



SPECIAL ISSUE ARTICLE

Review and perspective on polyhedron model for estimating thermodynamic properties of oxides

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Abstract

Knowledge of thermodynamics and phase equilibria of oxidic materials is crucial for advancement in the field of ceramics and glass. With the development of computational thermodynamics, predicting phase diagrams and chemical reactions of multicomponent systems has become possible. However, there are still plenty of oxides, the thermodynamic properties of which have not been identified due to the challenges in conducting experiments. Therefore, a key to the advancement in thermodynamic modeling would be to develop a universal model that can be used to estimate the thermodynamic properties of oxides with reliable extrapolation capacity. Atomistic (or molecular) scale models are still insufficient in predicting the thermodynamic properties of oxides at any scale. Alternatively, among group contribution-based methods, the polyhedron model has presented its potential in the estimation of the thermodynamic properties of ionic crystals. However, this model still demands improvements that increase the model's accuracy and extrapolation capacity. In this paper, the background and the state-of-the-art of polyhedron model will be presented together with its strengths and shortcomings. Subsequently, it will be briefly discussed how the field of artificial intelligence could be exploited to devise the next generation of the polyhedron model, the modified polyhedron model.

KEYWORDS

oxides, phase equilibria, thermodynamics

1 | INTRODUCTION

Thermodynamic modeling of phase equilibria and chemical reactions in multicomponent systems is an indispensable part of the development of advanced materials and processes. Oxide-based materials have many applications, such as glass,¹ ceramics,^{2,3} reinforcements in metallic matrix composites,⁴ thin films and coatings,^{5,6}

materials for magnetic recording,⁷ fuel cells,^{8,9} high-temperature superconductors,^{10,11} health,^{12,13} cement,^{14,15} energy storage,^{16,17} water decontamination,^{18,19} and process metallurgy.^{20,21} Despite the large volume of data available, there are numerous important oxide compounds with unknown thermodynamic properties. This is partly due to the fact that the experimental determination of thermodynamic properties is time-consuming and challenging (e.g.,

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hygroscopicity and impurities). Therefore, a universal model with reliable extrapolation capacity that can be used to estimate the thermodynamic properties of oxides would be a key to the advancement in thermodynamic modeling.

Several theoretical models have been developed to estimate the thermodynamic properties of the compounds.^{22–24} These models can be categorized into quantum mechanics and classical mechanics methods such as the density functional theory (DFT) and molecular dynamic (MD) simulations, respectively. These approaches are computationally expensive and ineffective for estimating thermochemical properties at elevated temperature. For example, incorporating temperature effect in DFT calculations, which are typically restricted to 0 K temperature, is an active area of research. Moreover, the calculations often take more time than doing actual experiments. The interatomic potentials in MD simulations, as another example, are not reliable in systems with more than three elements. Although these techniques could be ideal for the compounds that are difficult to conduct experiments on (e.g., extremely hygroscopic materials), they are still far to be considered practical and general.

In addition, several empirical models were also developed using the group contribution-based methods to predict the thermodynamic properties of compounds and minerals.^{25–29} The Neumann–Kopp rule (NKR), although developed as early as the 19th century, is still widely used as a first approximation in the estimation of thermodynamic properties of compounds.²⁵ The NKR is employed to calculate the unknown standard entropy and heat capacity of a compound from its constituent oxides. Most of the studies among the group contribution methods were based on the simple additivity rules, modifications of structural analogs, or regression-based correlations between the thermodynamic properties and structural data (e.g., atomic mass, molar volume, cation coordination, electronegativity, and lattice dilatation)^{25–27,30–52} to estimate the enthalpy, entropy, or heat capacity of solids. The thermodynamic properties of the constituents could be obtained directly from experiments or indirectly from regression analysis over the existing databases. These methods are thought-provoking because they are computationally less expensive, could be rather practical, and be easily applied to the prediction of the thermodynamic properties of new compounds.

Most of the group contribution models consider the lattice vibrational mode as the major contributor to heat capacity and entropy, and the lattice mode can be a function of the mode of the cation-oxygen polyhedra (i.e., groups of cations surrounded by anions), which roots back in the Pauling model of ionic solids.³⁰ According to Pauling, first-nearest neighbor (FNN) bonding plays a

crucial role in determining the structure and properties of ionic crystals. Among several group contribution-based models developed until now, the polyhedron model of Holland³¹ is quite distinctive as it is based on the physical structure of ionic compounds as demonstrated by Pauling and has been applied to predict the thermodynamic properties of large groups of oxides, hydroxides, carbonates, and phosphates with uncertainties often reportedly lower than those of other methods of estimation and comparable with experimental uncertainties.^{27,31–35} The polyhedron model assumes that polyhedra are the main building blocks of an ionic crystal, as shown in Figure 1 for the TiSiO_4 compound. The thermodynamic properties of the compound can be therefore predicted from the summation of the corresponding thermodynamic properties of its component polyhedra, Ti^{4+} -octahedra, and Si^{4+} -tetrahedra as demonstrated in Figure 1.

In this study, we aim to trace the development of the polyhedron model over the years and determine its state-of-the-art, highlight its strengths and shortcomings, and identify key avenues to propel further research and development. In the end, some potential areas, overlooked so far, are presented to improve the accuracy of the estimated thermodynamic properties of oxides.

2 | THEORY

If the Gibbs energies of all phases of a chemical system, including stoichiometric compounds and solution phases, are known, the phase equilibria, phase stability, and chemical reactions among its many components can be calculated under a set of conditions (e.g., X , T , P) via minimization of the Gibbs energy functions. Figure 2 shows the stable phase assemblages obtained by minimizing the Gibbs energies of multiple phases. If all stable phase assemblages are calculated as a function of temperature under atmospheric pressure, the thermal stability of phases can be revealed.

