



EMA5001 Lecture 23

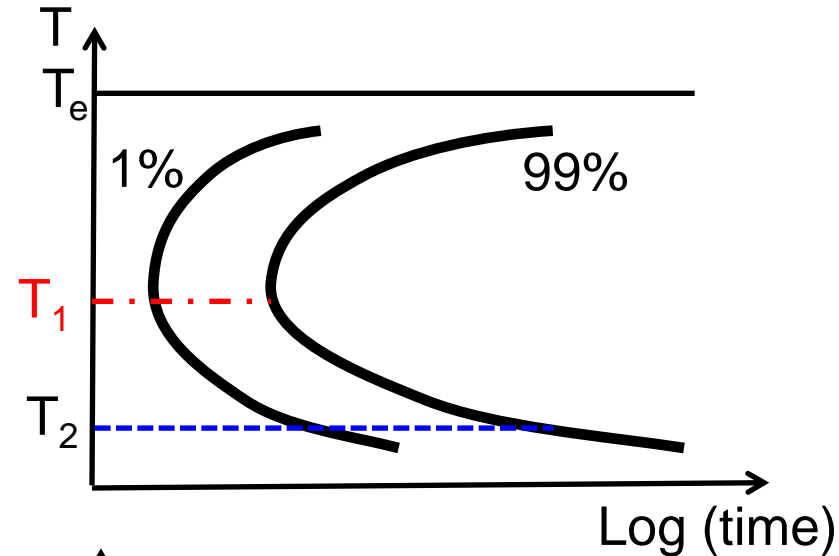
Models for Transformation Kinetics



TTT Curve vs. Conversion Curve

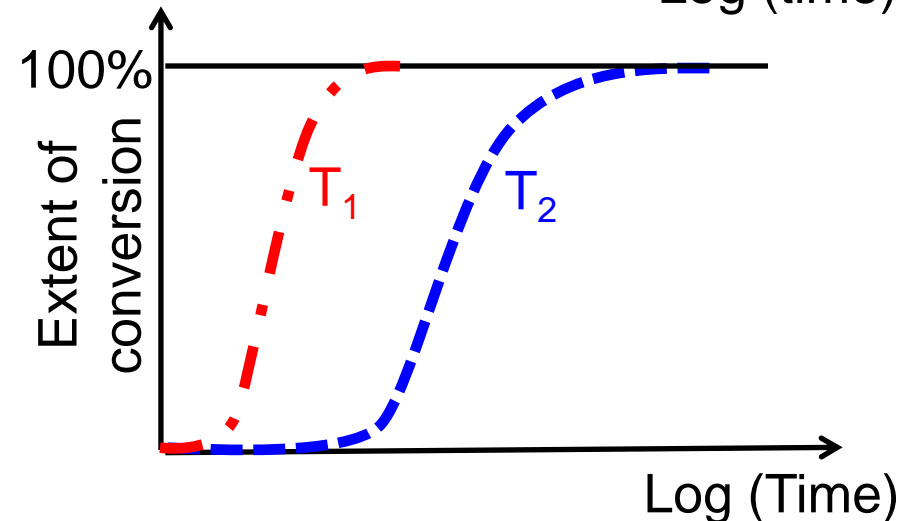
□ Temperature – Time – Transformation (TTT) Curve

- “Nose” shaped
 - Very high T: low driving force
 - Very low T: Slow diffusion
- For reactions happen during the cooling process



□ Conversion – Time (CT) Curve

- “S” shaped when time in log scale
- For any reactions
Usually for isothermal reactions (can be in undercooling or in superheating)





Kinetics Under Very Low Conversion Condition (1)

Assumptions

- Spherical β nuclei
- β nucleation rate constant of N
- Growth rate of nucleus radius constant of ν
- Very low conversion and negligible “overlapping”

At time t , the volume of a β precipitate nucleated at time τ ($0 \leq \tau \leq t$) is

