New Insights into the Traditional Charge Compensation Theory: Amphoteric Behavior of TiO$_2$ under the Guidance of Supply–Demand Relationship

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ABSTRACT: Polymerization degree theory and traditional charge compensation theory are the most fundamental principles to understand the structure and properties of oxide melts. It can well explain the behavior characteristics of acidic oxides and basic oxides in a melt. However, the amphoteric behavior of oxides cannot be explained well by these two theories. Herein, the octahedral connection mode and the behavior of the amphoteric transition of TiO$_2$ are analyzed by molecular dynamics simulation, and then, a calculation model which can quantitatively calculate the amphoteric transition of the oxide is established by analyzing a large number of data. On the basis of the model, a novel theory of supply and demand is put forward, which can explain the amphoteric transition behavior of oxides very well. To a great extent, the supply and demand theory makes up for the deficiency of the atomic structure theory of oxide melts and provides mechanism explanation and model prediction for the oxide amphoteric transformation behavior.

1. INTRODUCTION

Ti$^{4+}$ ions tend to form TiO$_6$ octahedrons, and Si$^{4+}$ ions tend to form SiO$_4$ tetrahedrons. The stability of the SiO$_4$ tetrahedron is much higher than that of the TiO$_6$ octahedron. When the system is surrounded by certain ions, the TiO$_6$ octahedrons will disappear. Therefore, the stability of the TiO$_6$ octahedron also reflects the proportion of network modifier components in the system. In addition, there are many kinds of oxides in the melt and the production is pretty huge (more than one billion tons per year), which makes it extremely important to clarify the behavior characteristics of various oxides in the oxide melt. The structure of silicate melts provides a basis for understanding the relations between the structure and the physical, chemical, and thermal properties of the melts. The discovery and utilization of silicate melt resources have been widely concerned. In addition to the silicate melt industry, the formation and evolution conditions of magma on the earth and terrestrial planets also need to clarify the atomic structure and physical and chemical properties of silicate melt. The metal cations in silicate melts may be divided into network formers and network modifiers, and the transition between the property of network formation and the property of network destruction is called amphoteric transition.

There are generally two types of octahedral connection of perovskite oxide with ABO$_3$ structures, namely, corner-sharing connection and edge-sharing connection. In the CaO–SiO$_2$–TiO$_2$ (CST) systems, TiO$_2$ is regarded as a network former when the content of TiO$_2$ exceeds 28 wt % in the CST system. As the pressure increases, the bond-lengths of Ti–O and Ti–O in TiO$_6$ octahedrons decrease with different speeds and equal to each other at about 22.0 GPa, forming a normal octahedron. Polymerization degree theory and traditional charge compensation theory are the most fundamental principles to understand the structure and properties of oxide melts. It can well explain the behavior characteristics of acidic oxides and basic oxides in a melt. However, the amphoteric behavior of oxides cannot be explained well by these two theories. Herein, the octahedral connection mode and the behavior of the amphoteric transition of TiO$_2$ are analyzed by molecular dynamics simulation, and then, a calculation model which can quantitatively calculate the amphoteric transition of the oxide is established by analyzing a large number of data. On the basis of the model, a novel theory of supply and demand is put forward, which can explain the amphoteric transition behavior of oxides very well. To a great extent, the supply and demand theory makes up for the deficiency of the atomic structure theory of oxide melts and provides mechanism explanation and model prediction for the oxide amphoteric transformation behavior.