The Gibbs energy of a compound can be obtained from enthalpy and entropy of formation of the compound in the standard state (298 K, 1 atm) and the heat capacity as a function of temperature. The Gibbs energy of a stoichiometric compound is expressed by

$$G_T^o = H_T^o - TS_T^o \quad (1)$$

$$H_T^o = \Delta H_{298\text{ K}}^o + \int_{298\text{ K}}^T C_p(T) dT \quad (2)$$

$$S_T^o = S_{298\text{ K}}^o + \int_{298\text{ K}}^T \left(\frac{C_p(T)}{T} \right) dT \quad (3)$$

where $\Delta H_{298\text{ K}}^o$ is the standard enthalpy of formation of a given stoichiometric compound from pure elements

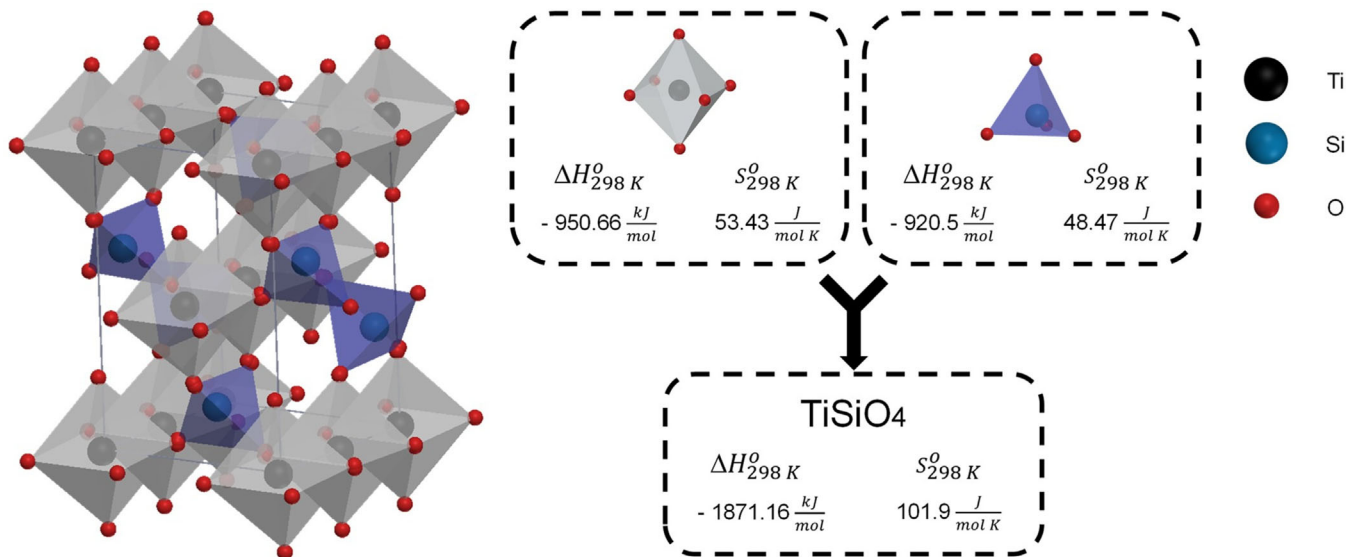


FIGURE 1 Schematic presentation of the polyhedron method and constituent polyhedra of TiSiO_4 crystal structure, showing Ti^{4+} -octahedra and Si^{4+} -tetrahedra.

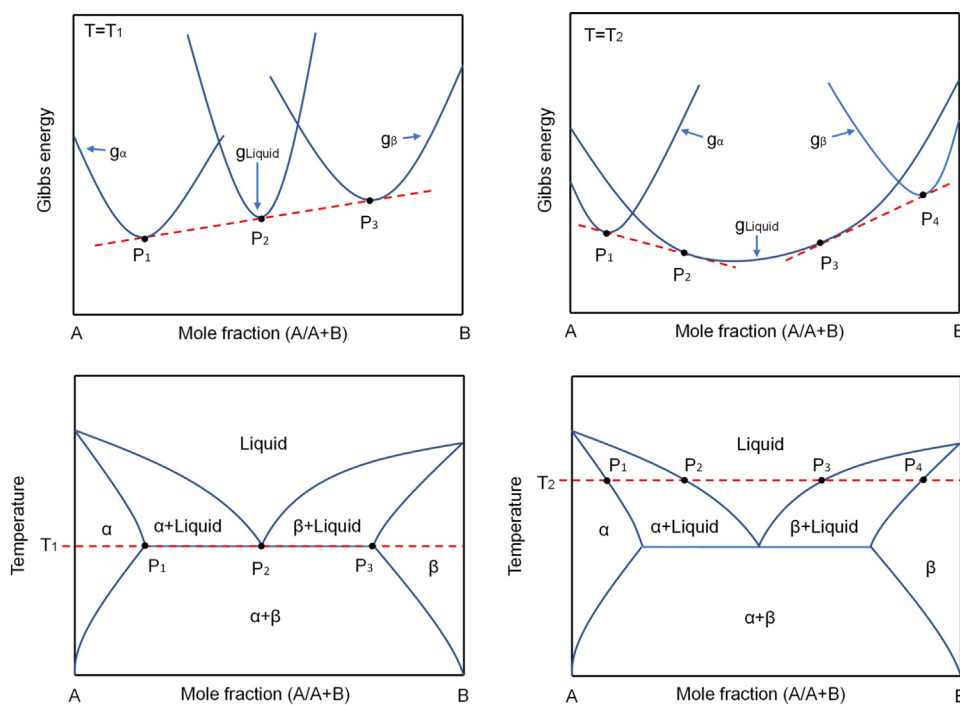


FIGURE 2 Relation between Gibbs energy and phase stability for a constant temperature and pressure.

at 298 K and 1 atm, $S_{298\text{ K}}^{\circ}$ is the standard entropy at 298 K and 1 atm, and $C_p(T)$ is the heat capacity as a function of temperature. An ideal model will be able to calculate the $\Delta H_{298\text{ K}}^{\circ}$, $S_{298\text{ K}}^{\circ}$, and $C_p(T)$ to estimate the Gibbs energy within the experimental uncertainty.

