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# CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

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## Estimation of thermodynamic properties of oxide compounds from polyhedron method

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### ARTICLE INFO

#### Keywords:

Polyhedron method  
Thermodynamic properties  
Oxide compounds

### ABSTRACT

This paper describes a method to calculate the thermodynamic properties like enthalpy, entropy and molar volume of oxide mineral phases from their constituent polyhedra. Based on thermodynamic properties of 48 silicate and 19 titanate compounds collected from the critically evaluated and optimized FactSage database, thermodynamic properties of 18 polyhedra were optimized by weighted multiple linear regression analysis. The optimized properties of constituent polyhedra accurately reproduced the entropy, enthalpy and molar volume of all compounds, and were used for the prediction of thermodynamic properties of ternary oxide compounds in titanate systems.

### 1. Introduction

Thermodynamic database built by the thermodynamic modeling of oxide phase diagrams, thermodynamic properties and chemical reactions using CALPHAD method has become an important tool for new materials design and process optimization in many fields of ceramics and metallurgy. Accurate thermodynamic predictions of all compounds and solution phases are necessary for building an accurate and self-consistent database. Although a remarkable number of experimental determinations of thermodynamic properties such as heat capacities, enthalpies and entropies of oxide compounds have been accumulated, there are still numerous oxide phases for which thermodynamic data are unavailable. Experimental determinations of thermodynamic properties are labor-intensive and time-consuming processes, and some of oxide compounds are even difficult to be synthesized under conventional conditions. Although the first principles calculations have been widely used in metallic systems, its applications to oxide systems are still rather limited.

To estimate the thermodynamic properties of oxide minerals, several techniques have been devised. Heat capacities and calorimetric entropies of binary and ternary mixed oxides can be estimated by the summation of the heat capacities of constituent oxides or elements based on the Neumann-Kopp rule (NKR) which was first presented by Kopp in 1865 [1]. By comparing experimental values of heat capacity at 298.15 K and values estimated using the NKR for more than 300 mixed oxides, Leitner et al. [2] showed that NKR provides an estimate of heat capacity with an average error of 3.3%. However, Stevens et al. [3,4]

and Richet and Fiquet [5] pointed out that the NKR can give a much larger error at both lower and very higher temperatures than room temperature. Leitner et al. [6] also analyzed the error of NKR approach for heat capacity with temperature.

Regarding entropy, Latimer [7,8] used entropies of elements to estimate entropies of oxide compounds. Fyfe et al. [9] calculated the entropies of binary or ternary oxides from their constituent oxides and found the correlation between excess entropy and molar volume. Helgeson et al. [10] improved the accuracy of entropy estimation by taking structurally analogous minerals as components instead of constituent oxides and considering differences in coordination state between the components. A significant improvement was achieved when the coordination of the different oxide components was taken into account. Holland and Richardson [11] considered different effects between Al in octahedral and tetrahedral sites on the mineral stability. Robinson and Haas [12] determined a set of fractional entropy of polyhedral components with varying coordination states to accurately reproduce the entropies of silicates and other type of oxides by a multiple regression technique. However, their analysis neglected the volume correction which potentially induced more errors in the estimation.

Hazen [13] expounded that structures and properties of oxide minerals can be modeled by considering cation polyhedra with specific coordination as basic building blocks. This so-called “polyhedron method” assumes: (i) each polyhedron has its own characteristic properties which are invariant from structure to structure and (ii) thermodynamic properties of an oxide compound can be derived from

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Received 19 October 2016; Received in revised form 3 February 2017; Accepted 10 March 2017

Available online 01 April 2017

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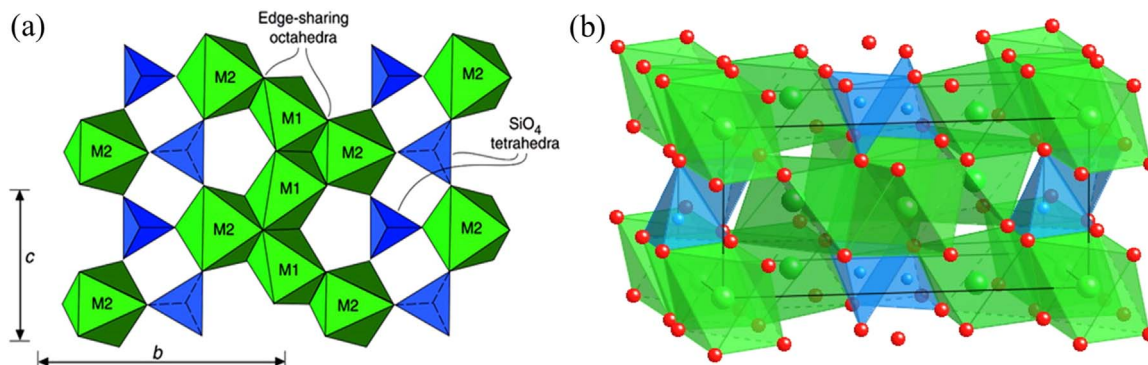


Fig. 1. Schematic representation of  $\text{Mg}_2\text{SiO}_4$  forsterite crystal structure. (a) 2-dimensional view, and (b) 3-dimensional view.

Table 1

Polyhedron components defined in the model as the oxide building blocks.

