

Thermodynamics of fluid-rock interactions with a metamorphic petrology point of view: Example with H₂O – CO₂ – NaCl mixtures

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Modelling the reciprocal solubilities of gases and the mineral-fluid reactions taking place in the context of CO₂ injection in geological reservoirs requires well-constrained thermodynamic databases and activity models for both minerals and aqueous species. By applying the thermodynamic formalism of Holland and Powell [1] originally derived for high-grade metamorphic rocks, it is possible to calculate phase diagrams for H₂O – CO₂ mixtures at conditions relevant to CO₂ storage independently from the uncertainties associated with the thermodynamic properties of the pure phases. Activity models for mixing fluids can thus be accurately constrained from experimentally measured solubilities. They are similar in essence to the activity models used for minerals showing solid solutions although varying non-linearly with pressure and temperature.

A refinement to this formalism, proposed by Evans and Powell [2] to account for speciation in fluids, has been successfully applied to model halite solubility over a large range of pressure and temperature. It takes into account the speciation of dissolved NaCl varying with concentration, pressure and temperature, by using macroscopic interaction parameters independent of the concentration. The relative simplicity of this thermodynamic formalism make it possible to differentiate uncertainties on activity models from uncertainties on the standard-state properties and then to use the thermodynamic properties of minerals and fluids from the THERMOCALC database [1]. Uncertainties can then be propagated to predictive calculations. It appears that the uncertainties on the thermodynamic properties of aqueous species, taken as given in the THERMOCALC database, are the major source of uncertainty in solubility calculations.

[1] Holland & Powell (1998) *J. Met. Geol.* **16**, 309–343.

[2] Evans & Powell (2006) *GCA* **70**, 5488–5506.

Surface structure effects on gibbsite nanoparticle reactivity

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Potentiometric titration results reported for different gibbsite (α -Al (OH)₃) nanoparticle samples have exhibited significantly different surface charging behavior. This has led to substantially different multi-site complexation (MUSIC) models to explain the data. We have re-examined this problem by applying a new method for assigning intrinsic pK_a values and another method for accurately analyzing particle/aggregate surface areas and geometries using atomic force microscopy (AFM).

The method for estimating pK_a values involves *ab initio* molecular dynamics simulations of hydrated gibbsite surfaces, and takes into account progressive bond relaxation as H⁺ ions are added to the surface. Based on the results of this method, we predict that the gibbsite basal (001) surface should charge significantly in the environmental pH range. Also, the pK_a values are extremely sensitive to the local chemical environment, and may be more sensitive on surfaces perpendicular to shorter particle dimensions.

AFM surface area analysis provides evidence that gibbsite nanoparticles aggregate in suspension, but are held together loosely. This is consistent with the idea that in suspension individual particles in aggregates are held apart by hydration forces.

Taking these and other observations into account, we have constructed a surface complexation model that can predict gibbsite surface charging behaviour in samples whose aspect ratios differ by a factor of 4.