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charge compensation theory\textsuperscript{12,13} are the most fundamental theories to explain the structure of oxide melts. Polymerization degree theory is based on the microscopic calculations of the intermolecular structure of dense polymer melts with the nonperturbative continuum theory.\textsuperscript{10,11} The degree of polymerization theory is based on the complexity of the system’s atomic structure, the use of melt activity, ion distribution, and other properties to construct a function that predicts the thermodynamic properties of the melt.\textsuperscript{10,11} At the early development of the establishment of the degree of polymerization theory, only the binary system of SiO\textsubscript{2}–MO \textsuperscript{15,16} (M is a metal element) was studied and focused on the prediction of thermodynamic properties. Therefore, the degree of polymerization theory does not apply to the amphoteric behavior of oxides.\textsuperscript{14} When the Si\textsuperscript{4+} ions in the center of the SiO\textsubscript{4} tetrahedrons in the melt are replaced by Al\textsuperscript{3+} ions or Na\textsuperscript{+} ions, the polyhedral structure will generate excess negative charges. The charge compensation theory assumes that the alkaline earth metal oxide cations would balance the excess negative charges. The Al\textsubscript{2}O\textsubscript{3} content of the system studied at the initial stage of the establishment of the charge compensation theory has not reached the turning point of the amphoteric transition. Therefore, the charge compensation theory does not possess a good role in explaining the amphoteric behavior of oxides. These two theories can well explain the behavior characteristics of acidic oxides\textsuperscript{15,16} and basic oxides\textsuperscript{17–19} in melts. The latest research results showed that Al\textsubscript{2}O\textsubscript{3} and B\textsubscript{2}O\textsubscript{3} represent an obvious amphoteric behavior in oxide melts.\textsuperscript{20} It should be emphasized that the amphoteric transition of oxide refers to the transition between the network former and network modifier. However, the amphoteric behavior of oxides cannot be well explained by both the polymerization degree theory and charge compensation theory.

On the basis of confirming that TiO\textsubscript{2} does have an obvious amphoteric behavior, through the analysis of the radial distribution functions (RDFs), coordination numbers (CNs), bond angle, and the statistical analysis of a large number of data, a set of calculation model of supply and demand balance is established, and a novel theory of oxygen supply and demand balance of oxygen is proposed. This model and theory can essentially explain the causes of the oxide amphoteric behavior and quantitatively calculate and predict the turning point of amphoteric transformation.

2. SIMULATION METHODS

Initially, the software PACKMOL\textsuperscript{23} was employed to do the simulations. Subsequently, the software LAMMPS package [version 2019]\textsuperscript{24} was employed, with a time step of 1 fs. The long-range Coulomb interactions were evaluated by the Ewald summation method with a cut-off distance of 10 Å and the corresponding cut-off distances for the short-range Born and van der Waals was chosen to be 8.0 Å. Initially, the system was heated to 5000 K for 100 ps, then cooled down to 2273 K within 322.7 ps, and then kept at 2273 K for more than 500 ps. This cycle was repeated to ensure equilibrium of the system. After reaching equilibrium, the system was kept system at 2273 K and data were collected. In order to ensure a long enough time to collect data, the whole system was balanced and iterated at 2273 K for 1 ns.

All molecular dynamics simulations were carried out using the Born Mayer Huggins model.\textsuperscript{25,26} This potential can be written as

\[ U_{ij} = \frac{Z_i^* Z_j^* e^2}{4 \pi \varepsilon_0 r_{ij}} + A_{ij}^* \exp\left(-B_{ij}^* r_{ij}\right) - \frac{C_i^* C_j^*}{r_{ij}^6} + \frac{D_i^* D_j^*}{r_{ij}^8} \]  

(1)

The first term on the right side of the equation is long-term Coulomb potential, the second term is the van der Waals forces, and the latter two terms represent repulsive forces. Where i and j represent two interacting atoms, respectively; \(Z_i\) and \(Z_j\) are the effective charge numbers of atoms i and j, respectively. The \(r_{ij}\) is the interatomic distance between atoms i and j, \(A_{ij}\), \(B_{ij}\), \(C_i\), \(C_j\), \(D_i\), and \(D_j\) are the special parameters between atomic pairs. Various parameters used have been listed in Table S2.

3. RESULTS AND DISCUSSION

3.1. Structural Factor Curve. In order to verify the simulation, the total structural factor curve of the sample is drawn, as shown in Figure 1. In addition, the high-temperature neutron diffraction experimental result of Hennet et al.\textsuperscript{27} is also plotted in Figure 1. The high-temperature neutron diffraction experimental results and the structural factor curve obtained by the simulation overlap well with each other, which also proves the effectiveness of the simulation.

