Estimation of missing third-law standard entropy of apatites using the optimized Volume-based Thermodynamics

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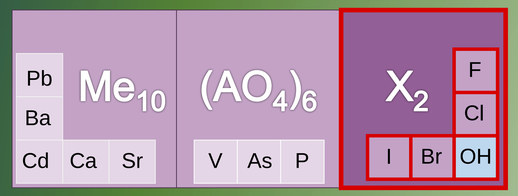
RESEARCH MOTIVATION

Apatite is well - known and one of the most numerous supergroup of minerals with given chemical formula as $\mathbf{Me_{10}(AO_4)_6X_2}$. Given it's abundance, only a small percentage of apatite group endmembers are studied for thermodynamic properties. The least number of experimental data is for **standard entropy *S*°** (Puzio & Manecki 2022). Due to the **growing need** for thermodynamic data, we are stepping forward to meet this challenge and propose a **new prediction method** for standard entropy for selected endmembers belonging to the apatite supergroup based on their **molar volume** V_m and **optimized** Volume-based Thermodynamics (**VBT**).

APATITE SUBGROUPS SYSTEM



In **this procedure**, apatites are **divided** into **subgroups**. The **apatites** within the subgroup have the same Me^{2+} and AO_4^{3-} but **different X**. Apatites having hydroxyl **group OH** at X position are in most cases excluded since they usually **do not follow** the linear **trend** defined by halides (Puzio & Manecki 2022).

VOLUME-BASED THERMODYNAMICS

Assumption: there is a linear relationship between standard entropy and molar volume for inorganic compounds, which can be described by the equation:

$$S°_{298.15K}\left(\frac{J}{mol \cdot K}\right) = 1262 \times V_m(nm^3) + 13 \qquad (1)$$

Adventage: The possibility of **estimating** the standard entropy **for any compound** based on molar **volume alone** (Fig. 1).

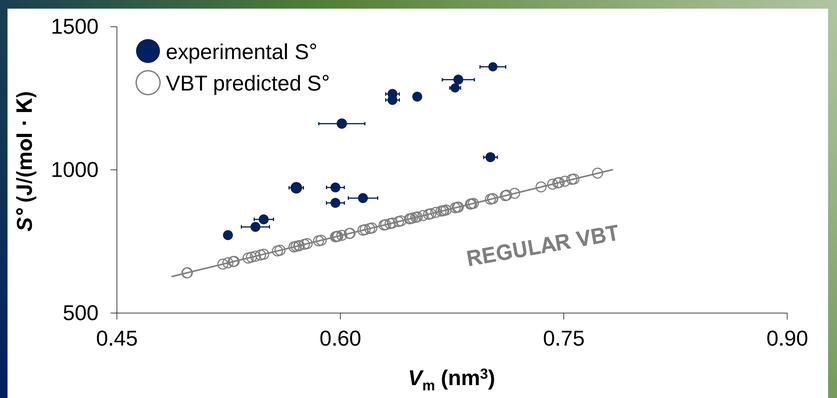


Fig. 1 Comparison of standard entropy (*S*°) predicted for apatites using Volume-based Thermodynamics (VBT, Eq. 1) along with existing experimental data against the molar volume (V_m).

Disadvantage: The **proxy** is subject to **considerable error** due to the treatment of compounds as a single population regardless of e.g., crystal system.

Hypothesis: VBT gives **accurate** estimated *S*° results if **applied to** narrow **subgroups** of compounds with the same crystal system, i.e., morphology.

RESEARCH OBJECTIVES

A. To investigate the relationship of **standard entropy versus molar volume** of apatite for **experimental** data **and** data **estimated** by available predictive methods e.g., Simple Salt Approximation (Glasser 2019).

B. To optimize the **Volume-Based Thermodynamics** method by applying and calibration Equation 1 with new ***a*** and ***b*** coefficients respect to selected **apatite subgroups**.

C. To propose a simple **one-step** method to **predict** missing **standard entropy** data for selected apatites and compounds with apatite-like structure.

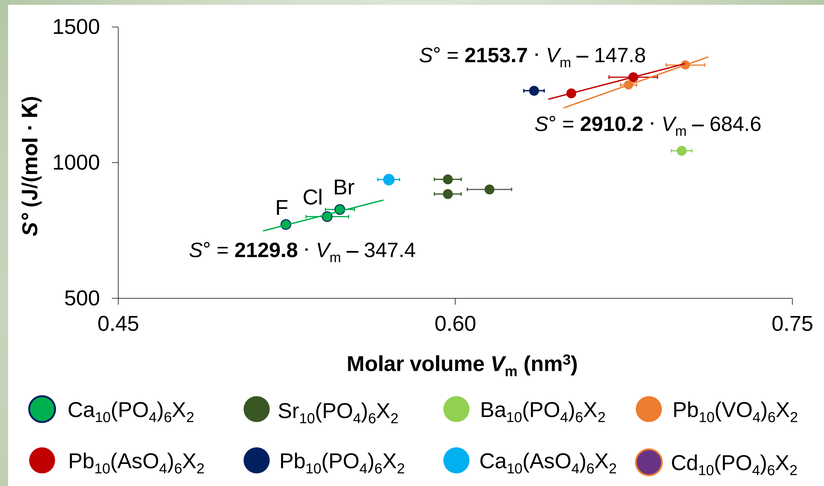


Fig. 2 Experimental standard entropies against their molar volume within apatite subgroups.

