

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

R. Myhill, C. Beyer

Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth, Germany

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 pyroxene, garnet and melt solutions, showing that inclusion of a variable excess volume is vital to simulate observed phase relations and seismic velocities. Heuristics are sug-

*Corresponding author: R. Myhill

Email address: myhill.bob@gmail.com (R. Myhill, C. Beyer)

gested for intermediate compounds where individual thermodynamic properties are poorly constrained.

Keywords: high pressure, excess properties

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.

In many circumstances, these shortcomings are unimportant. However, there
10 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 inconsistent 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.

15 2. The Extended Subregular Margules (ESM) model

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 (Helffrich and Wood, 1989):

$$\mathcal{G}^{xs} = W_{12}X_1X_2^2 + W_{21}X_1^2X_2 \quad (1)$$

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

$$W_{ij} = a_{ij} + b_{ij}P + c_{ij}T \quad (2)$$

dropbox 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
 25 compounds are fictional. The interaction terms are now defined as:

$$W_{ij}^{\mathcal{G}} = 4(\mathcal{G}_{ij} + T\mathcal{S}_{ij}^{\text{conf}}) - 2(\mathcal{G}_i + \mathcal{G}_j) \quad (3)$$

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 (Helffrich and Wood, 1989)

$$\mathcal{G}^{xs} = \sum_{i=1}^n \sum_{j>1}^n X_i X_j \left(W_{ij} X_j + W_{ji} X_i + 0.5(W_{ij} + W_{ji}) \sum_k^n (1 - \delta_{ik})(1 - \delta_{jk}) X_k \right) \quad (4)$$

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

$$\mathcal{G} = \sum_i X_i \mathcal{G}_i + \mathcal{G}^{xs} \quad (5)$$

$$\mathcal{H} = \sum_i X_i \mathcal{H}_i + \mathcal{H}^{xs} \quad (6)$$

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

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

$$C_P = \sum_i X_i C_{P_i} + T \left(\frac{\partial \mathcal{S}}{\partial T} \right)_P^{xs} \quad (9)$$

$$\alpha = \frac{1}{\mathcal{V}} \left(\sum_i X_i \alpha_i \mathcal{V}_i + \left(\frac{\partial \mathcal{V}}{\partial T} \right)_P^{xs} \right) \quad (10)$$

$$K_T = \frac{\mathcal{V}}{\sum_i \frac{X_i \mathcal{V}_i}{K_{T_i}} - \left(\frac{\partial \mathcal{V}}{\partial P} \right)_T^{xs}} \quad (11)$$

$$C_V = C_P - \mathcal{V} T \alpha^2 K_T \quad (12)$$

$$K_S = K_T \frac{C_P}{C_V} \quad (13)$$

$$\gamma = \frac{\alpha K_T \mathcal{V}}{C_V} \quad (14)$$

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 4), with interaction terms defined as follows:

$$W_{ij}^{\mathcal{S}} = 4(\mathcal{S}_{ij} - \mathcal{S}_{ij}^{\text{conf}}) - 2(\mathcal{S}_i + \mathcal{S}_j) \quad (15)$$

$$W_{ij}^{\mathcal{V}} = 4\mathcal{V}_{ij} - 2(\mathcal{V}_i + \mathcal{V}_j) \quad (16)$$

$$W_{ij}^{\partial \mathcal{V} / \partial P} = -4\mathcal{V}_{ij} / K_{Tij} + 2(\mathcal{V}_i / K_{Ti} + \mathcal{V}_j / K_{Tj}) \quad (17)$$

$$W_{ij}^{\partial \mathcal{V} / \partial T} = 4\alpha_{ij} \mathcal{V}_{ij} - 2(\alpha_i \mathcal{V}_i + \alpha_j \mathcal{V}_j) \quad (18)$$

$$W_{ij}^{\partial \mathcal{S} / \partial T} = \frac{4C_{Pij} - 2(C_{Pi} + C_{Pj})}{T} \quad (19)$$

35 Finally, excess enthalpy is defined as

$$\mathcal{H}^{xs} = \mathcal{G}^{xs} + T\mathcal{S}^{xs} \quad (20)$$

2.1. 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
40 this study, we suggest that the following heuristics be used:

$$\mathcal{S}_{ij} = 0.5(\mathcal{S}_i + \mathcal{S}_j) + \mathcal{S}_{ij}^{\text{conf}} \quad (21)$$

$$C_{Pij} = 0.5(C_{Pi} + C_{Pj}) \quad (22)$$

$$\alpha_{ij} = 0.5\mathcal{V} \left(\frac{\alpha_i}{\mathcal{V}_i} + \frac{\alpha_j}{\mathcal{V}_j} \right) \quad (23)$$

$$K'_T = -\frac{\partial}{\partial P} \left(\mathcal{V} \left(\frac{\partial P}{\partial \mathcal{V}} \right)_T \right) \sim \mathcal{V} \left(\sum_i \frac{X_i \mathcal{V}_i}{K'_{Ti} + 1} \right)^{-1} - 1 \quad (24)$$

If excess volumes are zero, the bulk modulus is given by Equation 11, with the differential term equal to zero. However, non-zero excess volumes are unlikely

