# Beyond Equilibrium

## Reaction Kinetics in Geodynamic Models

Collab:

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# Evidence of disequilibrium in rocks

Meta-igneous (anorthosite), Bergen Arcs, Holsnøy Norway  plagioclase + pyroxene → garnet

# Solid-state reactions in rocks

## Thermodynamics

Q: What *should* happen?

## Kinetics

Q: Does it *actually* happen on geodynamic timescales?

## Aspirational goal for ASPECT

**Go beyond equilibrium:**
Parameterize reaction progress in a physically meaningful and computationally tractable way

# The basis of kinetic theory

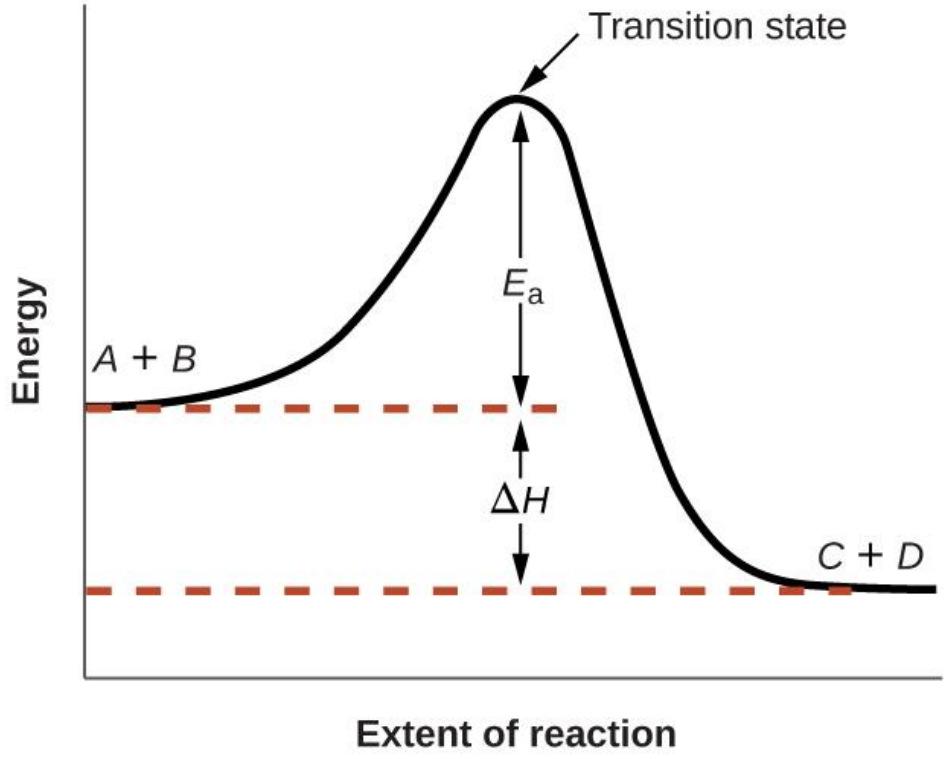
Transformation rate of the reaction:

$$A + B \rightarrow C + D$$

depends on the number of atoms that can achieve the transition state

$$\frac{dy}{dt} \propto A \exp\left(\frac{-E_a}{RT}\right)$$

*y:* volume fraction transformed
*A:* frequency factor
*Ea:* activation energy



# The basis of kinetic theory

A more general form of transformation rate is:

