

Solid-aqueous equilibrium in the BaSO₄-RaSO₄-H₂O system: first-principles calculations and a thermodynamic assessment

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Phase relations in the BaSO₄-RaSO₄-H₂O system are important for the understanding of the role of barite-type minerals in controlling concentrations of Ra²⁺ in ground waters. These relations are extremely sensitive to the degree of non-ideality of the solid solution phase, which commonly is expressed in terms of the regular mixing parameter, W_{BaRa} . The experimentally based W_{BaRa} values differ by up to one order of a magnitude. In this study W_{BaRa} is computed from first principles. The regular mixing parameter, W_{BaRa} , is interpreted as the slope of the enthalpy of mixing in the limit of infinite dilution ($x_{\text{Ra}} = 0$) and is calculated from the change in the enthalpy of a 2x2x2 supercell of BaSO₄ due to the insertion of a single substitutional defect of Ra. The method is validated by computing W values for a wider range of binary solid solutions with barite and aragonite structures. The predicted values agree with the available experimental data within the confidence limit of 30%. The W parameters computed for barite- and aragonite-type solid solutions correlate linearly with the square of the relative difference in the standard volumes of the end-members, $\delta = ((V_1 - V_2)/(V_1 + V_2))^2$. The linear regression equations are W (kJ/mol) = (2260 ± 150)δ and W (kJ/mol) = (1960 ± 80)δ for the barite and aragonite series, respectively. Our value ($W_{\text{BaRa}} = 2.2 \pm 0.70$ kJ/mol; $a_0 = 0.89 \pm 0.30$) falls within the range of the previous estimates of 0.9 kJ/mol [1] and 3.7-6.2 kJ/mol [2] obtained from solid – aqueous equilibrium data. The value of $a_0 = 0.89 \pm 0.30$ implies that the solid – aqueous equilibrium in the BaSO₄-RaSO₄-H₂O system has an alyotropic point in close proximity to the BaSO₄ end-member.

The calculations were performed at Jülich Supercomputing Centre.

[1] Zhu, Ch. (2004) *Geochim. et Cosmochim. Acta*, 68: 3327–3337

[2] Curti, E, Fujiwara K., Iijima K., et al. (2010) *Geochim. et Cosmochim. Acta*, 74: 3553–3570