![Figure 1](https://doi.org/10.1021/acsomega.2c02252)  
Figure 1. Comparison of the total structural factor of sample B4T4 (sample number details shown in the Supporting Information) with the results of the high-temperature neutron diffraction experiment. The SiO\textsubscript{2} content in the Hennet’s experimental system is 27 wt % which is similar to the that of sample B4T4 (27.78 mol % SiO\textsubscript{2}). The test temperature for Hennet’s molten systems is 1823 K.

3.2. Local Atomic Structure. The distribution state of TiO\textsubscript{6} octahedron in the system is shown in Figure 2a. It can be estimated that the volume of the octahedron is about 9.89 (Å\textsuperscript{3}) and that of the tetrahedron is about 2.10 (Å\textsuperscript{3}) according to the bond length (Ti–O 1.95 Å,\textsuperscript{28} Si–O 1.6 Å,\textsuperscript{29} Figure S1). The large difference in volume makes the Ti–O bond angle only 74.5° (Figure S6d), which will produce a larger bond angle tension and destroy the stability of the structure. It should be emphasized that the atoms and their display colors are in one-to-one correspondence in all figures, that is, Si-blue, Ca-silver, Ti-yellow, and O-red.

The previous results indicate that the TiO\textsubscript{6} octahedron tends to be connected with another TiO\textsubscript{6} octahedron. Meanwhile, a large number of structures as shown in Figure 2b will be produced. With the increase of TiO\textsubscript{2}, the structure in Figure 2c(A) gradually changes to the structure in Figure 2c(B). When the oxygen atoms of the system cannot meet the
oxygen atom number demanded by the corner-sharing connection, the TiO₆ octahedrons are forced to share two BO atoms to reach the equilibrium state of the system, thus producing the two connection forms in Figure 2c. Figure 2d(A) shows that the Ti−O−Ti bond angle is reduced from 148.5° to 131° by TiO₆ octahedrons pulling as the TiO₂ content increases (Figure 4a). It can be seen that there is no significant change of the Ti−O−Ti bond angle in Figure 2d(B).

3.3. RDFs and CNs. It can be found from the partial enlarged view in Figure 3a that with the increase of TiO₂ contents, the bond length of Ti−O chemical bonds in TiO₆ octahedrons tends to decrease, indicating that both the bond energy and strength increase. The same trend appears in Figure S1. The bond lengths of all samples in this simulation are depicted in Figure 3a, due to the large volume of TiO₆ octahedron, the system will become saturated with TiO₂ content, and the Ti−O−Ti bond angle will obviously decrease during the attraction of external cations to BO atoms and the mutual extrusion of TiO₆ octahedrons itself. It can be seen from Figure 4b that the influence of basicity on the bond angle ② is just the opposite. As the internal stress of octahedron, bond angular tension is related to the extension direction of electrons. Ca²⁺ ions are used to stabilize the charge balance of an octahedron. When Ca²⁺ ions are sufficient, the bond angular tension of the octahedron will be partially eliminated. Therefore, the bond angle will increase with the increase of basicity. Further details of more bond angles are shown in Figure S4.

3.4. TiO₆ Octahedron Bond Angle and Connection Form. It can be seen from Figure 4 that there are four obvious sizes of Ti−O−Ti bond angles in the simulated system, namely, ①, ②, ③, and ④. On the premise that there are enough cations in the system, oxygen ions would not form chemical bonds with each other. According to the analysis of O−O RDFs (Figure S3), the calculated Ti−O−Ti bond angle should be greater than 80° when the distance between O−O reaches the limit value. Therefore, only ①, ③, and ④ are true and effective. For the bond angle ④ depicted in Figure 3a, due to the increase of basicity mainly leads to the increase of Ca²⁺ ions in the system, while Ca²⁺, as the charge compensation ion of the octahedron structure, is directly related to the charge stability of octahedrons, affecting the structural stability of the octahedrons.

3.5. Supply−Demand Relationship Calculation Model. BO is defined as the middle oxygen atom connecting two polyhedrons. It should be noted that both polyhedrons can only form one chemical bond with this BO atom. The number of BO atoms in the system can directly reflect the complexity of the atomic structure of the system. Therefore, the components that can increase the BO content of the system are regarded as the network forming components and increase the degree polymerization; the components that can reduce the BO content of the system are regarded as the network modifier components and reduce the degree of polymerization of the system. In summary, the turning point of the BO curve is the turning point of the transition of the properties of the components.