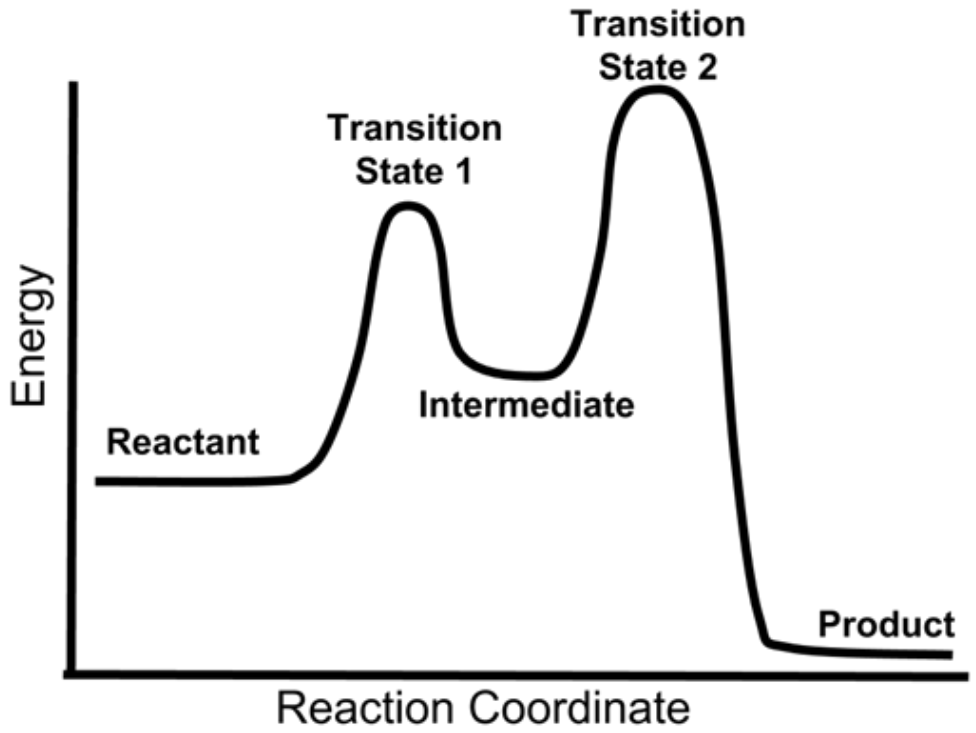
$$\frac{dy}{dt} = k(P,T)\, f(y)$$

*k:* rate constant (**pathway dependent**)

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$

*f(y):* how reaction progress feeds back on rate

- availability of reactants
- evolving interface area
- site saturation
- transport distances



# Mechanisms and pathways

**Reaction mechanism:** how atoms move

**Reaction pathway :** sequence of steps (mechanisms) to complete reaction

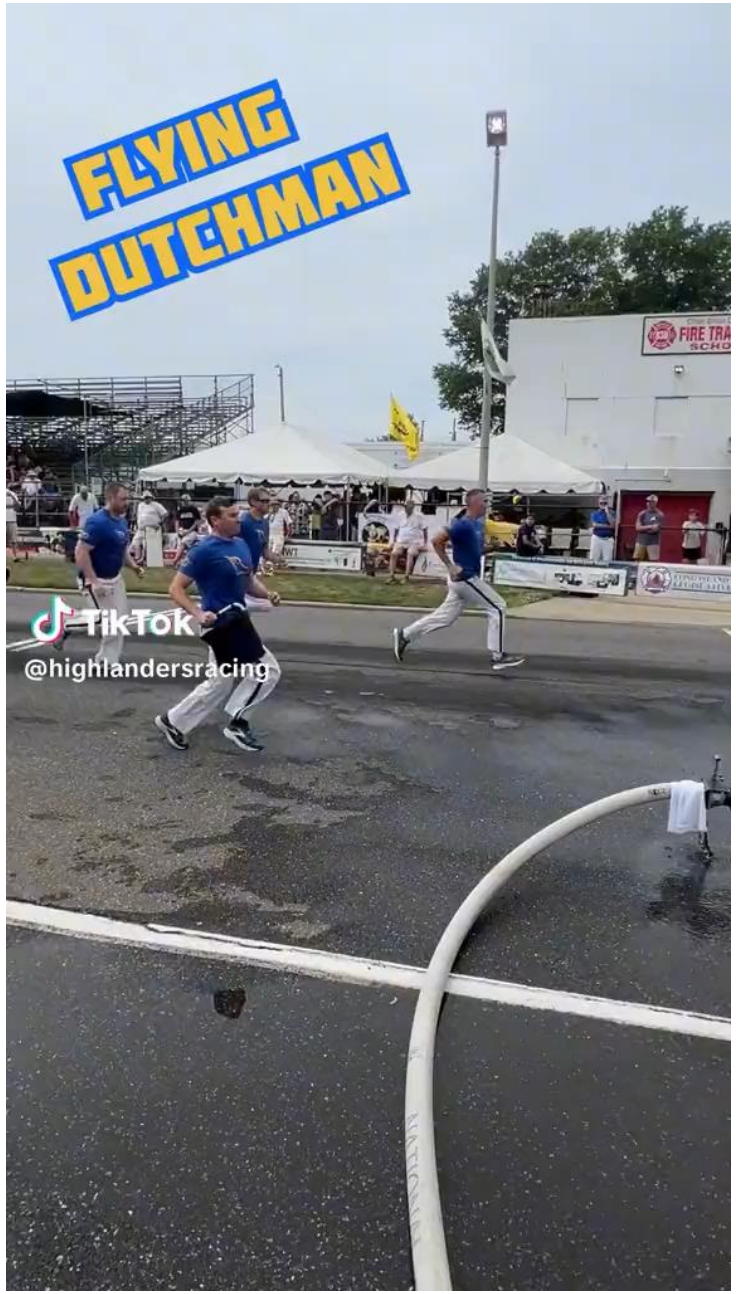
- Can be complex
- Slowest step limits overall reaction rate*

