Outline

• Thermogravimetric Analysis
• Thermal analytical methods vs. kinetics
• Models and mechanisms in solid-state kinetics
• Methods for studying solid-state kinetics
• Controversies in solid-state kinetics
• Summary
Definitions

• Homogeneous Reaction
  – Involves one phase

• Heterogeneous Reaction
  – Multiple phases, reaction usually occurs at the interface between phases.

• Irreversible Reaction
  – Proceeds in only one direction and continues in that direction until the reactants are exhausted.

• Reversible Reaction
  – Can proceed in either direction, depending on the concentrations of reactants and products present relative to the corresponding equilibrium constants.
Rate Laws - Principles

• A **rate law** is an algebraic equation that relates $-r_A$ to species concentrations.

\[ -r_A = [k(T)] \cdot [f(C_A, C_B, \ldots)] \]

• $k(T)$ is the **reaction rate constant**
  – Species specific, therefore subscripted to reflect to which species constant is making reference
  – NOT really a constant, but $\neq f(C_i)$
  – Described by kinetic theory of gases
Reaction Order

\[-r_A = kC_A^\alpha C_B^\beta\]

order in A = \(\alpha\)
order in B = \(\beta\)
overall order = \(\alpha + \beta\)

\[-r_A = \frac{kC_A}{1 + k'C_B}\]

Low \(C_B\)
\(n = 1\) (w.r.t A)

High \(C_B\),
\(n_A = 1, n_B = -1\)
(apparent orders)
<table>
<thead>
<tr>
<th>Order</th>
<th>Rate Eqn</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>zero</td>
<td>(-r_A = k)</td>
<td>(\text{mol} \cdot \text{V}^{-1} \cdot \text{s}^{-1})</td>
</tr>
<tr>
<td>first</td>
<td>(-r_A = kC_A)</td>
<td>(\text{s}^{-1})</td>
</tr>
<tr>
<td>second</td>
<td>(-r_A = kC_A^2)</td>
<td>(\text{V} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})</td>
</tr>
<tr>
<td>third</td>
<td>(-r_A = kC_A^3)</td>
<td>((\text{V} \cdot \text{mol}^{-1})^2 \cdot \text{s}^{-1})</td>
</tr>
</tbody>
</table>
Elementary Rate Laws

• A reaction order for which each specie is identical to its stoichiometric coefficient

\[
aA + bB \rightarrow cC + dD
\]

\[
-r_A = kC_A^aC_B^b
\]
Molecularity

• The term *molecularity* refers to number of atoms, ions, or molecules involved in the rate-limiting step of the reaction.
  – unimolecular – one reactant involved in reaction
  – bimolecular – two reactants must collide to react
  – termolecular – three reactants must interact for reaction to occur
Reversible Reactions

- All reversible reaction rate laws must reduce to the thermodynamic relationship relating reacting species concentrations at equilibrium.
- At equilibrium, the net rate of reaction is zero for all species involved in the reaction.

\[ aA + bB \leftrightarrow cC + dD \]

\[ K_C = \frac{C_c^c C_d^d}{C_a^a C_b^b} \]

\[ -r_{ie} = 0 \]
Reversible Reactions

\[ 2A \rightleftharpoons B + C \]

Forward rate law

\[ -r_A = k_A C_A^2 \]

Reverse rate law

\[ r_A = k_{-A} C_B C_C \]
Reversible Reactions

net rate law

\[ r_{A,\text{net}} = r_A + r_{-A} = -k_A C_A^2 + k_{-A} C_B C_C \]

forward rate law

\[ -r_A = k_A C_A^2 \]

reverse rate law

\[ r_A = k_{-A} C_B C_C \]
Reversible Reactions

net rate law

\[ r_{A,\text{net}} = r_A + r_{-A} = -k_A C_A^2 + k_{-A} C_B C_C \]

\[ r_{A,\text{net}} = 0 = -k_A C_A^2 + k_{-A} C_B C_C \]

\[ k_A C_A^2 = k_{-A} C_B C_C \]
Reversible Reactions

equilibrium condition

\[ k_A C_A^2 = k_{-A} C_B C_C \]

equilibrium relationship

\[ \frac{k_A}{k_{-A}} = \frac{C_B C_C}{C_A^2} = K_C \]

2A ⇌ B + C
Reversible Reactions

equilibrium relationship

\[ \frac{k_A}{k_{-A}} = \frac{C_B C_C}{C_A^2} = K_C \]

rate law in terms of equilibrium relationship

\[-r_A = k_A \left( C_A^2 - \frac{C_B C_C}{K_C} \right)\]
Thermogravimetric Analysis

- Thermogravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere.
- Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C.
- The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration.
What is it for?