As shown in Figure 5a, when the basicity is 1.7, the BO⁵⁺ contents of the system increase with the increase of TiO₂ contents. Under these conditions, the role of the Ti⁴⁺ ion in the system is to form TiO₆ octahedrons and increase the BO contents of the system. The concentration of BO is always higher for acid melts. When the basicity decreases to 0.5, the BO of the system under the same TiO₂ content is higher than when the basicity is 1.7. There will be more Ca²⁺ ions in the system with high basicity, and Ca²⁺ ions will destroy the BO structure of the system, making the BO content of the system with 1.7 basicity lower than that of another system with 0.5 basicity. However, the BO of the system with 0.5 basicity decreases with the increase of TiO₂ contents. In this case, the
O$_2^-$ ions in the system cannot meet the demand from all cations in the polyhedral structure. This is because TiO$_2$, as a amphoteric oxide, possesses an electronegativity weaker than that of SiO$_2$. Due to the influence of Si$^{4+}$ ions and the global structural balance$^{36}$ (stability and balance of the whole system network structure) of the system, most of TiO$_2$ has to change from capturing O$_2^-$ ions to providing O$_2^-$ ions, which makes the BO contents of the system decrease at all TiO$_2$ values. Just as the basicity is low (Figure S2), the coordination number decreases with the increase of the TiO$_2$ content. The decrease of the coordination number is due to the appearance of TiO$_{1x}$ ($x < 6$) type structure in Figure 2a. As the basicity increases from 0.5 to 0.9 and 1.3, the O$_2^-$ ion concentration in the system basically meets the needs of polyhedron formation when the content of TiO$_2$ is low. Therefore, the BO contents of the system will first show an upward trend. However, when the TiO$_2$ content exceeds the maximum load of the system (a limit when all Ti$^{4+}$ ions can be allocated to the value of sufficient O$_2^-$ ions), the excess Ti$^{4+}$ ions begin to interact with other polyhedral structures because they cannot distribute O$_2^-$ ions, trying to compete for O$_2^-$ ions, resulting in the decrease of BO contents (Figure 5b).

The behavior just observed suggests the development of a calculation model of oxide amphoteric transformation (more details in the Supporting Information). There are three basic facts or assumptions in this model. First: the oxygen ion is the only negative charge carrier of the system. The balance between supply and demand of oxygen ions, $\Delta N(O)$, is the

Figure 3. RDFs and CNs under different TiO$_2$ contents and basicity. The first peak of each graph in figure is the most probable bond distance of the corresponding ion-pair, which is used to estimate the corresponding bond length. The first peak in figure (a) is enlarged and the vertical lines perpendicular to the abscissa axis in the enlarged view highlight the peak value under the corresponding RDFs. It should be emphasized that $B$ represents the basicity ($\text{CaO/\text{SiO}_2}$, mol %): (a) the RDFs of Ti$^-$O atoms ($B = 0.9$); (b) Ti$^-$O bond length under different TiO$_2$ contents and basicity; (c) the CNs ($B = 0.9$); and (d) the CNs under different TiO$_2$ contents and basicity.

Figure 4. Change situation of Ti$^-$O$^-$Ti bond angle under different TiO$_2$ contents and basicity surroundings. The atomic structure corresponded to the bond angle has been drawn in each figure: (a) change of bond angle with TiO$_2$ contents when basicity is fixed at 0.9; (b) change of bond angle with basicity when TiO$_2$ content is fixed at 35 wt %.
The core of the supply-demand relationship model is to break the complex network structure of the system (as shown on the right side of Figure 6a). Through $N(O)_{\text{demanded}}$, the number of equivalent oxygen atoms demanded by the polyhedron in the system can be clarified, then defining $N(O)_{\text{supplied}}$ to calculate the number of equivalent oxygen atoms that the system can supply. The difference is the balance between the supply and demand. First, we equate all initial oxygen atoms as BO atoms, and two polyhedrons share a BO atom. Therefore, the equivalent oxygen atom that the system can supply is the product of twice the initial oxygen atoms and a limit factor. It should be emphasized that the initial oxygen atom is the number of oxygen atoms when the system is set; however, not all oxygen atoms in the system are BO atoms, so the limit factor $R$ is used for correction.