In the polyhedron model, an ionic compound is divided into constituent polyhedra. The basic assumption is

that the thermodynamic properties of ionic compounds (primarily silicate minerals) could be calculated from the linear summation of the corresponding thermodynamic properties of their constituent polyhedra as expressed in the following equations:

$$\Delta H_{i,298\text{ K}}^{\circ} = \sum n_j \Delta h_{j,298\text{ K}}^{\circ} \quad (4)$$

$$S_{i,298\text{ K}}^{\circ} = \sum n_j s_{j,298\text{ K}}^{\circ} \quad (5)$$

$$C_p(T) = \sum n_j c_{p,j}(T) \quad (6)$$

where i is the ionic crystal, the thermodynamic properties of which are unknown, j is the constituent polyhedron, and n_j is the stoichiometry of the constituent polyhedron. The letters H , S , and $C_p(T)$ stand for enthalpy, entropy, and heat capacity, respectively, and h , s , and $c_p(T)$ are the molar properties of the constituent polyhedra.

3 | REVIEW OF POLYHEDRON-BASED MODELS

3.1 | Estimation of $\Delta H_{298\text{ K}}^{\circ}$

Robinson and Haas²⁷ estimated the standard enthalpy of silicate minerals via the summation of the properties of polyhedra. They used the weighted, simultaneous, multiple, least-squares regression method to derive the thermodynamic properties of polyhedra. Between 298 and 1500 K, the technique has higher precision for enthalpy (2%–3% errors) than the NKR (up to 5% errors). Chermak and Rimstidt³⁶ calculated the enthalpy of silicate minerals at 298 K from the polyhedron method, the continuation of the polyhedron method of Robinson and Haas.²⁷ They derived the enthalpies of certain oxide and hydroxide polyhedra, used to estimate the thermodynamic properties of complex or impure silicates such as clay minerals and zeolite, challenging to be measured. The average residuals for calculated and experimented $\Delta H_{298\text{ K}}^{\circ}$ were calculated to be 0.24%. However, they mentioned that the enthalpy of Ca–Al pyroxene, forsterite, cordierite, andradite, and gehlenite could not be calculated with accuracy. La-Iglesia and Felix³³ applied the polyhedron method to derive the enthalpy of 20 polyhedra at 298 K and 1 atm to predict the enthalpy of carbonate minerals. The average calculated relative error for the enthalpy was 0.25%. Van Hinsberg et al.³⁷ determined the enthalpy for 35 polyhedra using weighted multiple linear regression (LR) analysis on published mineral thermodynamic properties. As a result, the enthalpy of a large number of phases could be calculated at 298 K and 1 atm with an associated uncertainty of less than 5%. Only reasonable results for silicate minerals and double oxides were obtained, and the correlation could not be used to predict the thermodynamic properties of other minerals, simple oxides (AO_x), and hydroxides ($\text{A}(\text{OH})_x$). For the two latter, the calculated difference between the experiments and prediction was more than 10%. For example, the thermodynamic properties of SiO_2 polymorphs (quartz, tridymite, and cristobalite) could

not be well reproduced. In all three, Si is located in the tetrahedral sites, but they have different thermodynamic properties. It is possible that the cation sites are not the same in the three polymorphs or that long-range ordering in these minerals is more important than the phases with multi-cations. La-Iglesia³² expanded the polyhedron method using a method of least-squares to derive the contribution of 15 polyhedra to estimate the enthalpies of phosphates at 298 K and 1 atm. The calculated residual errors for the enthalpy were less than 1%. Wu et al.³⁵ expanded the polyhedron method to derive the enthalpy of 18 polyhedra based on the weighted multiple LR of 48 silicates and 19 titanates, critically assessed and available in the FactSage database.³⁸ The standard deviation for enthalpy at 298 K was 0.56%. The standard enthalpies of 6 ternary alkali–silicate–titanate phases were predicted.

3.2 | Estimation of $S_{298\text{ K}}^{\circ}$

Fyfe et al.²⁶ method of estimation of entropy, although not a polyhedron-based model, deserves elaboration because it inspired the work of Robinson and Haas²⁷ pioneering the polyhedron method. Fyfe et al.²⁶ reported some deviations in the calculated entropy values based on the Latimer³⁹ table from the experimental values. Latimer⁴⁰ estimated the entropies of solid compounds considering the mass, size, and charge of cations and anions. For example, for albite $\text{NaAlSi}_3\text{O}_8$ or jadeite $\text{NaAlSi}_2\text{O}_6$, the estimated entropy values based on the constituent oxides' summation were 205.8 and 133.0 J/deg mol, against the calculated values of 187.0 and 145.2 J/deg mol, respectively. That implied that additivity rules based on elemental or oxide constituents would not always work. That is, there are other parameters that may contribute to the entropy in addition to the phase constituents. Therefore, Fyfe et al.²⁶ demonstrated that the contribution of volume should be considered in the entropy value. Entropy is associated with short distances and bond tightness, reflected in low compressibility values. They proposed that if the actual molar volume and the standard molar volume (i.e., from the summation of constituent oxides) agree with each other, no entropy correction should be required. In the opposite case, the volume effect should be considered in the entropy value. If the molar volume of a compound is higher than the standard molar volume, the actual entropy of the compound should be higher than the value obtained from the summation of oxides and vice versa. In general, higher volumes correspond to higher entropy values. It might be that high-temperature compounds have lower coordination than low-temperature compounds as an increase in coordination needs a shorter distance between cation and anion and higher density as a result.²⁶ Fyfe et al.²⁶

proposed a volume-corrected model of entropy where the difference between a compound entropy and its constituent oxides is proportional to the difference between the compound molar volume and the molar volumes of its constituent oxides as the following:

$$S_j = \sum n_i S_i + k(V_j - \sum n_i V_i) \quad (7)$$

where k is the volume correction parameter to be derived from experimental data. This technique was further improved by Helgeson et al.,⁴¹ Robinson and Haas,²⁷ and Holland.³¹