- Composition of Multicomponent Systems
- Thermal Stability of Materials
- Oxidative Stability of Materials
- Estimated Lifetime of a Product
- Decomposition Kinetics of Materials
- The Effect of Reactive or Corrosive Atmospheres on Materials
- Moisture and Volatiles Content of Materials
Block diagram of a thermobalance
TGA and DTG
Enthalpy of reaction and activation energy
Thermal analytical methods vs. kinetics

• Solid-state kinetics can be studied with thermal analytical methods by measuring a sample property as it is heated or held at a constant temperature.
• If a reaction involves weight loss, then weight is followed and the kinetics are usually studied by thermogravimetry (TGA).
• Heat (evolved or consumed) is another measurable property that is used for kinetic evaluation using differential scanning calorimetry (DSC) or differential thermal analysis (DTA).
• Weight loss or heat flow data are converted to a normalized form called conversion fraction ($\alpha$).
• The conversion fraction ranges from 0 and 1 and is a measure of reaction progress as a function of time or temperature.
Mass loss in coal pyrolysis at different heating rates
• For isothermal thermogravimetric analysis, the conversion fraction \( (\alpha) \) at any time is:

\[
\alpha = \frac{m_0 - m_t}{m_0 - m_\infty}
\]

• Where, \( m_0 \) is the initial sample weight, \( m_t \) is the sample weight at time, \( t \), and \( m_\infty \) is the final sample weight.

• Nonisothermally, the conversion fraction \( (\alpha) \) at any temperature is:

\[
\alpha = \frac{m_0 - m_T}{m_0 - m_\infty}
\]
Experimental TGA curve and calculated reaction extend
Rate law

• Using conversion fraction, rate expressions can be written as:

\[
\text{Rate } = \frac{d\alpha}{dt} = k(1 - \alpha) \quad (1)
\]

\[
-\ln(1 - \alpha) = kt
\]
• Unlike rate laws in homogenous kinetics which usually depend on reaction order (i.e. first, second, etc.), a rate law for an elementary solid-state reaction could depend on factors such as rate of nuclei formation, interface advance, diffusion, and/or geometrical shape of solid particles.

• These factors lead to several decomposition models that do not exist in homogenous kinetics.

• Kinetic equations can be generally expressed as:
Where, $f(\alpha)$ is the differential reaction model and $g(\alpha)$ is the integral reaction model. In some references, $f(\alpha)$ and $g(\alpha)$ definitions may be reversed.

The temperature dependence of the rate constant ($k$) is usually given by the Arrhenius equation:

$$
\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (2)
$$

$$
g(\alpha) = k \cdot t \quad (3)
$$

Where, $f(\alpha)$ is the differential reaction model and $g(\alpha)$ is the integral reaction model. In some references, $f(\alpha)$ and $g(\alpha)$ definitions may be reversed. The temperature dependence of the rate constant ($k$) is usually given by the Arrhenius equation:

$$
k = A e^{-\frac{E_a}{RT}} \quad (4)
$$
• Where, $A$ is the pre-exponential (frequency) factor, $E_a$ is activation energy, $T$ is absolute temperature and $R$ is the gas constant.

• Finally rate equation is:

$$\frac{d\alpha}{dt} = A e^{\frac{E_a}{RT}} f(\alpha)$$  \hspace{1cm} (5)$$

and

$$g(\alpha) = A e^{\frac{E_a}{RT}} t$$  \hspace{1cm} (6)$$
Models and mechanisms in solid-state kinetics

• A model is a theoretical, mathematical description of what occurs experimentally.

• In solid-state reactions, a model can describe a particular reaction type and translate that mathematically into a rate equation.

• Many models have been proposed in solid-state kinetics and these models have been developed based on certain mechanistic assumptions. Other models are more empirically based and their mathematics facilitates data analysis with less mechanistic meaning.