Figure 5c is the result of the supply-demand model, in which the calculation result of $R$ is 0.93 (more details in the Supporting Information). In Figure 5c, there are two zero points of $\Delta N(O)$, which are two curves with basicity values of 0.9 and 1.3. Remarkably, the position of these points coincides with the turning point of BO in Figure 5a, which validates the theory of supply and demand and amphoteric transformation in existing publications.21,22

### 3.6. Supply–Demand Relationship Theory and Essential Mechanism

Based on Figure 6a, there are three situations regarding the supply-demand model, as shown in Figure 6b−d. When the number of free oxygen ions supplied by the system is larger than that demanded by polyhedral

\[ \Delta N(O) = N(O)_{\text{supplied}} - N(O)_{\text{demanded}} \]  

(2)

In which $\Delta N(O)$ is the function of oxygen atoms supplied and demanded. $N(O)_{\text{supplied}}$ and $N(O)_{\text{demanded}}$ represent the number of equivalent oxygen atoms supplied and demanded in the supply-demand relationship, respectively.

\[ N(O)_{\text{supplied}} = 2 \times R \times N_O \]  

(3)

In which $N_O$ represents the initial number of oxygen atoms. $R$ represents the limit factor, that is, the maximum ratio of all oxygen atoms equivalent to BO. The basic idea of $R$ is that all types of oxygen atoms in all samples are assumed to be BO, and then, the percentage of all samples is taken as an average value. The NBO is equivalent to 0.5 BO, and the TO is equivalent to 1.5 BO. Data statistics of NBO, BO, and TO are performed for all samples, and the equivalent calculation in eq 4 is performed.

\[ R = \frac{\sum (0.5 \times P_{\text{NBO}} + P_{\text{BO}} + 1.5 \times P_{\text{TO}})}{N_{\text{sample}}} \]  

(4)

In which $N_{\text{sample}}$ represents the sample size. The larger the sample size, the closer the limit factor is to reality. $P_{\text{NBO}}, P_{\text{BO}}$, and $P_{\text{TO}}$, respectively, represents the percentage content of NBO, BO, and TO in the sample.

\[ N(O)_{\text{demanded}} = \sum (N_i \times P_i \times i) \]  

(5)

In which $N_i$ is the total number of cations corresponding to different coordination structures. $P_i$ is the percentage content, and the $i$ is the coordination number of polyhedrons.

The concentration of polyhedrons in the system can be clarified as the turning point of BO in Figure 5a, which validates the calculations in the model. By taking parameters from different systems, the turning point position of the corresponding system could be calculated and predicted. As shown in Figure S6, it can be proved that the supply-demand model is also applicable to the amphoteric transformation in existing publications.21,22

### Figure 5

Concentrations of various types of oxygen under different TiO$_2$ contents and basicity: (a) effect of basicity and TiO$_2$ contents on BO contents; (b) the unification of local octahedral structural changes and global BO content changes. $\bigcirc$ represented that the non-bridge oxygen (NBO)$^{14}$ transforms into BO, $\bigcirc$ represented that corner-sharing transforms into edge-sharing, and $\bigcirc$ represented that edge-sharing transforms into tri-cluster; and (c) quantitative calculation of supply and demand relationship of oxygen atoms in the system.