Moreover, Fyfe et al.²⁶ reported that the contribution of order–disorder at low temperatures should be added to the entropy value. The third law of thermodynamics assumes that the entropy value of a pure crystal at 0 K is zero. However, entropy values from calorimetric measurements and spectroscopy do not always match, and sometimes the entropy values from spectroscopy exceed the values from low-temperature heat capacity measurements. This was related to the existence of randomness down to the temperature as low as 0 K (i.e., the residual entropy). Residual entropy should exist in all crystal structures where there is randomness in the distribution of two or more types of cations on equivalent sites. For example, Al can replace Si in the fourfold tetrahedral site. For example, in silicates, Al can replace Si in the fourfold tetrahedral site. If the disorder related to the existence of randomness in the distribution of cations in the sublattices happens at high temperatures, it will be reflected in heat capacity data and thus entropy value. However, if this disorder happens at a low temperature, the residual entropy should be calculated and added to the experimental value.

Robinson and Haas²⁷ in a similar way to enthalpy estimated the standard molar entropy of silicate minerals via summation of the properties of basic polyhedra. Between 298 and 1500 K, the technique has a precision better than 5% for entropy. This indicates that the cation type and coordination number affect the mineral thermodynamic properties. They evaluated the coordination numbers for cations in each mineral group. Although this was a rather path-independent approach, where predicted results are independent on the choice of reactants, in comparison to analogous mineral constituents of Helgeson et al.,⁴¹ it neglected the effect of volume on entropy taken into account by Fyfe et al.²⁶ and Helgeson et al.⁴¹ They derived an equation for calorimetric entropies of polyhedra associated with the heat capacity function:

$$S' = a \ln T + 2bT - \frac{c}{T^2} + e + \frac{fT^2}{2} - \frac{2g}{T^{1/2}} \quad (8)$$

The entropies of pyroxenes and amphiboles were not well predicted (errors between 10 and 45 J/K were

obtained) and the components like MnO, TiO₂, and Fe₂O₃ were also missing in the model.

Chermak and Rimstidt³⁶ reported that the positive correlation between entropy and volume presented by Fyfe et al.²⁶ can be justified by considering the role of lattice vibrations in the heat capacity and entropy of crystalline solids. They based the entropy of a crystalline compound on the Einstein quantum model or the Debye model for heat capacity. They found an average value for explaining the relationship between the entropy and molar volume as 1.0 J/K cm³ from low to high temperatures. The obtained value is consistent with the k constant value obtained by Fyfe et al.²⁶ and is also in agreement with the Einstein and Debye solid behavior.

Holland³¹ further improved the polyhedron model of Robinson and Haas²⁷ by allowing coordination changes and incorporating the volume-corrected entropy and non-lattice vibrational contributions (magnetic and site order–disorder transitions). The dependency of entropy on volume was taken into account by including the volumetric contribution in the summation of different polyhedra. The uncertainties of estimated entropy values were about ± 2 –3 J/Kmol for silicates and double oxides. The uncertainties were in the range of ± 3 –6 J/K mol for phases containing transition metal oxides. These uncertainties are lower than other methods of estimation and comparable with experimental uncertainties.

Holland³¹ evaluated the effect of the molar volume of cation polyhedra on the third law of entropy within the framework of the lattice vibration theory of Einstein and Debye. Via regression analysis of 60 measured entropies and volumes of silicates and oxides, he found a value of 1.0 J/K cm³ for $(\Delta S/\Delta V)_{298\text{ K}}$ similar to that obtained from Einstein and Debye models and work of Fyfe et al.²⁶ Holland reported that molar volume can represent the average bonding and vibrational state of minerals, and the entropy is the function of the average vibrational spectrum. Therefore, the molar volume can be used to predict the entropies of crystals. Holland³¹ used 60 compounds for the regression to derive the parameter S – V for each polyhedron and its uncertainty. He also compared the volume-corrected results with the model of Robinson and Haas²⁷ ignoring the volume effect. He reported that the standard deviation of the residuals and the mean absolute deviation of residuals were two times the values of the volume-corrected model. For example, the difference between octahedral and tetrahedral Al₂O₃ in the model of Robinson and Haas was about 28.3 J/K mol in comparison to 6.3 J/K-mol from the volume-corrected model.

Holland³¹ also removed two non-lattice vibrational contributing factors to entropy (i.e., magnetic and site order–disorder transitions). The following equation could be used to ideally consider the contribution of magnetic

transformation at $T < 298$ K to the entropy:

$$S_{\max}^{\text{magnetic}} = R \sum n \ln(2s + 1) \quad (9)$$

where s is the spin quantum number, R is the gas constant, and n is the number of moles of Fe^{2+} , Fe^{3+} , and Mn^{2+} in the given oxide. Significant magnetic ordering can happen below 15 K down to 1 K in some minerals. He also considered the site-configurational entropy terms, for example, as occurs because of the distribution of Al and Si on the same sublattices. The maximum contribution of site order–disorder transition at $T < 298$ K to entropy can be calculated via the following equation:

$$S_{\max}^{\text{disorder}} = -mR \sum X_i \ln X_i \quad (10)$$

where X_i is the mole fraction of species i in a certain sublattice site, and m is the multiplicity of that lattice site at which cations or anions mixing occurs.⁴² Subsequently, the contribution of both magnetic and site order–disorder transitions at $T < 298$ K to the enthalpy can be calculated as follows:

$$\Delta H_{\max}^{\text{ex}} = \frac{2}{3} (S_{\max} T_c) \quad (11)$$

where T_c is the temperature of magnetic and/or site order–disorder transition, that is, T_{mag} and T_{dis} .

