

# **The Structural and Thermodynamic Basis of Ostwald's Rule**

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Ostwald's Rule, namely that the least stable rather than the most stable polymorph will crystallise first, has been widely quoted and misquoted for more than a century. The behaviour of crystallisation of melts and solutions can be justified on grounds of irreversible thermodynamics, structural resemblances, or on a combination of statistical thermodynamics and structure. The limitation of Ostwald's original justification by analogy with gas-liquid behaviour will be demonstrated. The conclusion is that Ostwald's Rule is just that, not more, and not a universal Law.