Table 1: Jadeite-Aegirine mixing parameters to fit the room temperature data of Nestola et al. (2006). $K_0'' = -K_0'/K_0$.

	jadeite	aegirine	jd50ae50	ae50jd50
V_0 (cm ³ /mol)	60.5640 ± 0.0001	64.6261 ± 0.0004	62.3641 ± 0.0005	62.4522 ± 0.0005
K_0 (GPa)	133.5 ± 0.2	116.0 ± 0.2	124.8 ± 0.5	126.7 ± 0.4
K_0'	4.6	4.4	4.4785	4.4785

to remain constant with pressure and temperature. Mixing of elements with
45 different ionic radii and chemical bonding on sites affects not only the packing
efficiency, but also the mechanisms of compression. A positive excess volume
implies a more open structure which will be more prone to volume decrease on
compression.

We suggest that, in the absence of other data it should be assumed that
50 $\left(\frac{\partial V}{\partial P}\right)_T^{xs} \rightarrow 0$ as $P \rightarrow \infty$. Bulk moduli for intermediates can then be constrained.

$$K_T \sim 0.5(K_{Ti} + K_{Tj}) + a \left(\frac{K_{Ti}\mathcal{V}_j + K_{Tj}\mathcal{V}_i}{\mathcal{V}_i + \mathcal{V}_j} - 0.5 * (K_{Ti} + K_{Tj}) \right) \quad (25)$$

The factor a before the second term on the RHS of Equation 25 modifies
the rule of thumb proposed by Anderson and Anderson (1970) to estimate the
compressibility of endmembers based on their molar volumes. A value of $a = 4$
serves as a good first approximation to that required to satisfy our proposed
55 heuristic.

3. Examples

3.1. Pyroxene

Our first example is that of jadeite-aegirine pyroxene, an almost ideal solid
solution (from a volumetric perspective). We use this model to illustrate that
60 even when excess volumes are extremely small, excess bulk moduli are resolvable.
The experimental data is that of Nestola et al. (2006), and the equation of state
used is the Modified Tait (Holland and Powell, 2011).

3.2. Garnet

Our second example is the pyrope-grossular join, which is well-known to
65 have significant non-ideality and volumes of mixing. Here we use the excess
volume of Du et al. (2015), approximating the solid solution as symmetric and
using the heuristics described above.

3.3. Fe-O melt

Our final example is that of Fe-FeO melt. This liquid solution is extremely
70 important for understanding partitioning of oxygen into the Earth’s core. At
pressures <25 GPa, the solution exhibits significant non-ideality, with a large
miscibility gap between ionic and metallic Fe-O liquids (Frost et al., 2010). As
pressure increases, this miscibility gap disappears, indicating a negative excess
volume of mixing. Komabayashi (2014) uses an ideal model at high pressure,
75 and obtains a more-or-less reasonable fit to the available experimental data.

To model processes of mantle differentiation and core formation, it would be
extremely useful to have a single model describing the properties of melts over
relevant pressure and temperature ranges. Clearly a high pressure ideal model
cannot be reconciled with a low pressure model with large excess volumes of
80 mixing without incorporating excess bulk moduli and thermal expansivities.

?

4. Conclusions

References

- Anderson, D.L., Anderson, O.L., 1970. Brief report: The bulk modulus-volume
85 relationship for oxides. *Journal of Geophysical Research* 75, 3494–3500.
- Du, W., Clark, S.M., Walker, D., 2015. Thermo-compression of pyrope-grossular
garnet solid solutions: Non-linear compositional dependence. *American
Mineralogist* 100, 215–222. [http://ammin.geoscienceworld.org/content/
100/1/215.full.pdf+html](http://ammin.geoscienceworld.org/content/100/1/215.full.pdf+html).
- 90 Frost, D.J., Asahara, Y., Rubie, D.C., Miyajima, N., Dubrovinsky, L.S.,
Holzapfel, C., Ohtani, E., Miyahara, M., Sakai, T., 2010. Partitioning of
oxygen between the Earth’s mantle and core. *Journal of Geophysical Re-
search (Solid Earth)* 115, 2202.
- Helfrich, G., Wood, B.J., 1989. Subregular model for multicomponent solutions.
95 *American Mineralogist* 74, 1016–1022.
- Holland, T.J.B., Powell, R., 2011. An improved and extended internally con-
sistent thermodynamic dataset for phases of petrological interest, involving a
new equation of state for solids. *Journal of Metamorphic Geology* 29, 333–383.
- Komabayashi, T., 2014. Thermodynamics of melting relations in the system
100 Fe-FeO at high pressure: Implications for oxygen in the Earth’s core. *Journal
of Geophysical Research (Solid Earth)* 119, 4164–4177.
- Nestola, F., Boffa Ballaran, T., Liebske, C., Bruno, M., Tribaudino, M., 2006.
High-pressure behaviour along the jadeite $\text{NaAlSi}_2\text{O}_6$ -aegirine $\text{NaFeSi}_2\text{O}_6$
solid solution up to 10 GPa. *Physics and Chemistry of Minerals* 33, 417–
105 425.