

## **Solid-aqueous equilibrium in the BaSO<sub>4</sub>-RaSO<sub>4</sub>-H<sub>2</sub>O system: first-principles calculations and a thermodynamic assessment**

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Phase relations in the BaSO<sub>4</sub>-RaSO<sub>4</sub>-H<sub>2</sub>O system are important for the understanding of the role of barite-type minerals in controlling concentrations of Ra<sup>2+</sup> 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,  $W_{\text{BaRa}}$ . The experimentally based  $W_{\text{BaRa}}$  values differ by up to one order of a magnitude. In this study  $W_{\text{BaRa}}$  is computed from first principles. The regular mixing parameter,  $W_{\text{BaRa}}$ , 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 BaSO<sub>4</sub> 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) =  $(2260 \pm 150)\delta$  and  $W$  (kJ/mol) =  $(1960 \pm 80)\delta$  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 BaSO<sub>4</sub>-RaSO<sub>4</sub>-H<sub>2</sub>O system has an alyotropic point in close proximity to the BaSO<sub>4</sub> 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