*If pathway is sequential

**Example:**

dissolution → grain-boundary diffusion → precipitation

scoop bucket → move bucket up ladder → pour bucket



# JMAK model

Johnson–Mehl–Avrami–Kolmogorov (1937–1941)

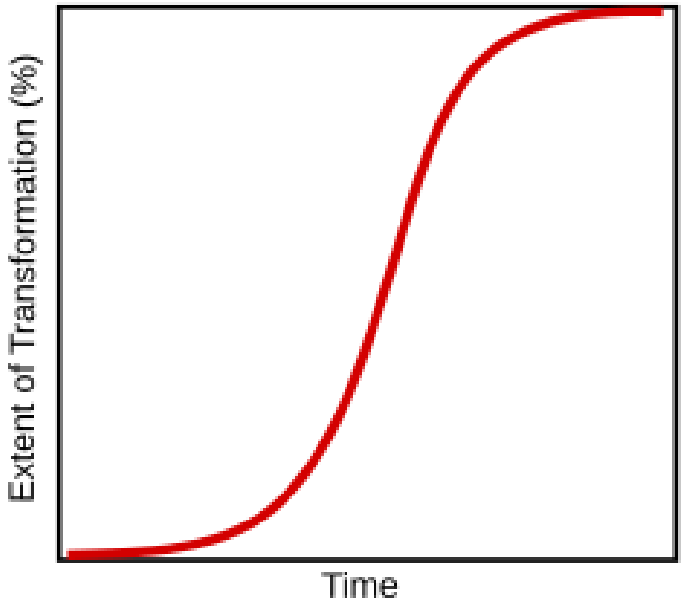
Many reactions $\alpha$ → β generally follow:

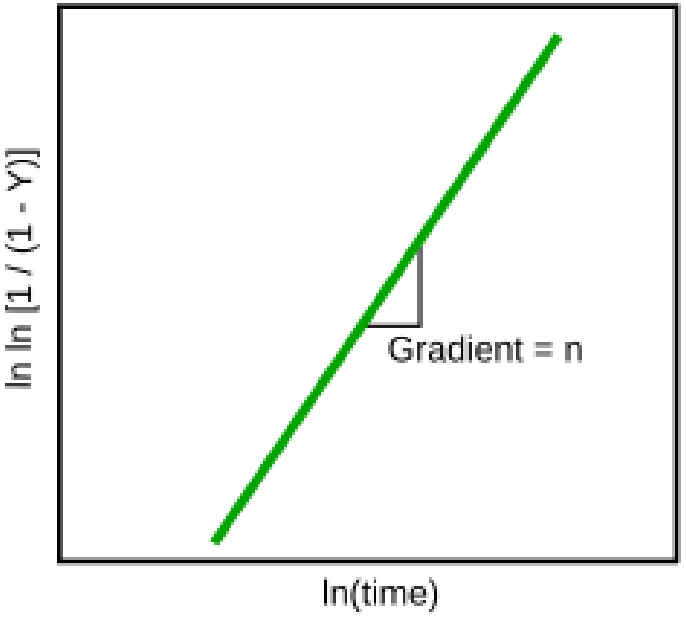
$$y = 1 - \exp(-kt^n)$$

$k$ : rate constant (Arrhenius)
$n$ : Avrami exponent*

*Interpreted as relating to geometry + mechanism

$n$ = 4 : nucleation + 3d growth (spheres)
$n$ = 3 : 3d growth (spheres)
$n$ = 2 : 2d growth (plates)
$n$ = 1 : 1d growth (needles)



# JMAK model

Updated for nucleation at preferred sites (Cahn, 1956):