Some minerals such as hematite and magnetite show magnetic transition above 298 K with a long tail to the lambda anomalies down to below 298 K, which could lead to a possible small contribution to the entropy below 298 K. The Landau theory can be used to calculate the contribution of both magnetic and site order–disorder to the entropy as explained by Carpenter⁴³:

$$C_p^{\text{ex}} = \frac{TS_{\max}}{2\sqrt{T_c}} (T_c - T)^{-1/2} \quad (12)$$

$$S_{\text{Landau}}^{\text{ex}} = S_{\max} (1 - Q^2) \quad (13)$$

where C_p^{ex} is the excess heat capacity with respect to the fully ordered phase, S_{\max} is the maximum entropy of transformation, and $Q = (1 - \frac{T}{T_c})^{1/4}$. The magnetic order–disorder is very common in minerals containing transition metal oxides and leads to the Lambda peaks and heat capacity anomalies. The contributions of magnetic and site order–disorder transitions at $T > 298$ K to the enthalpy can be obtained as the following equation⁴²:

$$H^{\text{ex}} = 2S_{\max} T_c \left(\frac{Q^6}{6} - \frac{Q^2}{2} - \frac{1}{3} \right) \quad (14)$$

La-Iglesia and Felix³³ also utilized the polyhedron model of Holland and derived the entropy of 20 polyhedra

at 298 K and 1 atm to predict the entropy of carbonate minerals. Van Hinsberg et al.³⁷ also determined the entropy and molar volume for 35 polyhedra using weighted multiple LR analysis on published mineral thermodynamic properties. They described the OH-bearing minerals by partial and total hydroxide coordinated components and obtained better results than previous models. However, they precluded the need for an S – V term to improve estimates of entropy as suggested by Holland.³¹ Wu et al.³⁵ also used the polyhedron method to derive the entropy, and molar volume of 18 polyhedra based on the weighted multiple LR of 48 silicates and 19 titanates. The reported standard deviations for entropy and molar volume at 298 K were 3.5% and 4.2%, respectively.

3.3 | Estimation of C_p

Robinson and Haas²⁷ estimated the standard molar heat capacity of silicate minerals via the summation of the properties of polyhedra. Between 298 and 1500 K, the technique has a high precision (2%–3% errors) for heat capacity. They used the following equation to fit the heat capacity of constituent polyhedra of minerals:

$$C'_{p,i} = a_i + 2b_i T + c_i/T^2 + f_i T^2 + g_i/T^{1/2} \quad (15)$$

where T is the absolute temperature, and a – g are the coefficients obtained from the least-square analysis (c and f coefficients are often zero). The calculated heat capacities of olivines and high-symmetry silica (i.e., β -quartz and β -cristobalite), having very rigid interconnection between the polyhedra, showed errors of more than 2%. The phase α -quartz was the worst case scenario where all polyhedra are loosely interconnected. In the polyhedron model, the volume changes with temperature are related to the variation in cation–anion bond lengths rather than the changes in polyhedra linkage. Van-Hinsberg et al.³⁴ estimated the heat capacity of minerals between 200 and 1200 K using the LR of constituent polyhedra within $\pm 2\%$ of the input values better than the values obtained from the NKR. Leitner et al.^{44,45} assessed the temperature dependency of the heat capacity of mixed oxides from the NKR. They revealed that this method leads to accurate heat capacities at 298 K, whereas the values largely deviate from the heat capacity values at low and high temperatures. They listed several parameters that contribute to the heat capacity of a solid compound at constant pressure all of which cannot be considered in the simple additivity method of NKR, such as the lattice vibration (harmonic and anharmonic) and lattice dilatation. Lattice dilatation and anharmonic vibration are important factors at high temperatures where the harmonic lattice vibration reaches the Dulong–Petit limit.

At low temperatures, vibrational frequencies change in a mixed oxide with respect to its binary oxides leading to a nonzero value for heat capacity difference. At low temperatures, the acoustic mode of a mixed oxide is different from its constituent oxides due to changes in the coordination number and site symmetry of the large cation between the binary oxides and their mixed oxides. Recently, Zhu et al.⁴⁶ used the polyhedron method to calculate the heat capacity of five different sodium magnesium silicates.

4 | DISCUSSION

The goal would be to estimate the three thermodynamic properties, that is, $\Delta H_{298\text{ K}}^o$, $S_{298\text{ K}}^o$, and $C_p(T)$, for a wide range of oxides within experimental uncertainties. Subsequently, the Gibbs energies of stoichiometric solids as functions of temperature, $G(T)$, could be calculated from the three thermodynamic properties (see Equations 1–3). The predicted Gibbs energies of stoichiometric compounds can be stored in thermochemical software, such as FactSage³⁸ and Thermo-Calc.⁴⁷ These Gibbs energies in combination with the thermodynamic properties of solid and liquid solutions will be employed to calculate phase equilibria, phase stability, and complex chemical reactions under a set of predefined conditions (T , X , P). According to the analysis of the literature, the polyhedron method of Holland³¹ could be a potential approach to predicting the thermodynamic properties of a wide range of ionic compounds such as oxides.