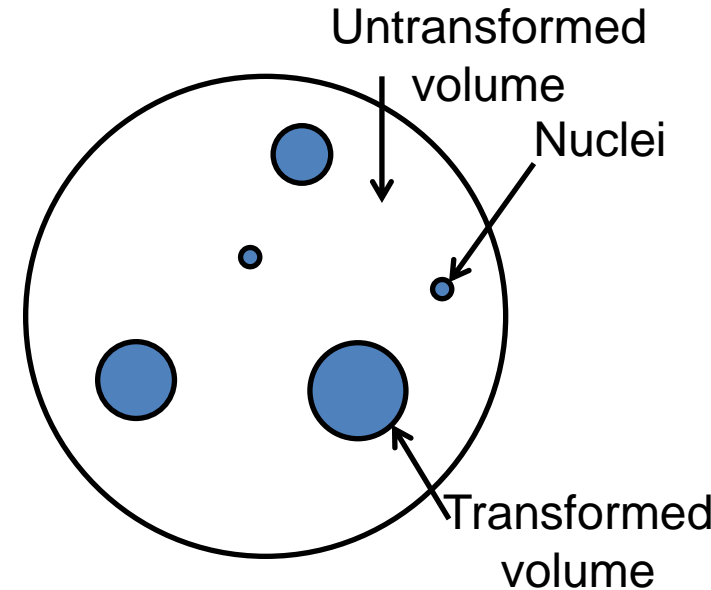
$$V_\tau = \frac{4}{3} \pi [\nu(t - \tau)]^3$$

Number of β precipitates nucleated in a small time period of $d\tau$ ($0 \leq \tau \leq t$) per unit volume is

$$dn = Nd\tau$$

Total volume of transformed β per unit volume of matrix at time t is

$$V_t = \int V_\tau dn = \int_0^t \frac{4}{3} \pi [\nu(t - \tau)]^3 Nd\tau = \frac{4}{3} \pi N \nu^3 \int_0^t (t - \tau)^3 d\tau$$





Kinetics Under Very Low Conversion Condition (2)

□ Continue from p.3

$$V_t = \frac{4}{3} \pi N v^3 \int_0^t (t - \tau)^3 d\tau$$

Integrate, we have

$$V_t = \frac{1}{3} \pi N v^3 t^4$$

For unit volume of starting matrix phase, the fractional of transformation (or extent of conversion) will be

$$f = \frac{V_t}{1} = \frac{1}{3} \pi N v^3 t^4$$

Note the above only applies when $f \ll 1$

Otherwise, the assumptions about constant nucleation rate, constant growth rate, and no overlapping would not apply



Kinetics Under Higher Conversion

JMA Equation (1)

Assumptions

- Spherical β nuclei
- β nucleation rate constant of N
- Growth rate of nucleus radius constant of ν

More precisely, the number of “real” β precipitates nucleated in a small time period of $d\tau$ ($0 \leq \tau \leq t$) per unit volume is

$$dn_r = N(1 - f)d\tau$$

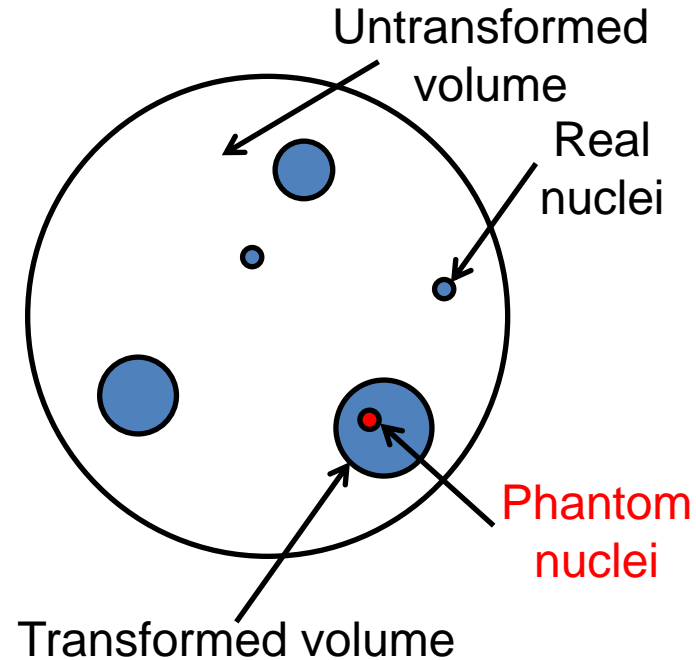
f volume fraction of “real” precipitates

