	11.3	13.6	15.9
M2	-3.0	-1.99	-388.2	-871	14.4	16.7	19.6
M3	-3.1	-2.09	-387.2	-879	14.5	16.8	19.7
M4-1	-1.7	-1.88	-386.6	-734	12.1	14.4	17.3
M4-2	-7.0	-1.88	-386.6	-1245	20.5	22.8	25.7
M4-3	-4.3	-1.88	-386.6	-985	16.2	18.5	21.4
M5	-1.2	-1.96	-387.3	-686	11.3	13.6	16.5

In the stage III, the reaction $2O = O_2$ takes place. The values ΔG_3 at 1823 K are also shown in Table III. They are found to be equal to -387 ± 1 kJ/mol O_2 (about -4 eV).

The total Gibbs free energy ΔG for the reaction (9) calculated as a sum $\Delta G_{10}+\Delta G_2+\Delta G_3$ is presented in Table III. The data for models 1-1 and 1-2, and 4-1, 4-2, and 4-3 were obtained in different runs of models 1 and 4 correspondingly.

The activity coefficients of titanium ions in dilute solutions do not depend on the titanium concentration. Then, the equilibrium constant K_a could be found and titanium partitioning between Ti^{3+} and Ti^{4+} valency states in the redox equilibrium calculated as

$$\ln[\frac{c(Ti^{3+})}{c(Ti^{4+})}]_{equi} = -\frac{\Delta G}{4RT} - \frac{1}{4}\ln p(O_2) \qquad (12)$$

The calculated ratii $s = c(Ti^{3+})/c(Ti^{4+})$ are shown in Table III. An error in the ΔG calculations with potentials (1) can be estimated to be 1-2 eV, this gives an error of 1.6-3.0 for the values of $\ln Ti^{3+}/Ti^{4+}$.

To determine the effect of titanium concentration on results of the MD simulation, the titanium concentration was increased to 20 Ti ions in a model. This changed ΔG values only by about 2 eV and had no visible effect on the titanium distribution between 3+ and 4+ valency states.

At oxygen potential 1 atm, the values $\ln s$ were found to be 14.3 ± 3.0 for very wide range of the $CaO\text{-}SiO_2$ compositions, from pure SiO_2 to $2CaO{\cdot}SiO_2$ (Table III). In all models titanium predominantly exists as Ti^{3+}, what contradicts to the experimental data.[13] This implies that the Born-Mayer potential is not adequate for the MD modelling of titanium redox reaction in the $CaO\text{-}SiO_2$ system.

The MD simulation was also conducted using the Lennard-Jones potential to describe interaction of titanium with O^{2-} ion and O^* atom (pairs 2-4 and 2-5). The Lennard-Jones potential has the following form:

$$u_{ij}(r) = 4\, B_{24}\, [(r_o/r)^{12} - (r_o/r)^{6})] \qquad (13)$$

The coefficient B_{24} was found to be 1.00 + 0.842λ eV. At this B_{24} value, the $r_1(Ti^{4+} - O^{2-})$ distance is 189-190 pm for all compositions of the $CaO\text{-}SiO_2$ system. The calculated $Ti^{3+} - O^{2-}$ distance was about 200 pm instead of expected 194-195 pm. However, experimental data for the $Ti^{3+} - O^{2-}$ pair are unknown, and this is a reasonable result.

The models with the ratii CaO/SiO_2 = 0/1, 1/2, 1/1, and 2/1 are designated now as M11, M21, M31 and M41 respectively. Results obtained with the potential (13) are shown in Table IV. They are in better agreement with the experimental data[13] than results obtained with the Born-Mayer potential. Particularly, the Ti^{4+} valency state dominates at $p(O_2)$ = 1 atm in models M31 and M41 as it observed experimentally. The effect of slag basicity is also more profound, increase in the slag basicity stabilises the Ti^{4+} valency state.

Table IV The Gibbs free energy of reaction (9) and equilibrium Ti^{3+}/Ti^{4+} ratio for $CaO - SiO_2 - TiO_x$ models at 1823 K and different oxygen pressures calculated with the Lennard-Jones potential for Ti-O pairs

Model	ΔG_{10} eV	ΔG_2 eV	ΔG_3 kJ	ΔG kJ	$\ln(Ti^{3+}/Ti^{4+})$		
					1 atm	10^{-4} atm	10^{-9} atm
M11	2.7	-1.9	-387	-310	5.1	7.4	10.3
M21	5.1	-2.0	-388	-89	1.5	3.8	6.7
M31	7.1	-2.1	-387	95	-1.6	0.7	3.6
M41	6.1	-1.9	-387	18	-0.3	2.0	4.9

5. CONCLUSION

Molecular dynamics is an effective method of investigation of structure and properties of oxide systems. The approximation of the ionic model with simple pair potential like the Born-Mayer potential is appropriate for systems with relatively high degree of ionization (approximately, above 50%) including pure silica. However, in the case of P_2O_5, the difference in electronegativity of oxygen and phosphorous is rather small, and ionization is only 39% (according to Pauling). For such systems MD simulation with the Born-Mayer potential does not give satisfactory results.

The thermodynamic analysis of oxides performed in this work involved the calculation of difference in the Gibbs free energy of the oxide system in two different states in accordance with equation (3). This method was employed to calculate (i) thermodynamic properties of oxides of the MeO_2 series; (ii) to analyse activity coefficients of oxides of MeO and MeO_2 series in the $CaO\text{-}SiO_2$ system in context of the basicity of this system, and (iii) to calculate titanium distribution between Ti^{3+} and Ti^{4+} valency states in the dilute $CaO\text{-}SiO_2$ solutions.

It was suggested that basicity of the $CaO\text{-}SiO_2$ system my be characterised on the basis of thermodynamic activities of solutes of MeO or MeO_2: in the area of basic solution activity coefficients of MeO solutes should increase with increasing basicity of solute, for example, from MgO to BaO, while in the acidic solutions activity coefficients of MeO solutes are expected to decrease from MgO to BaO. It was revealed that with respect to oxides of MeO series, the $CaO\text{-}SiO_2$ system may be regarded as a basic solution when $x_{CaO}>0.8$, neutral at $x_{CaO}\cong 0.8$ and acidic when $x_{CaO}>0.8$. However, with respect to oxides of MeO_2 series, the $CaO\text{-}SiO_2$ system may be regarded as a basic solution at $x_{CaO}>0.3$. This indicates, that with respect to the solute oxides, the universal scale of basicity does not exists.

The MD simulation of titanium redox equilibrium with the Born-Mayer potential predicts that titanium in the wide range of $CaO\text{-}SiO_2$ compositions from pure SiO_2 to $2CaO{\cdot}SiO_2$ predominantly exists as Ti^{3+} even at oxygen partial pressure of 1 atm. This contradicts to the experimental data. Better results were obtained with the use of the Lennard-Jones potential. The selection of the potential to describe the inter-ionic interactions in the oxide system is a crucial element of the MD simulation.

ACKNOWLEDGEMENT

Financial support for this work was provided by the Australian Research Council and the University of New South Wales.

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