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 $\beta$ nuclei
- $\beta$ nucleation rate constant of $N$
- Growth rate of nucleus radius constant of $v$
- Very low conversion and negligible “overlapping”

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

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

Number of $\beta$ 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 $\beta$ per unit volume of matrix at time $t$ is

$$V_t = \int V_\tau d_n = \frac{4}{3} \pi \int [v(t - \tau)]^3 N d\tau = \frac{4}{3} \pi Nv^3 \int (t - \tau)^3 d\tau$$
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 \( f << 1 \)
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 $\beta$ nuclei
- $\beta$ nucleation rate constant of $N$
- Growth rate of nucleus radius constant of $v$

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

$$\frac{dn_r}{dn_i} = 1 - f$$
Continue from p.5

We have

\[ \frac{dn_r}{dn_i} = 1 - f \]

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

\[ \frac{dn_r}{dn_i} = \frac{dV_r}{dV_i} = \frac{df}{df_i} \]

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,

\[ f = 1 - \exp \left( - k t^n \right) \quad n = \sim 1-4 \]

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
\[ \ln[-\ln(1 - f)] = \ln k + n \ln t \]
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:

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

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:

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

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 \(-\ln(1-f) = k't^{2.5} \) \[ -\ln(1-f) \right]^{1/2.5} = kt \]
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)

\[ f = \frac{x}{L_0} = \frac{\sqrt{k'} \cdot t^{\frac{1}{2}}}{L_0} \]

We have

\[ f = k'' t^2 \]

Or

\[ f^2 = kt \]
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
\[
f = \frac{\frac{4}{3} \pi r_0^3 - \frac{4}{3} \pi (r_0 - x)^3}{\frac{4}{3} \pi r_0^3}
\]
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
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

\[ f = \frac{4}{3} \pi r_0^3 - \frac{4}{3} \pi r^3 \]
Continue from p.2

Remember that transformed portion radius \( r = r_0 - kt \)

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

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

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

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

The JMA Equation is given by:

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

### Growth Geometry

<table>
<thead>
<tr>
<th>Growth Geometry</th>
<th>Nucleation rate</th>
<th>Interface-controlled</th>
<th>Diffusion-controlled</th>
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<tr>
<td>3D</td>
<td>Constant nucleation rate</td>
<td>4</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Zero nucleation rate (site saturation)</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Decreasing nucleation rate</td>
<td>3-4</td>
<td>1.5-2.5</td>
</tr>
<tr>
<td>2D</td>
<td>Constant nucleation rate</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Zero nucleation rate (site saturation)</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Decreasing nucleation rate</td>
<td>2-3</td>
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<td>1D</td>
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<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Decreasing nucleation rate</td>
<td>1-2</td>
<td>0.5-1.5</td>
</tr>
<tr>
<td>No growth</td>
<td>Constant nucleation rate</td>
<td>1</td>
<td>0.5</td>
</tr>
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