4.1 | Strengths and shortcomings of the polyhedron model

It has been already shown that the polyhedron method was inspired by the physical structure of ionic compounds demonstrated by Pauling,³⁰ boosting its extrapolation capacity and reliability. Considering the cation coordination, it became possible to estimate enthalpy, calorimetric entropy, and heat capacity without data about representative minerals in similar structural classes, making this model path-independent. That is, the thermodynamic properties of a target compound do not change based on the choice of constituents. The polyhedron model is rather practical and can be used to estimate the properties of several different families of ionic crystals (e.g., oxides, hydroxides, carbonates, and phosphates). The residual errors are often less than those calculated by other well-established and widely used methods of summation based on oxides or minerals such as NKR. For some compounds and minerals, residual errors as low as the experimental uncertainties were reported.

However, Hanzen⁴⁸ specified that polyhedra have specific vibrational frequencies and amplitudes, and fictive thermochemical properties assigned to each polyhedron, vary by temperature and pressure. He also reported that each cation polyhedron has certain predetermined properties (i.e., compressibility, expansion, and volume), which could vary by a few percentages from one structure to another. For example, 2% variations in average bond distance, 4% in polyhedron volume, and 15% in O–O edge lengths are common for divalent polyhedra in minerals. In general, cations with larger valence show less change in the polyhedra geometry from structure to structure. The variations are the largest in this order: Si tetrahedra < Al octahedra < Mg octahedra < Be tetrahedra.

According to Hanzen,⁴⁹ the limitations of the polyhedron method can be listed as follows: (1) The polyhedron method assumes that the properties of a polyhedron (e.g., size, shape, and fictive thermodynamic properties) are constant from one structure to another, (2) the effect of inter-polyhedra linkage (“linkage rigidity”) is missing, (3) polyhedron distortions are not allowed from structure to structure (i.e., the energies related to crystal field effects, Jahn–Teller distortions, ion pairs), (4) it is simply based on mechanical mixing of polyhedra (i.e., the excess properties of mixing are not predicted), and (5) it is only applicable to compounds that can be divided into different polyhedra (i.e., it cannot be applied to covalent sulfides and sulfosalts).

Hanzen introduced four different linkage topologies, a “shared face” (three or more common anions), a “shared edge” (two common anions), a “shared corner” (one common anion), or van der Waals forces (intermolecular forces and no shared elements). He classified the minerals’ structures based on the distribution of rigid versus deformable polyhedra linkages in the structure. A rigid linkage (e.g., AlO_6 octahedra sharing faces in corundum) does not go under a significant deformation as a result of a change in the composition of adjacent polyhedra, temperature, and pressure. However, a compliant linkage (e.g., the shared corners between two SiO_2 tetrahedra in α -quartz) significantly changes with respect to temperature and pressure. It can be said that ionic crystals with a few flexible linkages fit well with a polyhedron model but those with all flexible linkages like α -quartz or olivine with no flexible linkages show lower or higher thermodynamic properties. Figure 3 illustrates the four different linkage topologies between different polyhedra in BaCoO_3 (“shared-face”), $\text{Na}_2\text{Ti}_3\text{O}_7$ (“shared-edge”), CaTiO_3 (“shared-corner”), and Li_4SiO_4 (“van der Waals forces”). The enthalpy and entropy of $\text{Na}_2\text{Ti}_3\text{O}_7$ and Li_4SiO_4 were calculated using the polyhedron model and compared with the experimental data in Table 1. It is seen that the calculated residual error for Li_4SiO_4 with

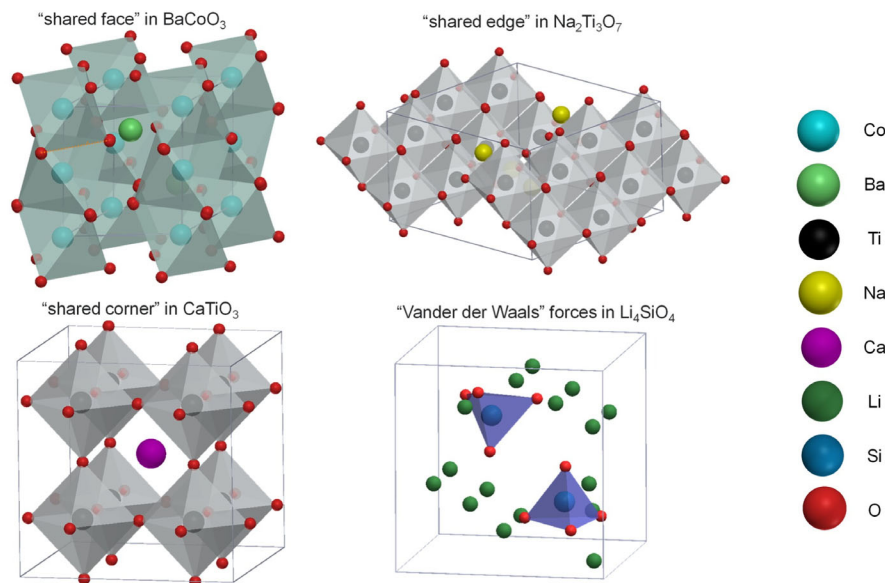


FIGURE 3 Ionic compounds with different inter-polyhedra linkages; “shared face” in BaCoO_3 , “shared edge” in $\text{Na}_2\text{Ti}_3\text{O}_7$, “shared corner” in CaTiO_3 , and “van der Waals forces” in Li_4SiO_4 .

TABLE 1 Predicted enthalpies of $\text{Na}_2\text{Ti}_3\text{O}_7$ and Li_4SiO_4 using the polyhedron model in comparison to experiments.

	$\text{Na}_2\text{Ti}_3\text{O}_7$	Li_4SiO_4
	$\Delta H_{298\text{ K}}^o$ (kJ/mol)	$\Delta H_{298\text{ K}}^o$ (kJ/mol)
Polyhedron model	−3474.41	−2328.80
Barin et al. ⁵⁵	−3490.47	–
Ihle et al. ⁵⁶	–	−2328.90
Residual error	0.46%	0.0%

“van der Waals forces” is negligible in comparison to that for $\text{Na}_2\text{Ti}_3\text{O}_7$ with “shared edge” where the effect of polyhedra linkage on the thermodynamic properties might be more important. However, this is subject to further investigation.