Introduce the concept of “imaginary (or extended) nucleation”, which includes both “real” nuclei and “phantom” nuclei

$$dn_i = Nd\tau$$

The number of “imaginary” β precipitates nucleated in a small time period of $d\tau$ at τ ($0 \leq \tau \leq t$) per unit volume is

$$\frac{dn_r}{dn_i} = 1 - f$$





Kinetics Under Higher Conversion

JMA Equation (2)

□ Continue from p.5

We have

$$\frac{dn_r}{dn_i} = 1 - f$$

On the other hand, for “real” nuclei and “imaginary” nuclei,

$$\frac{dn_r}{dn_i} = \frac{dV_r}{dV_i} = \frac{df}{df_i}$$

f_i volume fraction of “imaginary” (“real” + “phantom”) precipitates

Therefore,
$$\frac{df}{df_i} = 1 - f$$

Or
$$\frac{df}{1 - f} = df_i$$

Integrate, we have
$$f = 1 - e^{-f_i}$$



Kinetics Under Higher Conversion

JMA Equation (3)

□ Continue from p. 6

$$f = 1 - e^{-f_i}$$

Remember that the “imaginary” fraction of conversion f_i is essentially represented by the fraction of transformation in low conversion (i.e., neglecting overlapping) case

$$f_i = \frac{1}{3} \pi N v^3 t^4$$

We will have
$$f = 1 - \exp\left(-\frac{1}{3} \pi N v^3 t^4\right)$$

known as the Johnson-Mehl-Avrami (JMA) equation

In general,
$$f = 1 - \exp(-kt^n) \quad n = \sim 1-4$$

The number of n depends on geometry of nuclei/precipitates and whether the transformation involves only growth (i.e., “site saturation” scenario)



Kinetics Under Higher Conversion

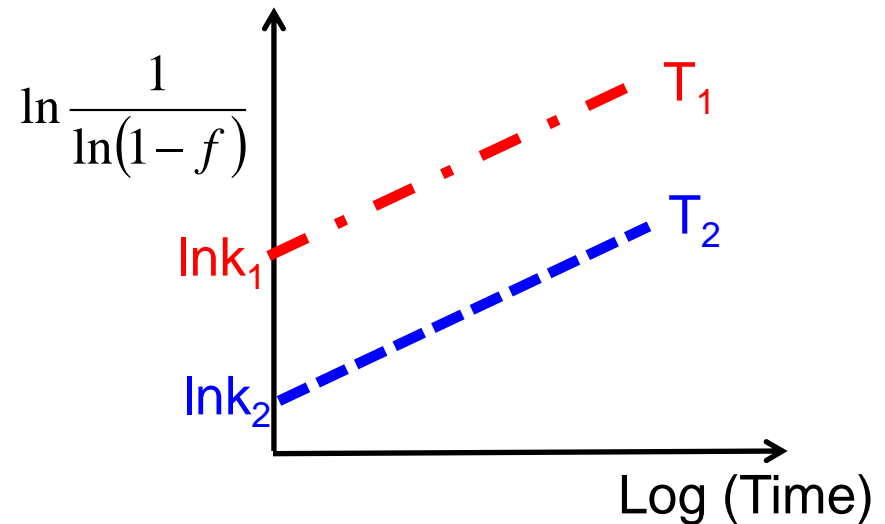
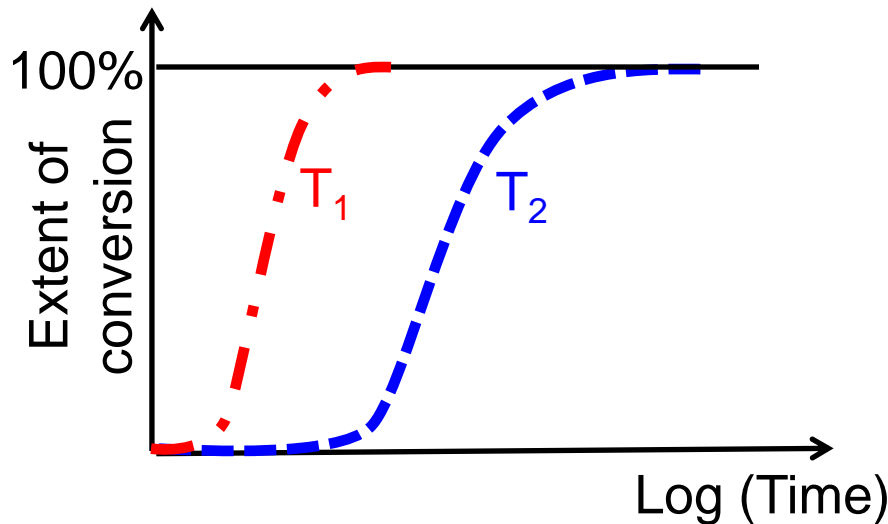
JMA Equation (4)