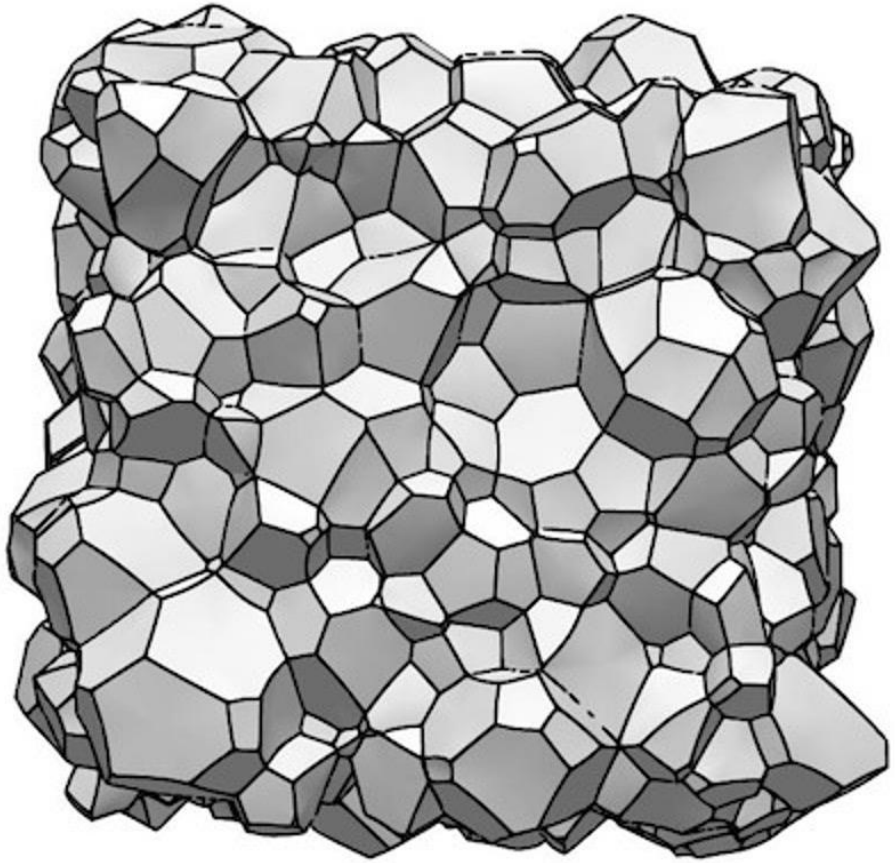
$$y = 1 - \exp\left(-\frac{1}{3}\pi \dot{N} \dot{G}^3 t^4\right)$$

$\dot{N}$ : nucleation rate per volume ($m^{-3}\ s^{-1}$)
$\dot{G}$ : growth rate of grain boundary ($m\ s^{-1}$)

After nuclei saturate grain surfaces:

$$y = 1 - \exp\left(-\frac{6.7}{d}\dot{G}t\right)$$

$d$ : mean grain size



# JMAK model

After nuclei saturate grain surfaces (Cahn, 1956):

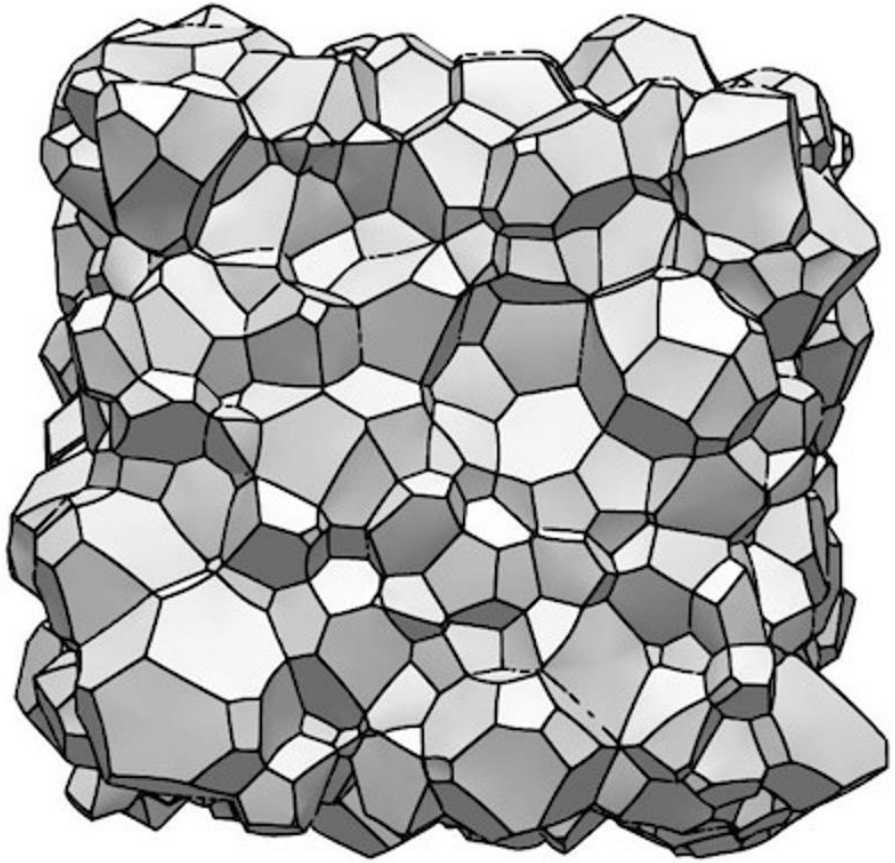
$$y = 1 - \exp\left(-\frac{6.7}{d}\dot{G}t\right)$$

