

Modelling excess properties of mineral and melt solutions over large P-T ranges: implications for phase relations and seismic velocities in the mantle

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Abstract

Thermodynamic models of solid and liquid solutions in the Earth Sciences are increasingly used to calculate phase relations and seismic properties over large pressure and temperature ranges. Calculations often span over 1000 K and 5 GPa in studies of exhumation processes and metamorphism in subduction zones. Research into mantle phase relations and differentiation of the early Earth frequently involves calculations over 3000 K and 100 GPa. Despite spanning such huge ranges, a common approximation is that excess thermodynamic derivatives within solid solutions (entropy and volume) are pressure-temperature invariant. If these excesses are large, the approximation can result in large errors in gibbs free energy at high pressure and temperature, and errors in seismic velocities even within the range of calibration conditions.

In this paper, we present a solution to this problem by extending the sub-regular Margules mixing model using intermediate compounds to define the thermodynamic properties of solid solutions. Mathematical derivations are provided for excess properties (H^{ex} , S^{ex} , V^{ex}) and their pressure and temperature derivatives (K_T^{ex} , α^{ex} , Cp^{ex} etc.). We provide examples of garnet and melt solutions, showing that inclusion of a variable excess volume is vital to simulate observed phase relations and seismic velocities. Heuristics are suggested for in-

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intermediate compounds where individual thermodynamic properties are poorly constrained.

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1. Introduction

Thermodynamic models of solid and liquid solutions in the Earth Sciences are an integral part of

The approximation of constant positive excess volume implicitly yields an
 5 excess positive bulk modulus and negative thermal expansion, in conflict with
 both intuition and experimental observations. This is a particular problem
 where thermodynamic data are used over pressure ranges exceeding a few GPa,
 and where they are used to compute seismic wave velocities.

2. Motivation

10 2.1. Bulk moduli

The regular solution model implicitly defines many of the thermoelastic properties of solid solutions. For example, it defines the bulk modulus as the Reuss average of the endmembers:

$$K_T = -V \left(\frac{\partial P}{\partial V} \right) \quad (1)$$

$$= \left(\sum_i n_i V_i + V_{\text{excess}} \right) \left(\frac{1}{\sum_i \left(n_i \frac{V_i}{K_{Ti}} \right)} + \frac{\partial P}{\partial V_{\text{excess}}} \right) \quad (2)$$

V_{excess} is often approximated as zero, or as a scalar term with no pressure
 15 dependence. There are potential problems with this approximation:

- Excess enthalpy terms may change sign and/or become very large as pressure increases. For example, pyrope-grossular in Green et al., 2012 has an enthalpy interaction of 31 kJ/mol, and an excess volume of 0.164 kJ/kbar/mol, leading to a doubling of enthalpy over its stability field.

- 20 • The model predicts an excess bulk modulus with the same sign as the excess volume, conflicting with the Anderson-Anderson (1970) rule of thumb that $V K_T = c$
- Higher order excess volume terms to fit excess bulk moduli cause large deviations from a given equation of state at high pressure, as polynomial
- 25 expansions of equations of state converge very slowly.

In many circumstances, these shortcomings are unimportant. However, there is a fundamental need to adjust the solid solution model where

- the stability range of the solid solution extends over pressure regimes large enough to contribute significantly to changes in excess enthalpy inconsis-
- 30 tent with data, or
- mineral phases exhibit significant excess bulk moduli. The latter is especially important for those studies where velocities are obtained from the models.

2.2. Shear moduli

35 Thermodynamic variables do not include any input/constraints on shear moduli, which appear to deviate significantly from Voigt and Reuss averages.

3. Strategies

Taylor expansion of EoS converges extremely slowly, and leads to rapid divergence at pressures greater than the last crossing. This is part of the reason

40 that Stixrude and Lithgow-Bertelloni (2011) set excess volumes as zero. Thus, simply adding a bulk modulus term is inappropriate.

Best fit elastic properties for an ideal intermediate can be found, from which deviations can be applied.

4. The Extended Subregular Margules (ESM) model

45 The subregular Margules mixing model within a binary system approximates excess Gibbs free energies at any given pressure and temperature as a cubic function of composition (?):

$$\mathcal{G}^{xs} = W_{12}X_1X_2^2 + W_{21}X_1^2X_2 \quad (3)$$

The terms W_{ij} describing the interaction between endmembers i and j are normally described by a function of the form

$$W_{ij} = a_{ij} + b_{ij}P + c_{ij}T \quad (4)$$

50 In the ESM model, we instead define properties for each binary pair based on two intermediate compounds with compositions $X_i = X_j = 0.5$. For the special case of a symmetric mixing model, the properties for both intermediates are the properties of a compound with that composition; otherwise, both compounds are fictional. The interaction terms are now defined as:

$$W_{ij}^{\mathcal{G}} = 4(\mathcal{G}_{ij} + T\mathcal{S}_{ij}^{\text{conf}}) - 2(\mathcal{G}_i + \mathcal{G}_j) \quad (5)$$

