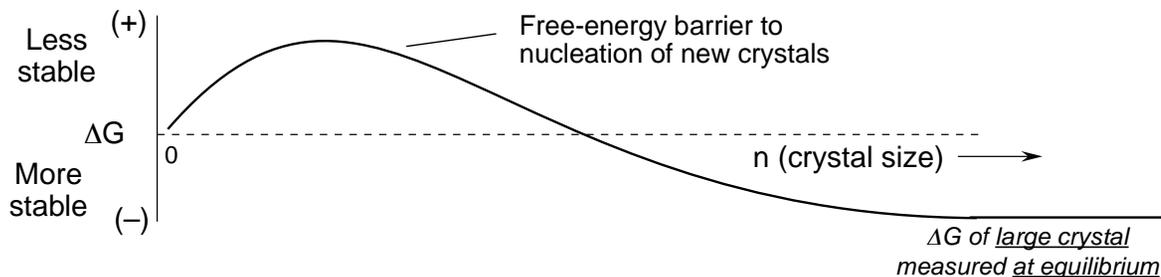
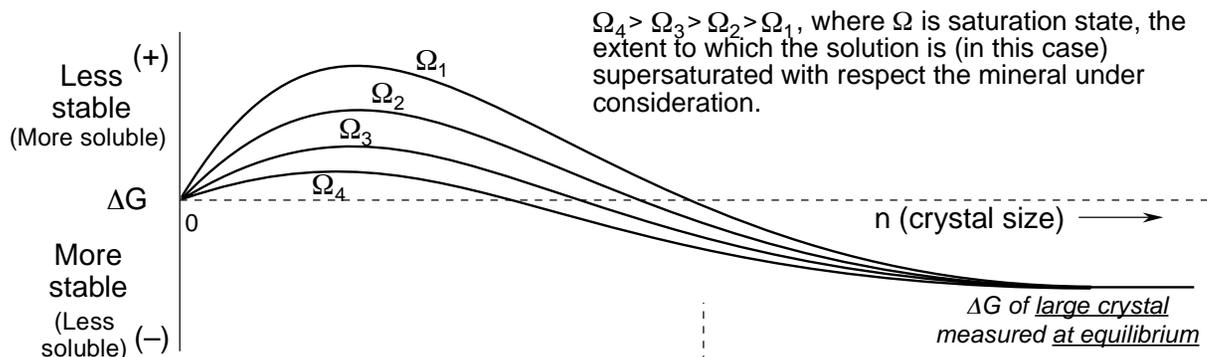


## An explanation of the free-energy barrier to nucleation of crystals

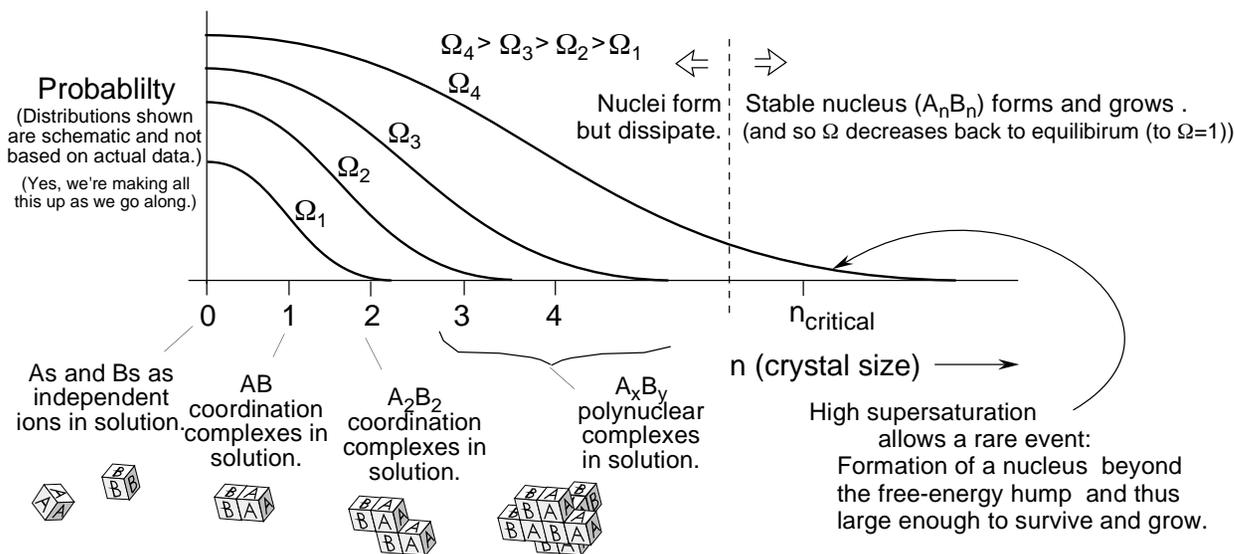
In a previous illustration of "Why very small particles are very soluble", we saw a curve for solubility as a function of crystal size. We can extend that curve to even smaller crystal sizes and, at least in theory, reach the curve at right showing the free energy of tiny crystals of any one mineral as a function of their size:



Such curves are commonly used in explaining the inhibition of nucleation of new crystals (e.g., Berner, 1980). The hump in the curve above represents an excess energy that destabilizes very small crystals (because such a large proportion of their atoms are weakly bonded outer atoms, at kinks and edges and on terraces). The size of that hump (and barrier) decreases with increasing saturation state of the solution, as is shown at right:



Another way to think about the figure above is to think in terms of probabilities that a nucleus will develop large enough to survive and grow. The horizontal axis of the diagram at right is the same as that for the one above. The vertical axis is probability of the existence of the various combinations of A and B, our two solutes that might form a nucleus of mineral AB. The greater the amount of A and B in solution (the greater  $\Omega$  is), the greater the probability of any given combination.



### Key points:

1. Formation of crystal nuclei is disfavored energetically.
2. Higher saturation state makes formation and growth of crystal nuclei more likely (or at least less improbable).

See also "Thermodynamics of nucleation of a new crystal vs. growth on an existing crystal"