If $\dot{G}$ is constant at fixed PT (no long-range diffusion):

$$\frac{dy}{dt} = \frac{6.7}{d}\,\dot{G}\,(1-y)$$

where $\dot{G}$ follows basis of kinetic theory:

$$\dot{G} = A\,T\exp\left(\frac{-E_a}{RT}\right)\left[1 - \exp\left(\frac{-\Delta G_{rxn}}{RT}\right)\right]$$



# Diffusion-controlled growth

If grain growth is not constant at fixed PT (long-range diffusion):

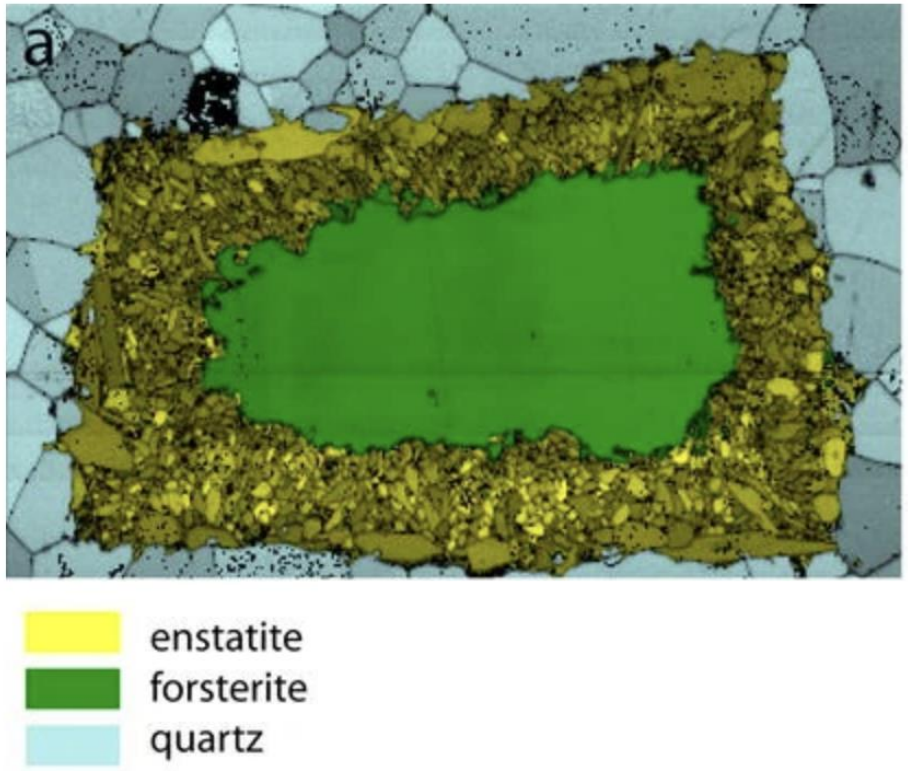
$$x \propto \sqrt{Dt}$$

$$\dot{G} \propto \frac{1}{\sqrt{t}}$$

then we have a different numerical problem altogether*

$$y = 1 - \exp\left(-kt^{1/2}\right)$$

*Still tractable without explicitly tracking rim width $x$ (e.g., Däßler & Yuen 1996; Reidel & Karato 1997)