□ Continue from p.7

We have $f = 1 - \exp(-kt^n)$

Take log $-\ln(1-f) = kt^n$

Take log again $\ln[-\ln(1-f)] = \ln k + n \ln t$





Nucleation & Growth Model - Instant Nucleation/ Site Saturation Case

- If all nucleation happen at the very beginning and only growth afterwards

For 3D growth, dimension of a precipitate under constant growth rate at time t

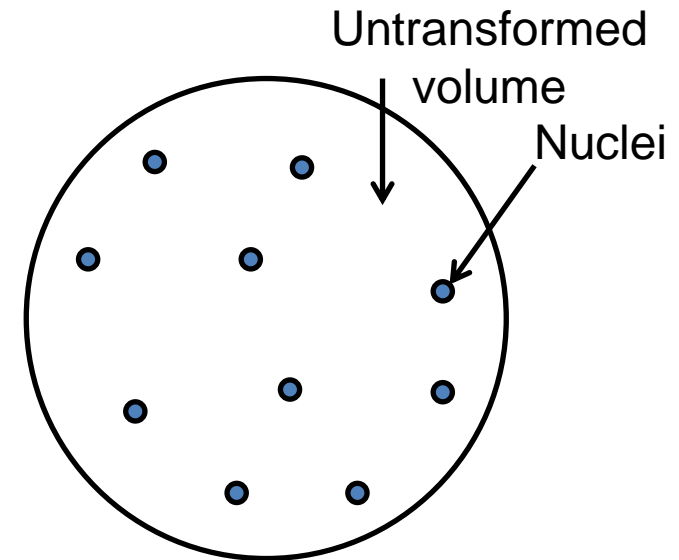
$$V_r = \frac{4}{3} \pi (vt)^3$$

N_0 is initial nuclei density, the “imaginary” (or extended) fractional conversion (real + phantom) will be:

$$f_i = \frac{\frac{4}{3} \pi (vt)^3 N_0}{V_0} = k' t^3$$

Real fractional conversion: $f = 1 - e^{-f_i}$

We have: $f = 1 - \exp(-k' t^3)$ or $-\ln(1 - f) = k' t^3$ $[-\ln(1 - f)]^{\frac{1}{3}} = kt$





Nucleation & Growth Model - Diffusion-Controlled Case

□ For diffusion-controlled 3D growth scenario for nucleation-growth:

