ELECTRONIC ANNEX EA1: RATES OF CRYSTAL NUCLEATION AND GROWTH
ESTIMATED BY AN ARRHENIUS-TYPE TEMPERATURE DEPENDENCE

If we assume that the rates of nucleation and growth can be approximated by an Arrhenius-type temperature dependence of the form $A_0 \cdot \exp\left(-\frac{E_{Ac}}{R \cdot T}\right)$ where $A_0$ is the pre-exponential factor and $E_{Ac}$ is the activation energy, then the rate constants for nucleation ($K_N$) and growth ($K_G$) can be expressed as:

$$K_N = A_N \cdot \exp\left(\frac{-E_N}{R \cdot T}\right) \quad K_G = A_G \cdot \exp\left(\frac{-E_G}{R \cdot T}\right)$$ (1)

At low to moderate temperatures the $R \cdot T$ term in the denominator in each exponent is typically small compared to the respective activation energies, $E_N$ and $E_G$, so that the exponential terms dominated the respective pre-exponential factors in determining the rate constant. Furthermore since the activation energy for nucleation is typically greater than that for growth, i.e., $E_N > E_G$, it follows that $\exp\left(\frac{-E_N}{R \cdot T}\right) \ll \exp\left(\frac{-E_G}{R \cdot T}\right)$. As a result at these temperatures the rate of growth is faster than the rate of nucleation and the formation of product from reactant is characterized by relatively few large crystals. Conversely, at higher temperatures where the $R \cdot T$ term becomes significant so that the reaction rates for nucleation and growth become dominated by the respective pre-exponential terms $A_N$ and $A_G$. If, as is typically the case, $A_N > A_G$ then the rate of nucleation is faster than of growth and the reactant phase is characterized by a relatively large numbers of small crystals.