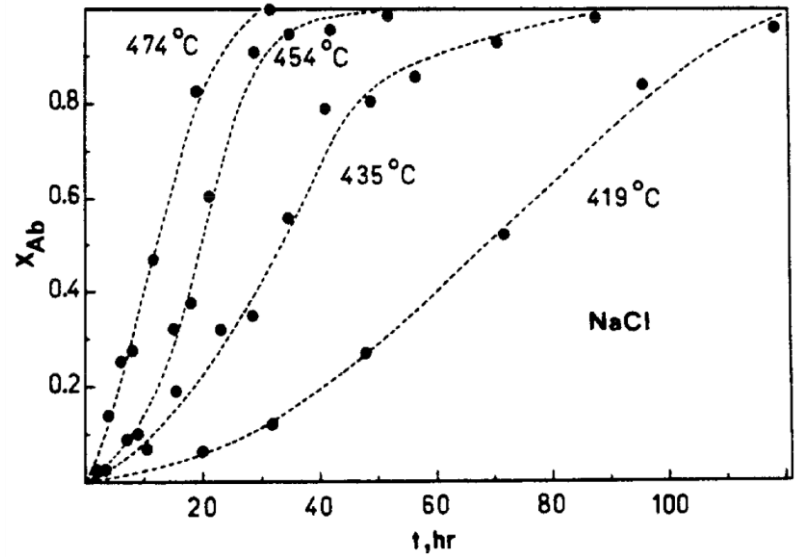
# Simpler models

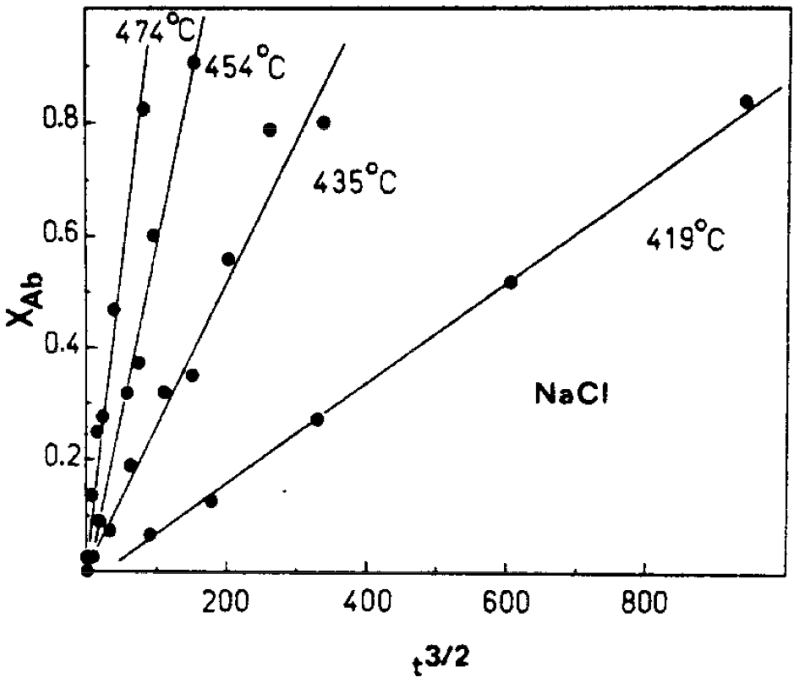
**Power law:**

$$y = kt^n$$

ex: zeolite + quartz → albite + H2O

Coefficients determined by measuring *y* during isothermal experiments at different *T*



# Summary

The following rate laws could be considered for implementation in ASPECT***

| | | |
|---|---|---|
| **Constant rate:** | $y = kt$ | simple; limited applications |
| **Power law:** | $y = kt^n$ | simple; no theoretical basis; limited data |
| **JMAK:** | $y = 1 - \exp(-kt^n)$ | nucleation + growth; many applications; limited data |
| **JMAK (Cahn):** | $y = 1 - \exp\left(-\frac{1}{3}\pi \dot{N} \dot{G}^3 t^4\right)$ | nucleation + growth; many applications; limited data |
| **JMAK (Cahn):** | $y = 1 - \exp\left(-\frac{6.7}{d}\dot{G}t\right)$ | growth; many applications; limited data |

***_**Requires many assumptions**_ about reaction pathways, microstructures, grain sizes, and more …

Ex: Li et al. (2026 in prep) Kerswell et al. (2026 in review)