Holland³¹ applied some modifications to the polyhedron model of Robinson and Haas²⁷ such as the volume-corrected entropy. However, this could only account for the nonzero value of the interaction entropy of constituent polyhedra for a specific compound at 298 K (see Equation 7). Afterward, the polyhedron method was utilized^{32,35,37} to estimate the thermodynamic properties of silicate, binary oxides, hydroxides, titanate, titanate-silicate, and carbonate minerals. Van Hinsberg et al.³⁷ rejected the necessity of volume-corrected entropy, which could be related to the choice of selected minerals for the regression analysis. As explained before, only if the difference between the actual molar volume of a compound and the standard molar volume from the summation of its constituent polyhedra is important, the volume effect can be reflected in the interaction entropy. However, Wu et al.³⁵ reported slightly better results considering the

volume-corrected entropy term. In our unpublished work, we obtained significant improvements in the predicted entropies of the compounds $\text{Li}_2\text{Si}_2\text{O}_5$, $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, and Fe_2TiO_4 considering the volume-corrected entropy.

It can be said that no further major developments were performed on the polyhedron model after Holland,³¹ and the model is still today based on the major assumption that the enthalpy and heat capacity of polyhedra interaction are equal to zero. This might provide a reasonable first approximation, but it could be further improved by incorporating physical structural data (e.g., electronegativity and molar volume) representing the enthalpy and heat capacity of reactions. You et al.²⁴ recently demonstrated that the calculated C_p values of $\text{Na}_2\text{MgSiO}_4$ from the polyhedron model agree well with the differential scanning calorimetry (DSC) results between 800 and 1200 K; however, deviation as large as approximately 20% from the DSC data was observed between 298 and 800 K. Although the polyhedron model of Holland in general provides estimates of thermodynamic properties better than previously well-established methods such as NKR, the residual errors in the thermodynamic properties propagate to the Gibbs energy, which might lead to largely erroneous phase equilibria and phase stability data. In addition, the residual $\Delta H_{298\text{ K}}^o$, $S_{298\text{ K}}^o$, $V_{298\text{ K}}$, and $S_{298\text{ K}}^o - V_{298\text{ K}}$ were calculated by Wu et al.³⁵ to be 0.56%, 3.50%, 4.20%, and 6.51%, respectively, versus 1.50%, 6.77%, 6.94%, and 9.28% by Van Hinsberg et al.³⁷ That is, in the present state, the enthalpy of compound can be predicted rather more accurately than the entropy and molar volume, which need further improvement.

4.2 | Outlook on future research

The main problem of the polyhedron model is that it does not distinguish the polyhedra linkages and the crystal energy contributions by cation–cation second nearest neighbor (SNN) and longer range interactions. That is, the present polyhedron method averages out energies associated with different inter-polyhedra linkages and SNN and longer range ordering in the form of FNN interactions among constituent polyhedra of a mineral. The SNN and inter-polyhedron rigidity could particularly vary from one compound to another. If this information is known, in combination with polyhedra characteristics, the thermodynamic properties of materials can be calculated. That is, the assumption that each cation polyhedron has specific properties that are constant from one structure to another, and that the bulk properties of ionic compounds can be predicted from the linear summation of the constituent polyhedra are only a first approximation.⁴⁸ Hence, the main challenge could be the development of proper summation methods for these different linkage topologies and SNN interactions. For example, Hanzen⁴⁸ proposed to include a simple polyhedron linkage coefficient that represents the flexibility of corner-shared structural elements.

As mentioned before, the polyhedron method of Holland³¹ focused on LR analysis of data. However, with the advancements in the field of artificial intelligence, nonlinear models can be used to improve the derived thermodynamic properties of polyhedra and the accuracy of the estimated thermodynamic properties of compounds. Machine learning (ML) or Deep Learning (DL) models could be efficient in the estimation of thermodynamic properties of compounds and enable calculations beyond the capacity of mathematical functions. For example, they can be used to estimate not only the FNN interactions (i.e., first-order interactions) but also the SNN interactions (i.e., the second-order interactions) and longer range ordering (e.g., third-order and fourth-order interactions) between constituent polyhedra of a crystalline phase. In addition, the DL algorithms (e.g., neural network [NN], decision tree) can be used to find complex correlations between the thermodynamic properties of compounds and physical structural data governing the thermodynamic properties of ionic solids. Subsequently, the related physical structural data can be used as input parameters to the polyhedron model to account for the nonzero values of reaction thermodynamic properties. This approach can be promising in studying and predicting the thermodynamic properties of compounds while obtaining the balance between computational time and accuracy.

Figure 4 shows the relationship between the three pillars (database, descriptors, and algorithm) in ML and the process of development of a modified polyhedron

model. The development of an ML model can be divided into four steps: (1) creating a database of thermodynamic properties, (2) selecting proper descriptors and algorithms, (3) training the algorithm based on the dataset and descriptors, and (4) utilizing the trained model to predict the thermodynamic properties of unknown compounds based on selected descriptors.

For creating ML algorithms, two sets of data (training vs. prediction) are required. Known thermodynamic properties of ionic compounds can be used as the training set to predict unknown thermodynamic properties of other compounds. The reliability of training set data largely influences the predictability of an ML model. Therefore, rigorous attention should be paid to the soundness of the available data. Thermochemical software and their databases such as FactSage contain a large number of thermodynamic properties of ionic compounds that have been critically evaluated, optimized, and amassed in the past decades. These data can be used as inputs to the ML process. These internally consistent databases and optimized and cleaned data are favored over the experimental measurements that are accurate within certain error ranges and are measured independently from other components of a chemical system. If thermodynamic properties of interest are not available in an internally consistent database, the data from original experimental values can be taken.