Linear dimension (e.g., radius) of a precipitate would follow

$$x = \frac{\Delta X_0}{X_\beta - X_e} \sqrt{Dt} = ut^{0.5}$$

For 3D growth with constant nucleation rate,
the imaginary (or extended) volume per unit volume of original phase will be:

$$V_i = \int V_r d_n = \int_0^t \frac{4}{3} \pi [u(t-\tau)^{0.5}]^3 N d\tau = \frac{4}{3} \pi Nu^{3/2} \int_0^t (t-\tau)^{3/2} d\tau$$

The imaginary (real + phantom) fractional transformation is $f_i = k't^{2.5}$

Real fractional conversion: $f = 1 - e^{-f_i}$

We have $f = 1 - \exp(-k't^{2.5})$ or $-\ln(1-f) = k't^{2.5}$ $[-\ln(1-f)]^{1/2.5} = kt$



Diffusion-Based Model Under Very Low Conversion – 1D Case

□ Diffusion-controlled growth of precipitate in 1D

$$x^2 = \frac{D(\Delta X_0)^2}{(X_\beta - X_e)^2} t$$

Dimension change follows parabolic law

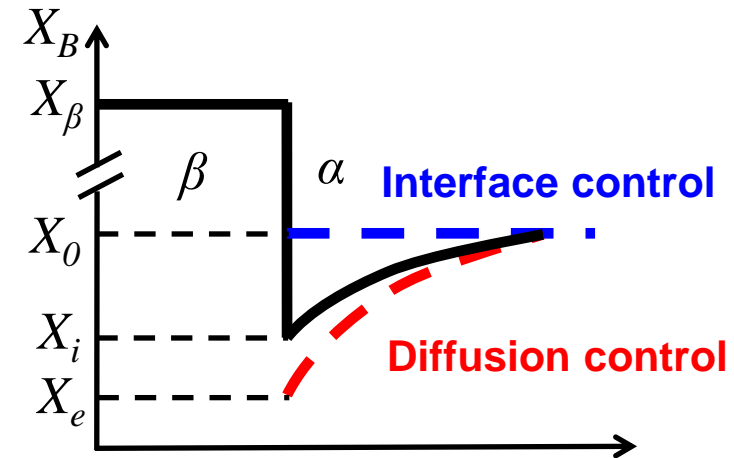
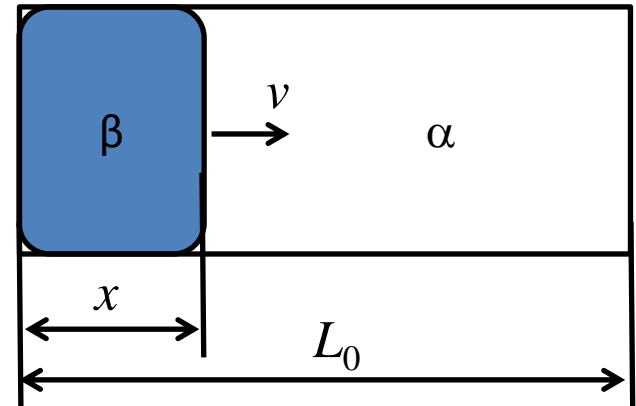
$$x^2 = k't$$

Fractional conversion (assuming low conversion)

$$f = \frac{x}{L_0} = \frac{\sqrt{k'} t^{\frac{1}{2}}}{L_0}$$

We have $f = k'' t^{\frac{1}{2}}$

Or $f^2 = kt$





Diffusion-Controlled “Grow In” Model with Thin Diffusion Field – 3D Case (1)

