

Mineralogical approaches to fundamental crystal dissolution kinetics

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ABSTRACT

We introduce a general kinetic model for crystal dissolution that explicitly tracks all the various atoms in the crystal structure as part of the reaction mechanism. This model will be used in this and subsequent articles to develop a theory for the treatment of experimental and field water-rock kinetic data. The model is based on a many-body reaction mechanism. It is built from both elementary reactions, i.e., bond-breaking and bond-forming, and basic reactions, i.e., dissolution of surface units, adsorption and incorporation of solution units, and mobility of units at the crystal surface. The full crystal structure is used to calculate the interactions of neighboring atoms as well as possible defects of the crystal lattice in the model. This approach is different from models based on either molecular precursor complexes or adsorption.

We analyze several fundamental concepts such as activation energy, surface free energy, the solubility product, inhibition/catalysis, and saturation-state dependence using our approach. In addition, surface features such as nucleation, steps, and defects are presented and put in a quantitative basis in this paper. The resulting kinetic framework can handle explicitly any crystal structure, treating the actual bonding and position of all atoms within a given surface orientation in the structure. Investigation of the properties of such a general kinetic model leads to new relations between the activation energy and the net energy changes in the hydrolyses reactions, between surface free energy and activation energies and between inhibition and the statistical mechanics of kink sites. The kinetic model can actually account for the emergence of a solubility product from a reaction mechanism involving independent kinetics for the different species using steady-state concepts on the behavior of surface sites. The possible ΔG dependence of the overall rate is studied with the general approach. Isotachs are used to exhibit the interplay of ΔG and inhibition within a simple AB mineral structure. The crystal-based reaction mechanism not only leads to a unified explanation of many observed water-rock features but also produce a series of modifications of kinetic results not fully understood before.