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Retrieval of stoichiometry and stability of solid-solution end members by “dual-thermodynamic” calculations

D.A. KULIK, E. CURTI AND J. TITS

Waste Management Laboratory (LES), Paul Scherrer Institute
5232 Villigen PSI, Switzerland (dmitrii.kulik@psi.ch)

Many environmental contaminants can be retarded by solid solution formation. Data on thermodynamic properties of solid solutions are still scarce, difficult to retrieve from experimental partition coefficients. This contribution aims at showing that the *dual-thermodynamic* (DualTh) calculations are helpful in determining the unknown solubility products of pure end-members or the parameters of non-ideal mixing.

GEM algorithm [1] solves chemical equilibria at given T, P and bulk composition of the system by computing mole amounts x_j of chemical species in phases (*primal solution*) simultaneously with the *dual solution* values u_i (chemical potentials of elements). At equilibrium, u_i values must be the same in all co-existing phases. Hence, the chemical potential $\mu_j^{(u)}$ of j -th solid-solution end member can be found from its chemical formula using the dual solution vector u for the co-existing aqueous phase of known bulk composition [2]. End-member mole fractions (χ_j) can be determined from the measured bulk composition of solid-solution phase. Either μ_j^0 (standard chemical potential) or γ_j (activity coefficient) of end-member j can be found from a DualTh equation:

$$\mu_j^0 + RT \ln \gamma_j = \mu_j^{(u)} - RT \ln \chi_j \quad (1).$$

If μ_j^0 is known (e.g. for a pure mineral end-member) then γ_j can be found [3]. Alternatively, if the parameters of mixing are available, the unknown μ_j^0 value can be determined [4]. It may also happen that the end-member stoichiometry is not known, but experimental partitioning data at different trace χ_j are available. Postulated end-member candidates can then be tested using Eq (1) by calculating a $G_j^* = \mu_j^0 + RT \ln \gamma_j$ estimate for each data point. Appropriate end-members must have (within $\pm 2 \text{ kJ} \cdot \text{mol}^{-1}$) the same G_j^* value for all data points [5]. *DualTh* calculations need the GEM-Selektor [2,6] or similar package to obtain elemental chemical potentials u_i .

From experimental viewpoint, the *DualTh* concept requires that compositions of coexisting aqueous and solid solutions are reported in sufficient detail to compute aqueous equilibria, and to estimate the extent of recrystallization and end-member mole fractions in solid solution. Partitioning of more than one minor element can be studied simultaneously.

References

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Solid solutions of trace Eu(III) in calcite: A thermodynamic study

E. CURTI, D.A. KULIK AND J. TITS

Waste Management Laboratory (LES), Paul Scherrer Institut
CH-5232 Villigen PSI, Switzerland (enzo.curti@psi.ch)

New results from our laboratory and published data on solid solution formation between trace Eu and calcite, obtained under widely different pH-pCO₂ conditions, were modeled using the Gibbs energy minimization (GEM) method [1]. In a first step (“forward” modeling), we tested ideal binary solid solutions between calcite and the prospective Eu end-members Eu₂(CO₃)₃, EuNa(CO₃)₂, EuOH(CO₃) or Eu(OH)₃. For these end-members, corresponding solid phases with independently measured solubility products are available. None of the four binary solid solutions could reproduce all experimental datasets simultaneously. In a second step (“inverse” modeling), ideal binary solid solutions were constructed between calcite and the candidate Eu end-members EuO(OH), EuH(CO₃)₂ and EuO(CO₃)_{0.5}, for which independent solubility or calorimetric data are not available. These end-members were selected based on crystal-chemical criteria. For each single data point and each end-member α , a molar free energy of formation with inherent activity term ($G_{\alpha}^* = G_{\alpha}^{\circ} + RT \ln \gamma_{\alpha}$) was estimated from *dual-thermodynamic* (*Dual-Th*) GEM calculations [1]. The statistical mean of G_{α}^* was then calculated for each of the three datasets considered. A specific end-member was considered to be acceptable if a standard deviation of $\pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ or less resulted for each single dataset, and if the mean G_{α}^* -values calculated for the various datasets were found to coincide. However, no binary solid solution with any of the above end-member candidates proved to satisfy both criteria.

The third step in our analysis involved the construction of ternary solid solutions with CaCO₃ as major end-member and any two of the seven Eu trace end-members mentioned above. It was found that an overall fit of all experimental data can be obtained only with the ternary ideal solid solution EuH(CO₃)₂ – EuO(OH) – CaCO₃, setting $G_{EuHCO_3}^* = -1733 \text{ kJ} \cdot \text{mol}^{-1}$ and $G_{EuO(OH)}^* = -955 \text{ kJ} \cdot \text{mol}^{-1}$. All other end-member combinations failed.

Our model is consistent with laser fluorescence data, indicating two distinct species for Cm(III) incorporated in calcite [2] (one partially dehydrated, the other completely dehydrated) and with Nd-calcite EXAFS data [3], showing an increase in coordination number and Nd-O distances. In conclusion, our study indicates that substitution of trivalent cations in carbonate crystal structures requires complex multicomponent thermodynamic models, the parametrization of which is facilitated by the inverse *DualTh* modeling.

References

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