• Therefore, different rate expressions are produced from these models.
List of the most common models

<table>
<thead>
<tr>
<th>Model</th>
<th>Differential form $f(\alpha) = \frac{1}{k} \frac{d\alpha}{dt}$</th>
<th>Integral form $g(\alpha) = kt$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation models</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power law (P2)</td>
<td>$2 \alpha^{(1/2)}$</td>
<td>$\alpha^{(1/2)}$</td>
</tr>
<tr>
<td>Power law (P3)</td>
<td>$3 \alpha^{(2/3)}$</td>
<td>$\alpha^{(1/3)}$</td>
</tr>
<tr>
<td>Power law (P4)</td>
<td>$4 \alpha^{(3/4)}$</td>
<td>$\alpha^{(1/4)}$</td>
</tr>
<tr>
<td>Avarami-Erofejev (A2)</td>
<td>$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$</td>
<td>$[-\ln(1-\alpha)]^{1/2}$</td>
</tr>
<tr>
<td>Avarami-Erofejev (A3)</td>
<td>$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$</td>
<td>$[-\ln(1-\alpha)]^{1/3}$</td>
</tr>
<tr>
<td>Avarami-Erofejev (A4)</td>
<td>$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$</td>
<td>$[-\ln(1-\alpha)]^{1/4}$</td>
</tr>
<tr>
<td>Prout-Tompkins (B1)</td>
<td>$\alpha (1-\alpha)$</td>
<td>$\ln[\alpha/(1-\alpha)]+c^b$</td>
</tr>
<tr>
<td>Geometrical contraction models</td>
<td>2(1-(\alpha))^{1/2}</td>
<td>[1-(1-(\alpha))^{1/2}]</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>-------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Contracting area (R2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contracting volume (R3)</td>
<td>3(1-(\alpha))^{2/3}</td>
<td>[1-(1-(\alpha))^{1/3}]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion models</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-D Diffusion (D1)</td>
<td>1/(2(\alpha))</td>
<td>(\alpha^2)</td>
</tr>
<tr>
<td>2-D Diffusion (D2)</td>
<td>[-\ln(1-(\alpha))]^{-1}</td>
<td>[(1-(\alpha))\ln(1-(\alpha))] + (\alpha)</td>
</tr>
<tr>
<td>3-D Diffusion-Jander (D3)</td>
<td>[3(1-(\alpha))^{2/3}] / [2(1- (1-(\alpha))^{1/3})]</td>
<td>[1-(1-(\alpha))^{1/3}]^2</td>
</tr>
<tr>
<td>Ginstling-Brounshtein (D4)</td>
<td>3/[2((1-(\alpha))^{-1/3} – 1)]</td>
<td>1-(2(\alpha)/3)-(1-(\alpha))^{2/3}</td>
</tr>
<tr>
<td>Reaction-order models</td>
<td>1</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------</td>
<td>----------</td>
</tr>
<tr>
<td>Zero-order (F0/R1)</td>
<td>(1-$\alpha$)</td>
<td>-ln(1-$\alpha$)</td>
</tr>
<tr>
<td>First-order (F1)</td>
<td>(1-$\alpha$)$^2$</td>
<td>(1-$\alpha$)$^{-1}$ - 1</td>
</tr>
<tr>
<td>Second-order (F2)</td>
<td>(1-$\alpha$)$^3$</td>
<td>0.5 [(1-$\alpha$)$^{-2}$ - 1]</td>
</tr>
</tbody>
</table>
Methods for studying solid-state kinetics
TGA data for a simulated dehydration reaction

Isothermal

Nonisothermal
Nonisothermal method

• This method employs a heating rate ($\beta$), usually linear, to raise the temperature. A linear heating program follows:

$$T = T_0 + \beta t$$

• Where, $T_0$ is the starting temperature, $\beta$ is the linear heating rate (K/min.), and $T$ is the temperature at time, “t”.
Differential form of the nonisothermal rate law

• The following relationship can be defined for nonisothermal experiments

\[ \frac{d \alpha}{d T} = \frac{d \alpha}{d t} \cdot \frac{d t}{d T} \]

(7)

• Where, \( d\alpha/dT \) is the nonisothermal reaction rate; \( d\alpha/dt \) is the isothermal reaction rate and \( dT/dt \) is the heating rate (\( \beta \)). Substituting Eq. (7) into Eq. (5) gives,

\[ \frac{d \alpha}{d T} = \frac{A}{\beta} e^{\frac{E_a}{RT}} f(\alpha) \]

(8)
Temperature integral

• Integrating the differential nonisothermal rate law (Eq. (8)) produces the integral form of the nonisothermal rate law:

$$ g(\alpha) = \frac{A}{\beta} \int_{0}^{T} e^{\frac{E_a}{RT}} \, d\, T $$

(9)

