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Clusters, nanoparticles and the solubility constant

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The solubility of minerals is conventionally presented in terms of a solubility constant. For a mineral A, the solubility constant, K_{sp} , is equivalent to the equilibrium constant for the reaction $aA = b\{X_1\} + c\{X_2\}$

$$K_{sp} = \frac{\prod\{X_i\}^{m_i}}{\{A\}^a} \quad (1)$$

where a , b and c are the number of moles in the balanced equation and $\{X\}$ refers to the activity of X.

Conventionally, the activity of a solid phase in its ideal state is defined as unity and (1) becomes

$$K_{sp} = \prod\{X_i\}^{m_i} \quad (2)$$

Deviations from the ideal state, where $\{A\} \neq 1$, are then contained in the solubility constant, K_{sp} .

The first condensed phase in many natural low temperature systems is nanoparticulate, and deviations from ideal behavior, included in a so-called "surface free energy" term, dominate the total free energy of the system. As the condensed phase becomes larger, the "surface free energy" term becomes less significant and the solubility begins to approach the solubility of the bulk phase. Even in the bulk phase, surface features and phases often control the solubility. In nanoparticles, the surface phase dominates the behavior of the solid and determines its solubility.

The solubility of nanoparticles changes continuously with time. In any aquatic environment, the measured concentration of solutes is then some sort of steady state sample which is only tenuously related to mineral solubilities as defined in (2).

Aqueous clusters are characterised by a spectrum of compositions which ultimately reach the mass of the first condensed phase. A stability constant for any individual cluster may be defined, if that particular configuration exists for a significant time or dominates the cluster spectrum. But the constants for the solution series are, by definition, variable and continuously changing. This means that the activity product of the dissolved species in an aquatic system is not constant but changing. Also, total metal and ligand in soluble clusters can be measured by different analytical procedures complicating interpretation of the activities of the aqueous metal and ligand conventionally used in (1).

The net result of these observations on the condensed and dissolved species in low temperature aquatic environments is that the solubility constant is at best not a constant value and at worst only an empirical measurement for a particular set of conditions at a particular time.

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Interface interactions in nanoparticle aggregates

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Mineral nanoparticle suspensions have a strong tendency towards aggregation. In natural settings, and in synthetic materials, diverse aggregate morphologies are observed. Aggregation will modify the transport properties and net surface reactivity of nanoparticles, and is the first step towards growth by attachment. We have studied aggregates of natural and synthetic metal sulfide and metal oxide nanoparticles. By observation and simulation of nanoparticle ensembles, we aim to understand the nature and consequences of particle-particle interactions.

Uncoated 3 nm ZnS nanoparticles synthesized at room temperature in both water and methanol form aggregates. Nanoparticle structure in water is crystalline. In contrast, nanoparticles in methanol possess considerable internal distortion, driven by strain at the nanoparticle surface. Weak solvent interactions do not relieve the strain. However, crystallinity increases significantly when the nanoparticles are aggregated by the removal of methanol. This is reversed when the nanoparticles are disaggregated. Molecular modeling of nanoparticle motion and structural changes in an assembly of nanoparticles provides insight to the surface interactions that accompany aggregation. When surface-solvent interactions are low, particle-particle interactions may have an associated stabilization energy due to reduction of strain throughout the interior of the nanoparticle. The stabilization energy is low, as it can be reversed at room temperature.

We have also investigated aggregation and crystal growth in oxide systems. Both iron oxyhydroxide and titanium dioxide grow via oriented aggregation under some conditions. Coarsening may be accompanied by transition to a stable phase that depends upon solution pH-controlled interfacial energy. Charge development, investigated by molecular simulations, appears to explain orientational relationships observed in TEM images of aggregating goethite crystals. Surface charge on iron oxyhydroxide nanoparticles is proposed to influence the thermodynamics and kinetics of acid-base, complexation, and redox reactions in these systems.