□ For diffusion-controlled reaction

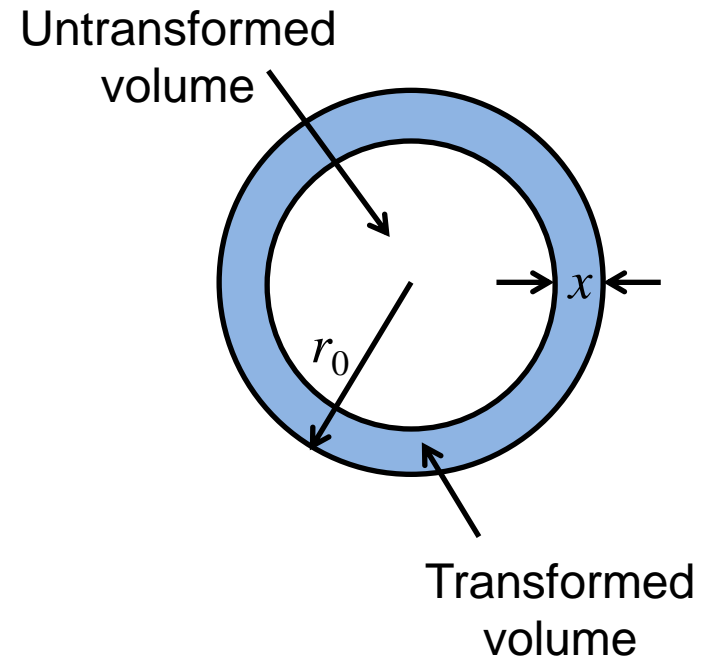
Assuming

- Spherical shape
- Thickness of the product (transformed) layer follow parabolic law
- NO change in volume in reaction

Volume of untransformed portion $V_r = \frac{4}{3} \pi r^3$

Fraction of transformation/conversion is given by $f = \frac{V_0 - V_r}{V_0}$

Consider $V_0 = \frac{4}{3} \pi r_0^3$ we have $f = \frac{\frac{4}{3} \pi r_0^3 - \frac{4}{3} \pi (r_0 - x)^3}{\frac{4}{3} \pi r_0^3}$





Diffusion-Controlled “Grow In” Model with Thin Diffusion Field – 3D Case (1)

□ Continue from p.2

We have
$$f = \frac{r_0^3 - r^3}{r_0^3} = \frac{r_0^3 - [r_0 - x]^3}{r_0^3} = 1 - \left(1 - \frac{x}{r_0}\right)^3$$

Re-arrange, we have
$$(1 - f)^{\frac{1}{3}} = 1 - \frac{x}{r_0} \quad x = r_0 \left[1 - (1 - f)^{\frac{1}{3}}\right]$$

Remember that thickness of product layer $x^2 = kt$

Another way to represent it
$$\left[1 - (1 - f)^{\frac{1}{3}}\right]^2 r_0^2 = kt \quad \left[1 - (1 - f)^{\frac{1}{3}}\right]^2 = \frac{k}{r_0^2} t$$

This is Jander’s equation:

Its limitations/assumptions are (i) low thickness of product (thin diffusion field), and (ii) constant volume in reaction

More rigorous models such as Ginstling-Brounshtein and Carter’s Models exist



Interface-Controlled “Grow In”/ “Shrinking-Core” Model – 3D Case (1)

□ For interface controlled “shrinking-core reaction

Examples: decomposition of solids

Assuming

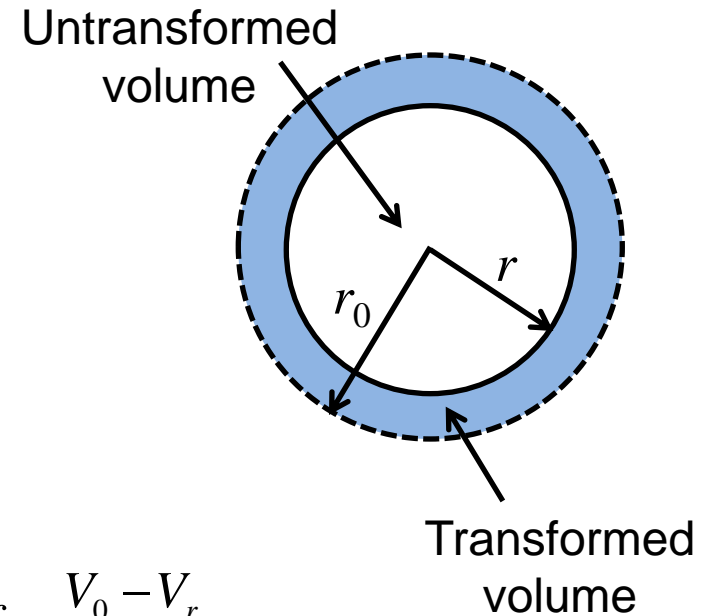
- Spherical shape
- Constant rate of growth for the product layer thickness i.e.,

