

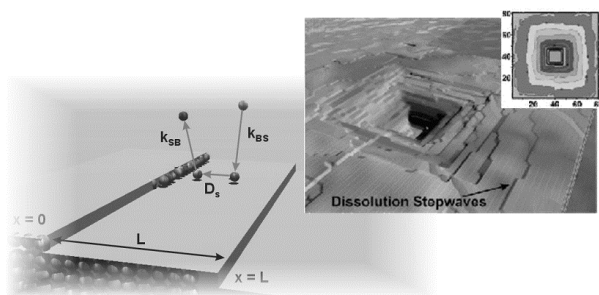
What is the role of free energy in reaction mechanism?

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In the description of reaction kinetics via phenomenological rate laws, it is common practice to express the rate's dependency on disequilibrium with a free energy term, $f(\Delta G_r)$, that is distinct from those that explicitly accommodate inhibition, catalysis, adsorption of impurities, pH dependence, etc. This mechanistic/non-mechanistic "division of labor" as a product series provides that the overall rate $r \rightarrow 0$ as $\Delta G_r \rightarrow 0$, satisfies a link between kinetics and thermodynamics, and in dissolution reactions yields a constant rate as $\Delta G_r \rightarrow -\infty$. This $f(\Delta G_r)$ function typically has an exponential form where the rate is proportional to $\exp(-\beta\Delta G_r)$. The problem with this treatment is that (1) it permits little insight into the control of reaction rate as the equilibrium condition (e.g., a given ion activity product) is approached, and (2) has the unfortunate implication that as $\Delta G_r \rightarrow 0$, the dissolution rate becomes independent of solution composition and thus of mechanism itself. For dissolution of even a simple ionic solid such as CaCO_3 this implies that extreme variations in the ratio of ionic activities should still yield a constant rate close to the solubility product. Under this assumption, alkaline soda lake water should yield the same dissolution rate as a CO_2 -rich subsurface brine, a result that satisfies neither our intuitive expectation nor our empirical results.

Here we apply a parameterized Monte Carlo model to investigate dissolution in the near-equilibrium region, providing a basis for understanding both the role of differences in ionic activity ratio as well as the role of common impurities.



Monte Carlo modeling of dissolution and etch pit formation at defect centers via attachment-diffusion-detachment processes at steps edges and terraces.