Component	Element	Coordination	Component	Element	Coordination
Ti-oct	Ti <sup>4+</sup>	Octahedral	Mg-tet	Mg <sup>2+</sup>	Tetrahedral
Si-tet	Si <sup>4+</sup>	Tetrahedral	Mg-oct	Mg <sup>2+</sup>	Octahedral
Al-tet	Al <sup>3+</sup>	Tetrahedral	Ca-oct	Ca <sup>2+</sup>	Octahedral
Al-oct	Al <sup>3+</sup>	Octahedral	Ca-multi	Ca <sup>2+</sup>	Multi-coordination
Fe3-oct	Fe <sup>3+</sup>	Octahedral	Li-tet	Li <sup>+</sup>	Tetrahedral
Fe-tet	Fe <sup>2+</sup>	Tetrahedral	Li-oct	Li <sup>+</sup>	Octahedral
Fe-oct	Fe <sup>2+</sup>	Octahedral	Li-multi	Li <sup>+</sup>	Multi-coordination
Mn-tet	Mn <sup>2+</sup>	Tetrahedral	Na-multi	Na <sup>+</sup>	Multi-coordination
Mn-oct	Mn <sup>2+</sup>	Octahedral	K-multi	K <sup>+</sup>	Multi-coordination

the linear summation of constituent polyhedron properties in a given formula unit of the oxide compound. Holland [14] further improved the entropy estimation by including a volume correction term and considering magnetic and configurational order-disorder contributions, and Chermak and Rimstidt [15] extended the method to calculate the Gibbs energies and enthalpies of silicate minerals. Recently, the polyhedron model was updated and expanded by Hinsberg et al. [16]. The enthalpies, entropies and molar volumes of 35 polyhedra were determined using a weighted multiple linear regression analysis on published thermodynamic properties of 47 silicates and double oxides and 57 OH-bearing minerals. They reported that the thermodynamic properties of silicates and double oxides were reasonably reproduced using the polyhedron method, but not for OH-bearing minerals.

Since the polyhedron model was first introduced by Hazen [13], only a few studies have been conducted by geochemists [14–16] to improve this model. Considering that *ab initio* calculations are still less satisfactory to predict the thermodynamic properties of complex oxide phases, the polyhedron model can be a suitable option for CALPHAD community to estimate/predict the thermodynamic properties of oxide compounds which have not been experimentally determined. In this study, the polyhedron method originally proposed by Hazen [13], Holland [14] and Hinsberg et al. [16] is further expanded to titanate systems. Total 48 silicates and 19 titanates were selected and their enthalpies, entropies and molar volumes at 298.15 K were collected to update and newly evaluate the properties of polyhedron constituents. In particular, the CALPHAD-type thermodynamic database which contains highly self-consistent thermodynamic data was used for the first time as the source of the present polyhedral analysis. The optimized polyhedron properties were used for the predictions of thermodynamic properties of ternary alkali-titanate-silicate compounds

where no thermodynamic data are available.

## 2. Polyhedron method

### 2.1. Concept of polyhedron method

The basic assumption of polyhedron method is that the thermodynamic properties and molar volume of mixed oxides (mostly silicates) can be described as linear combinations of the fractional thermodynamic properties and molar volume of their constituent polyhedra. That is, according to the polyhedron method,  $\Delta H_{i, 298.15K}^o$ ,  $S_{i, 298.15K}^o$  and  $V_{i, 298.15K}$  of mixed oxide compounds can be calculated:

$$\Delta H_{i, 298.15K}^o = \sum n_j \Delta h_{j, 298.15K}^o \quad (1)$$

$$S_{i, 298.15K}^o = \sum n_j s_{j, 298.15K}^o \quad (2)$$

$$V_{i, 298.15K} = \sum n_j v_{j, 298.15K} \quad (3)$$

where  $i$  is the mixed oxide phase,  $j$  is the constituent polyhedron,  $n_j$  is the stoichiometry of the polyhedron component  $j$ . The capital letters  $H$ ,  $S$ , and  $V$  represent enthalpy, entropy and molar volume of the mixed oxide, respectively, and small letters  $h$ ,  $s$ , and  $v$  represent the molar properties of polyhedron component.

Taking the  $\text{Mg}_2\text{SiO}_4$  forsterite phase for an example, as the schematic representation of the forsterite structure shown in Fig. 1, one mole of  $\text{Mg}_2\text{SiO}_4$  consists of two moles of Mg octahedra (M2 and M1;  $\text{MgO}_6$ ) and one mole of Si tetrahedron ( $\text{SiO}_4$ ). According to the polyhedron model, the thermodynamic and volumetric properties of  $\text{Mg}_2\text{SiO}_4$  can be determined from these polyhedron properties using Eqs. (1) to (3).

The oxide compound may have a magnetic spin order-disorder transition (for example, Curie temperature in  $\text{MgFe}_2\text{O}_4$ ) and disorder of cations or anions in its crystal lattice sites (for example, cation distribution of  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  between tetrahedral (T) and octahedral (O) sites in  $(\text{Mg}^{2+}, \text{Fe}^{3+})^T[\text{Mg}^{2+}, \text{Fe}^{3+}]_2\text{O}_4$ ). The magnetism and lattice disorder can contribute to the thermodynamic properties such as enthalpy, entropy and even molar volume. However, these contributions cannot be estimated directly from the constituent polyhedra. Therefore, in the evaluation and application of polyhedron method, such contributions should be carefully considered. For example, in the evaluation of the properties of each polyhedron, the corrected properties of the mixed oxide phase after subtracting the magnetism and lattice disorder contributions should be used. On the other hand, in the estimation of the properties of mixed oxide from the polyhedron method, the contributions of magnetism and disorder should be added on top of the estimated properties from polyhedron method. Therefore, strictly speaking, the values of  $\Delta H_{i, 298.15K}^o$ ,  $S_{i, 298.15K}^o$  and  $V_{i, 298.15K}$  in Eqs. (1)

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