

Multiphase transformation and Ostwald's rule of stages during crystallization of a metal phosphate

Authors: Sung-Yoon Chung, Young-Min Kim, Jin-Gyu Kim, Youn-Joong Kim
Nature Physics (23 Nov 2008), doi: 10.1038/nphys1148

**Recommended with commentary by Daan Frenkel,
Dept of Chemistry, U. Cambridge**

In 1897, Wilhelm Ostwald formulated his famous Step Rule. This empirical rule summarizes the findings of a large number of experimental studies that Ostwald had performed on crystal nucleation. Ostwald's Step Rule states that the crystal phase that nucleates is not the phase that is thermodynamically stable at that temperature and pressure but rather another metastable phase that is closest in free energy to the parent phase. This observation was (and is) certainly counter-intuitive: why would the system not immediately nucleate to form the phase that is thermodynamically stable? The thermodynamic driving force would be largest for such a direct transformation to the stable state. Ostwald offered no explanation. He just stressed the generality of his observation and mentioned (among other examples) the case of mercury-iodide that first crystallizes in the metastable yellow form and subsequently transforms to the stable red form. Ostwald addressed the fact that there was experimental evidence that appeared to contradict his Step Rule as, in some cases, nucleation experiments appeared to yield simply the most stable phase. Ostwald was undeterred – he wrote [my “loose” translation, DF]: *“There are undoubtedly examples of phase transformations where a metastable phase exists but does not form. In such cases we can always assume that the intermediate structure does form but then immediately transforms into another phase.* Ostwald realizes that this is a rather bold statement, certainly for a “positivist” who, under other circumstances, would dismiss things that cannot be observed – in particular atoms – as figments of the imagination. He continues: *Admittedly this way of dismissing the counterexamples of the Rule is somewhat questionable as it is based on a hypothesis that cannot be tested with the existing experimental techniques.* But Ostwald argues that it should often be possible to slow down the kinetics of the phase transformation and that then, surely, the intermediate metastable phase will be observed.

Now, more than a century after Ostwald formulated his conjecture, Kim et al. have managed to observe the ephemeral metastable crystal structures that Ostwald postulated but could not see. Kim et al. perform high-resolution electron microscopy (HREM) to follow the crystallization of amorphous LiFePO_4 . And they find that, the transformation of the amorphous parent phase to the stable (olivine) phase proceeds via the formation of a number of different metastable nano-crystals forms. With the macroscopic tools that were available to Ostwald, only the final (stable) phase would have been observable and hence Kim et al's experiment appear to vindicate Ostwald's rule in a regime that was inaccessible to nineteenth-century experiments. Ostwald would have been very pleased with these experiments. However, his posthumous victory in this field of science is, at the same time, one more nail in the coffin of Ostwald's opposition to the atomic hypothesis: HREM experiments allow us to “see” atoms. Yet Ostwald was one of the most vocal opponents of the atomic hypothesis. To him, only energy was real and he considered the belief in atoms equivalent to the worshipping of idols. At least, this was Ostwald's point of view at the time when he

formulated the “Step Rule”. However, after Perrin’s experiments Ostwald accepted the atomic hypothesis and so, most likely, he would have been delighted with the present experiments where atoms can be “seen”.

What remains is the question *why* Ostwald’s Step Rule works so well. One could look for a specific explanation in terms of Classical Nucleation Theory (as was done in the 1930's by Stranski and Totomanov). However, such an explanation does not really resolve the mystery but moves it (to the observation that metastable phases must have a low interfacial free energy). Another suggestion (that would be most relevant for simple atomic or colloidal crystals) is the one made almost 30 years ago by Alexander and McTague who argued that, in the metastable liquid phase, fluctuations with the local symmetry of a body-centered cubic (bcc) crystal are uniquely favored, even if that crystal is not the most stable structure: such fluctuations could act as a precursor to the nucleation of a (metastable) body-centered crystal. Of course, the Alexander-McTague conjecture also provides an argument *against* the Step Rule: if a bcc phase would be thermodynamically stable, it would still be the one to nucleate first. For more complex materials, the “explanation” of Ostwald's Step Rule may be more trivial: for all but the simplest materials, the number of possible crystal polymorphs is very large and, unlike proteins, crystals have not evolved to transform easily into their “native” structure. The more polymorphs exist, the more likely Ostwald's scenario becomes – except at very small supercooling, but there the rate of nucleation becomes negligible anyway.