An algorithm is a mathematical model that is employed to estimate a variable of a system (here, the unknown thermodynamic properties of a compound) based on other variables (properties of constituent polyhedra). The algorithm connects inputs, descriptors, and outputs either qualitatively or quantitatively. It might be not all the algorithms are suitable for one specific objective (i.e., a variable to be calculated). For example, algorithms that suit only the interpolation and not extrapolation might not be suitable for the modified polyhedron model because the estimated values cannot be outside the training set values for the target compounds, the thermodynamic properties of which can be very different from those of the training set.

To perform ML modeling with the information available in the dataset, it is necessary to use descriptors (often called “features”) to characterize the compounds in the algorithm. Descriptors are numerical representations of the included properties used for training and can be included into the ML algorithm as matrix (e.g., constituent polyhedra of compounds) values (e.g., $\Delta H_{298\text{ K}}^0$).^{50–52} For example, Peng et al.⁵³ predicted the thermal expansion coefficients of $\text{La}_2(\text{Zr}_{2-2x}\text{Ce}_{2x})\text{O}_7$ using the polyhedron approach, including descriptors such as constituent polyhedral, temperature, and lattice parameters. They demonstrated that a larger database may result in a remarkable increase in the accuracy of nonlinear ML

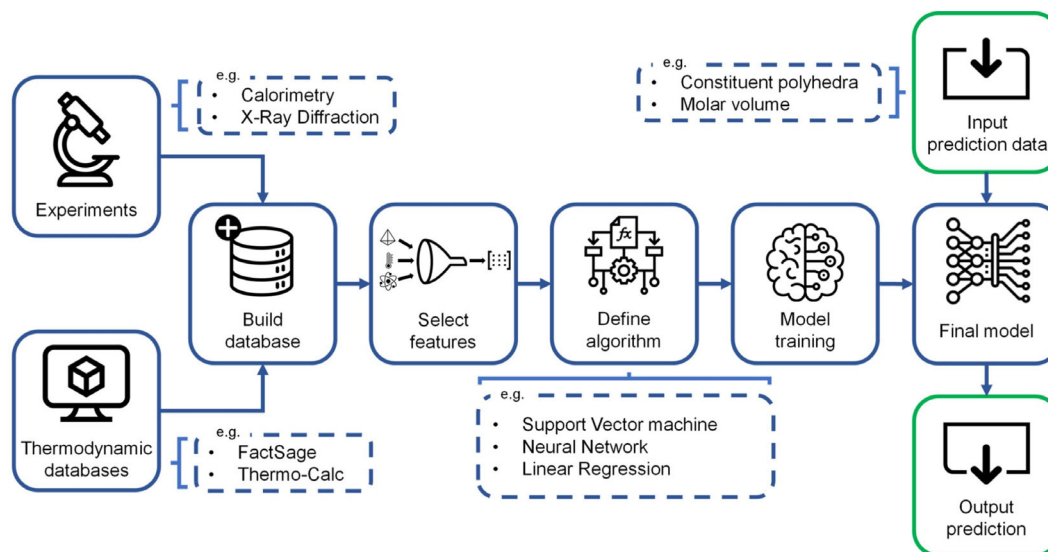


FIGURE 4 Process of developing a modified polyhedron model using machine learning.

TABLE 2 Comparison of predicted $\Delta H_{298\text{ K}}^0$ of stoichiometric compounds in the PbO–SiO₂ system to experimental measurements.

Compound	Polyhedron (kJ/mol)	Kother et al. ⁵⁴ (kJ/mol)	Error (%)
PbO	−219.43	–	–
SiO ₂	−920.88	–	–
Pb ₄ SiO ₆	−1800.13	−1813.37	0.09
Pb ₂ SiO ₄	−1360.51	−1378.53	0.46
PbSiO ₃	−1140.69	−1148.97	0.74

models (e.g., Support Vector Machine, and k -Nearest Neighbors [k -NN]) outperforming linear models.

As an example, the enthalpy of three lead–silicate stoichiometric compounds calculated from the hybrid ML–LR polyhedron method is provided in Table 2. The resulted errors are below 0.74% in comparison with the experimental data reported by Kother et al.⁵⁴

5 | CONCLUSION

The polyhedron method proposed by Holland could be a promising approach for the estimation of the thermodynamic properties of compounds because (1) it is rooted in the physical structure of ionic compounds, (2) considering the cation coordination without a need for data about representative minerals in similar structural classes makes this model path-independent, (3) it is rather practical in comparison to atomistic (or molecular) methods and can be used to estimate the properties of a wide range of ionic compounds, and (4) the calculated errors are often less than those calculated by

other well-established and widely used methods such as NKR.

The polyhedron model, however, only estimates the thermodynamic properties of compounds with a first approximation. It is based on the linear summation of polyhedra's thermodynamic properties taking into account merely the first-nearest neighbor interactions and ignoring the significance of second-nearest neighbor and longer range interactions and the nonzero values of the enthalpy, and heat capacity of polyhedra's interactions. The present polyhedron model also ignores the effect of inter-polyhedra linkages on the thermodynamic properties, which could be important in some compounds and minerals.

It could be possible to overcome some of the important shortcomings of the polyhedron model by taking advantage of the field of artificial intelligence and devise the modified polyhedron model. For example, exploiting ML algorithms, the SNN, and longer range ordering can be calculated in ionic crystals. Possible correlations between the physical structural data (e.g., molar volume and electronegativity) and thermodynamic properties can be revealed to account for the nonzero values of the thermodynamic properties of polyhedra's interactions while obtaining the balance between computational time and accuracy.

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CONFLICT OF INTEREST STATEMENT

The authors claim that there is no conflicts of interest.

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