### Figure 6

Theory of supply and demand and amphoteric transformation of TiO$_2$: (a) oxygen atoms supplied by the system and oxygen atoms demanded by the network structure, the demand of oxygen atoms in the relationship between supply and demand is determined by the coordination polyhedrons and the ratio of different coordination structures; (b−d) the difference between the oxygen atoms supplied by the system and the oxygen atoms demanded by the network structure.
connections, Ti$^{4+}$ ions perform as network forming, increasing the BO content and polymerization degree of the system (Figure 6b). With the increase of TiO$_2$, the octahedral angle connection structure will rotate and the connection gradually changes from corner-sharing to an edge-sharing connection structure, until the free oxygen ions supplied by the system balance the oxygen number required by the octahedral edge connection structure (Figure 6c). At this point, if TiO$_2$ continues to increase, the TiO$_x$ ($x < 6$) structure in Figures 2a and 6d will be produced, and even free Ti$^{4+}$ ions will appear. Combined with the previous calculation model of amphoteric transition, it can be seen that when the number of free oxygen ions supplied by the system is larger than the number of oxygen ions demanded by simple chain structure, both acidic oxides and amphoteric oxides in the system act as network forming components, and conversely, amphoteric oxides or oxides with weak electronegativity (significantly smaller than the electronegativity of silicon, which is 1.8$^{37,38}$) will change from network formers to network modifiers. However, the essence of this destruction is still to compete with the existing network structure for oxygen ions, resulting in the destruction of the network structure.

According to the analysis of Figures 5 and 6, a theory suitable for the amphoteric transformation of melt atomic structure is proposed. The principle is that the essence of oxide amphoteric transformation (from network former to network modifier) is that the supply of oxygen atoms cannot meet the demand of the oxygen atoms to achieve sufficient polyhedral connections. Therefore, the oxides with an electronegativity demand of the oxygen atoms to achieve su-

amphoteric transformation (from network former to network structure is proposed. The principle is that the essence of oxide suitable for the amphoteric transformation of melt atomic structure but also other certain properties of the melt. Through the previous analysis, it can be known that when the value of R or B is small, Ti$^{4+}$ ions act as network modifiers corresponding with a decrease of viscosity. In Figure 7a, when the value of R is greater than 1, it can be clearly observed that the viscosity of the system increases with the increase of TiO$_2$, as shown by the curves in Figure 7b with B values at 1.3 and 1.7. When the value R or B is larger, Ti$^{4+}$ ions act as network formers, increasing the BO structure of the system, corresponding to the increase in viscosity. On the one hand, TiO$_2$ ions could increase the BO structure and increase the viscosity of the system; on the other hand, Ti$^{4+}$ ions could destroy the existing [SiO$_4$]−[SiO$_4$] structure of the system, generate [SiO$_4$]−[TiO$_4$] structure, and reduce the viscosity of the system. When the TiO$_2$ content is less than 20 wt %, Ti$^{4+}$ ions possess a stronger ability to reduce the viscosity than to increase the viscosity of the system; when the TiO$_2$ content is higher than 20 wt % and less than 30 wt %, Ti$^{4+}$ ions possess the stronger ability to increase the viscosity than to reduce the viscosity of the system. In addition, when the TiO$_2$ content exceeds 30 wt %, both opposite effects result in a decrease in the viscosity of the system.

4. CONCLUSIONS

In summary, it can be seen that TiO$_2$ does have the ability to show amphoteric behavior. When the basicity of the system is 0.9 and 1.3, the content of TiO$_2$ is over 20 and 25 mol % respectively, the amount of oxygen atoms that can be supplied by the system cannot meet the demand of octahedral formation of all Ti$^{4+}$ ions, so excessive Ti$^{4+}$ acts as the network destruction component and attacks other polyhedral structures. Through the analysis of RDFs, CNs, bond angle, and a large amount of data analysis, a set of calculation models can quantitatively calculate and predict the turning point of the amphoteric transition of oxides is established, and the theory of supply and demand of the melt atomic structure is proposed. When $\Delta N(O)$ is always greater than or less than zero, there is no amphoteric transformation process in the system. When $\Delta N(O)$ has a zero point, the zero point is the turning point of amphoteric transformation.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.2c02252.

Simulation methods, components of the studied blast furnace slag system, BMH model parameters used in this simulation, calculation methods, RDFs and bond length, bond angle and local structure evolution, oxygen network structure and global structural stability, content of different types of oxygen atoms, calculation results of \( N(O)_{\text{supply}} \) and \( N(O)_{\text{demand}} \), results of model calculation, applicability verification of the supply–demand model, and results of the supply–demand relationship model (PDF)

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Notes
The authors declare no competing financial interest.

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