55 where $\mathcal{S}_{ij}^{\text{conf}}$ is the configurational entropy of the intermediate compound, which depends on the number of sites on which mixing occurs. For a solution with n independent endmembers, and ignoring ternary terms, the excess nonconfigurational Gibbs free energy is (?)

$$\mathcal{G}^{xs} = \sum_{i=1}^n \sum_{j>1}^n X_i X_j \left(W_{ij} X_j + W_{ji} X_i + 0.5(W_{ij} + W_{ji}) \sum_k^n (1 - \delta_{ik})(1 - \delta_{jk}) X_k \right) \quad (6)$$

Using this new model, we can now define the properties of the solid solution
60 as follows:

$$\mathcal{G} = \sum_i X_i \mathcal{G}_i + \mathcal{G}^{xs} \quad (7)$$

$$\mathcal{H} = \sum_i X_i \mathcal{H}_i + \mathcal{H}^{xs} \quad (8)$$

$$\mathcal{S} = \sum_i X_i \mathcal{S}_i + \mathcal{S}^{xs} \quad (9)$$

$$\mathcal{V} = \sum_i X_i \mathcal{V}_i + \mathcal{V}^{xs} \quad (10)$$

$$C_P = \sum_i X_i C_{Pi} + T \left(\frac{\partial \mathcal{S}}{\partial T} \right)_P^{xs} \quad (11)$$

$$\alpha = \frac{1}{\mathcal{V}} \left(\sum_i X_i \alpha_i \mathcal{V}_i + \left(\frac{\partial \mathcal{V}}{\partial T} \right)_P^{xs} \right) \quad (12)$$

$$K_T = \frac{\mathcal{V}}{\sum_i X_i \frac{\mathcal{V}_i}{K_{Ti}} - \left(\frac{\partial \mathcal{V}}{\partial P} \right)_T^{xs}} \quad (13)$$

$$C_V = C_P - \mathcal{V} T \alpha^2 K_T \quad (14)$$

$$K_S = K_T \frac{C_P}{C_V} \quad (15)$$

$$\gamma = \frac{\alpha K_T \mathcal{V}}{C_V} \quad (16)$$

With the exception of the enthalpy excess, excess terms (\mathcal{S}^{xs} , \mathcal{V}^{xs} etc) are derived in the same way as the excess Gibbs free energy (Equation 6), with interaction terms defined as follows:

$$W_{ij}^{\mathcal{S}} = 4(\mathcal{S}_{ij} - \mathcal{S}_{ij}^{\text{conf}}) - 2(\mathcal{S}_i + \mathcal{S}_j) \quad (17)$$

$$W_{ij}^{\mathcal{V}} = 4\mathcal{V}_{ij} - 2(\mathcal{V}_i + \mathcal{V}_j) \quad (18)$$

$$W_{ij}^{\partial \mathcal{V} / \partial P} = 4\mathcal{V}_{ij} / K_{Tij} - 2(\mathcal{V}_i / K_{Ti} + \mathcal{V}_j / K_{Tj}) \quad (19)$$

$$W_{ij}^{\partial \mathcal{V} / \partial T} = 4\alpha_{ij} \mathcal{V}_{ij} - 2(\alpha_i \mathcal{V}_i + \alpha_j \mathcal{V}_j) \quad (20)$$

$$W_{ij}^{\partial \mathcal{S} / \partial T} = \frac{4C_{Pij} - 2(C_{Pi} + C_{Pj})}{T} \quad (21)$$

Finally, excess enthalpy is defined as

$$\mathcal{H}^{xs} = \mathcal{G}^{xs} + T \mathcal{S}^{xs} \quad (22)$$

65 4.1. Heuristics

It is often the case that endmembers are particularly well studied, while the properties of the solid solution are constrained only by enthalpies of solution and

volumes at room temperature and pressure. In the absence of other data, heuristics are required to constrain the properties of the intermediate compounds. In
70 this study, we suggest that the following heuristics be used:

$$\mathcal{S}_{ij} = 0.5(\mathcal{S}_i + \mathcal{S}_j) + \mathcal{S}_{ij}^{\text{conf}} \quad (23)$$

$$C_{Pij} = 0.5(C_{Pi} + C_{Pj}) \quad (24)$$

$$K'_T = -\frac{\partial}{\partial P} \left(\nu \left(\frac{\partial P}{\partial \mathcal{V}} \right)_T \right) \sim \nu \left(\sum_i \frac{X_i \mathcal{V}_i}{K'_{Ti} + 1} \right)^{-1} - 1 \quad (25)$$

5. Conclusions

References

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