STANDARD ENTROPY VS. MOLAR VOLUME

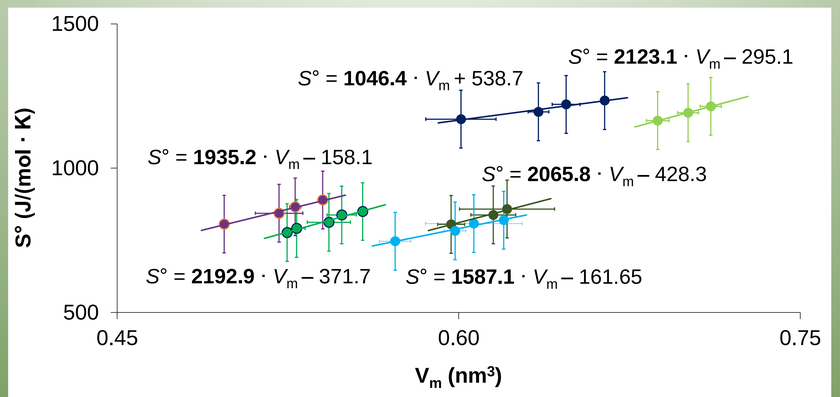


Fig. 3 Correlation of standard entropy predicted by Simple Salt Approximation with molar volume of apatites.

It is evident that apatites divide into halide subgroups also with respect to standard entropy. There is a strong linear relationship between *S*° and V_m. Regardless of the experimental variation of *S*° vs. V_m, the pattern for data estimated by Simple Salt Approximation is the same. Although the data obtained by the SSA method differ significantly from the experimental ones, the relationships between and within subgroups are preserved (Fig. 3). This is important output for further evaluation.

OPTIMIZED VOLUME-BASED THERMODYNAMICS

Although the absolute values of *S*° obtained by the SSA method differ from the experimental ones, the slope coefficients **„*a*"** of the regression lines for these two groups of data are similar. SSA slope coefficients can be used for calibration VBT equation for selected apatite subgroups where we cannot use **„*a*"** from experimental regression lines.

Based on the slope coefficients **„*a*"** of the **SSA** regression lines and single experimental data within selected **subgroups**, the coefficients **„*b*"** of the **optimized VBT** Equation (2) were calculated (Tab. 1) and **calculation** of **lacking S°**.

$$S°_{298.15K}\left(\frac{J}{mol \cdot K}\right) = a_i \times V_m(nm^3) + b_i \qquad (2)$$

Apatite subgroup	Slope coefficient a_i	b_i
$Ca_{10}(PO_4)_6X_2$	2129.8	-347.4
$Sr_{10}(PO_4)_6X_2$	2065.8	-332.2
$Ba_{10}(PO_4)_6X_2$	2123.1	-443.8
$Cd_{10}(PO_4)_6X_2$	1935.2	-158.1
$Pb_{10}(PO_4)_6X_2$	1046.4	579.5
$Ca_{10}(AsO_4)_6X_2$	1587.1	32.4
$Pb_{10}(AsO_4)_6X_2$	2153.7	-147.8
$Pb_{10}(VO_4)_6X_2$	2910.2	-684.6

Tab. 1 Optimized Volume-based linear regression coefficients for selected subgroups of apatites.

OPTIMIZED VBT - RESULTS

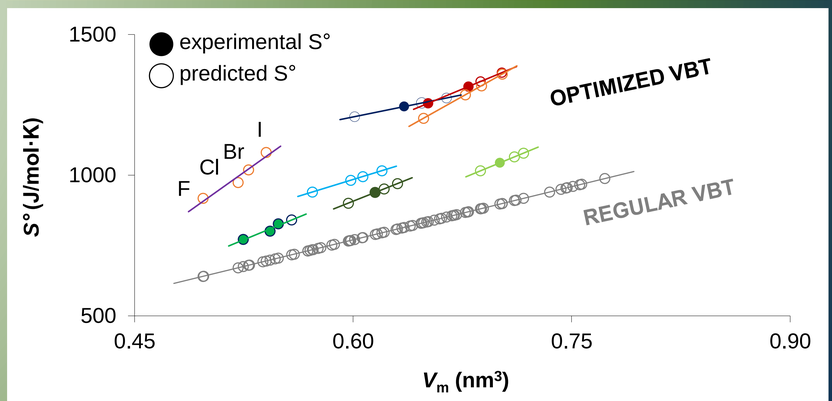


Fig. 4 Graphical comparison of the data obtained by the optimized and regular VBT method against molar volume along with experimental data.

SUMMARY

A. **Positive linear correlation** of standard entropy ***S*°** with molar volume $\boldsymbol{V_m}$ within apatite subgroups **allows** for **extrapolation** and interpolation of regression lines resulting in **new** so far unknown **data**.

B. **Optimized VBT method** gives **more accurate** predictions **than other** existing **methods**.

REFERENCES

Glasser, L. (2019). Apatite thermochemistry: the simple salt approximation. Inorganic Chemistry, 58(19), 13457-13463.

Puzio, B., & Manecki, M. (2022). The prediction method for standard enthalpies of apatites using the molar volume, lattice energy, and linear correlations from existing experimental data. Contributions to Mineralogy and Petrology, 177(11), 103.