$$r = r_0 - kt$$

Volume of unreacted portion $V_r = \frac{4}{3} \pi r^3$

Fraction of transformation/conversion is given by $f = \frac{V_0 - V_r}{V_0}$

Consider $V_0 = \frac{4}{3} \pi r_0^3$ we have $f = \frac{\frac{4}{3} \pi r_0^3 - \frac{4}{3} \pi r^3}{\frac{4}{3} \pi r_0^3}$





Interface-Controlled “Grow In”/ “Shrinking-Core” Model – 3D Case (2)

□ Continue from p.2

Remember that transformed portion radius $r = r_0 - kt$

We have
$$f = \frac{r_0^3 - r^3}{r_0^3} = \frac{r_0^3 - (r_0 - kt)^3}{r_0^3} = 1 - \frac{(r_0 - kt)^3}{r_0^3}$$

Therefore,
$$f = 1 - \left(1 - \frac{k}{r_0}t\right)^3$$

Another way to represent it
$$(1 - f)^{\frac{1}{3}} = 1 - \frac{k}{r_0}t$$

Therefore,
$$1 - (1 - f)^{\frac{1}{3}} = \frac{k}{r_0}t \quad 1 - (1 - f)^{\frac{1}{3}} = k't$$

Similarly, for interface controlled reaction for 2D case (such as decomposition of cylinder shaped particles), we have

$$1 - (1 - f)^{\frac{1}{2}} = \frac{k}{r_0}t$$



Summary of Kinetic Reaction Models

Kinetic Model	Equation	Additional Notes
Power law model	$f = kt^n$	$n = 1, 2, 3, \text{ etc.}$
Nucleation – Growth (grow out) model	$[-\ln(1-f)]^{\frac{1}{n}} = kt$	Scenario could be by geometry (1D, 2D, 3D), nucleation (constant nucleation vs. site saturation), and rate limiting step (diffusion controlled vs. interface control)
Diffusion-controlled 1D model	$f^2 = kt$	Planar growth
Diffusion-controlled (shrinking-core) 3D model: Jander's Equation	$\left[1 - (1-f)^{\frac{1}{3}}\right]^2 = \frac{k}{r_0^2} t$	Simplification of constant reaction volume and thin diffusion layer thickness
Interface-controlled (shrinking-core) model	$1 - (1-f)^{\frac{1}{n}} = \frac{k}{r_0} t$	$n=2$ for 2D (shrinking area) $n=3$ for 3D (shrinking volume)
Reaction order model	$\frac{df}{dt} = k(1-f)^n$	$n=1$ for 1 st order reaction $n=2$ for 2 nd order reaction



Summary of Physical Meaning for n Factor in JMA Equation

□ JMA Equation $f = 1 - \exp(-kt^n)$

Growth Geometry	Nucleation rate	Interface-controlled	Diffusion-controlled
3D	Constant nucleation rate	4	2.5
	Zero nucleation rate (site saturation)	3	1.5
	Decreasing nucleation rate	3-4	1.5-2.5
2D	Constant nucleation rate	3	2
	Zero nucleation rate (site saturation)	2	1
	Decreasing nucleation rate	2-3	1-2
1D	Constant nucleation rate	2	1.5
	Zero nucleation rate (site saturation)	1	0.5
	Decreasing nucleation rate	1-2	0.5-1.5
No growth	Constant nucleation rate	1	0.5

Hulbert, S. F., "Models for Solid-state Reactions in Powdered Compacts: A Review," *Journal of the British Ceramic Society*, Vol. 6, pp. 11 (1969)