• This integral is called the “temperature integral” and has no analytic solution.
• To transform the above integral to a more general form found in mathematical handbooks, the integration variable can be redefined as,

\[
x = \frac{E_a}{RT}
\]

and the temperature integral then becomes,

\[
g(\alpha) = \frac{AE_a}{\beta R} \int_{x}^{\infty} \frac{e^{-x}}{x^2} \, dx
\]  

(10)
• If,

$$p(x) = \int_{x}^{\infty} \frac{e^{-x}}{x^2} \, dx$$

• then Eq. (10) can be written as,

$$g(\alpha) = \frac{A \! E^a}{\beta R} \, p(x)$$
• Where, \( p(x) \) is the exponential integral which can be found in mathematical tables.

• The main approaches used for evaluating the temperature/exponential integral are:
  – Calculating values of \( p(x) \) numerically.
  – Converting \( p(x) \) to an approximate form that can be integrated.
  – Approximating \( p(x) \) by a series expansion.
The Doyle approximation

- The Doyle approximation is based on the observation that $\log p(x)$ is linear with respect to $x$ over a short range of $x$ values according to:

$$\log p(x) \approx -A - Bx \quad (11)$$

- Where, $A$ and $B$ are fitted linear constants. Doyle approximated values of $p(x)$ using the first three terms of series expansion. By interpolation, Doyle calculated parameters in Eq. (11) as, 2.315 and 0.4567 for $A$ and $B$, respectively.

- Therefore, Eq. (11) becomes,

$$\log p(x) \approx -2.315 - 0.4567x \quad (12)$$
Calculation methods

• There are two groups of methods used to analyze either isothermal or nonisothermal solid-state kinetic data – modelistic and model-free methods
Model-fitting methods

• For these methods, different models are fit to the data and the model giving the best statistical fit is chosen as the model of choice from which the activation energy ($E_a$) and frequency factor (A) are calculated.

• Model–fitting approach is often used for pyrolysis reaction description. As a result, a one set of kinetic parameters is derived for entire range of temperatures and respective extend of reaction. These are called apparent kinetic parameters.
Isothermal model-fitting methods

• This method is identical to that in homogenous phase kinetics. It involves two fits:
  – the first, determines the rate constant (k) of the model that best fits the data according to Eq. (3),
  – while the second determines specific kinetic parameters such as the activation energy \((E_a)\) and frequency factor \((A)\) using the Arrhenius equation (Eq. (4)).
Nonisothermal model-fitting methods

• There are many model fitting methods that extract the three kinetic parameters known as the kinetic triplet \((A, E_a\text{ and model})\) from nonisothermal data. These methods were used extensively earlier in solid-state kinetic analysis and they continue to appear.

• These methods have been critically evaluated and it’s been shown that the sole use of these methods is not recommended because:
  – They assume a constant kinetic triplet \((A, E_a\text{ and model})\).
  – They involve fitting three parameters \((A, E_a\text{ and model})\) which are determined from a single run (i.e., one hating rate).
  – They involve a single heating rate which is not always sufficient to determine reaction kinetics.
Model of coal pyrolysis

- The key assumption of the model is to assume that the thermal decomposition of coal takes place in accordance with the following kinetic equation:

\[ \frac{dV}{dt} = A(V^0 - V) \]  \hspace{1cm} (13)

where: \( V \rightarrow V^0 \) if \( t \rightarrow \) infinity

Unknown parameters: \( A \) – reaction rate constant and released volatile matter \( V \) are the subject for experimental determination.
• V0 means the effective amount of volatile components contained in coal, which in many cases is different from the volatile content specified by standard analytical procedures.

• In the case of fast pyrolysis processes conducted with the participation of smaller particles, eg. in a fluidized bed V0/VM ratio is between $1 \div 1.3$.

• In the case of coking coal at the slow heating rate, which contributes to secondary reactions and therefore V0/VM is between $0.9 \div 1.0$. 
After separation of variables this equation can be subjected to sided integration:

\[
\int_{V^0}^{V} \frac{dV}{V^0 - V} = \int_{T_{tot}}^{T} \frac{1}{\beta} A \exp \left( \frac{-E_a}{(MR)T} \right) dT
\]

After integration:

\[
\Delta V = \frac{V^0 - V}{V^0} = \exp \left[ \frac{-1}{\beta} A \int_{T_{tot}}^{T} \exp \left( \frac{-E_a}{(MR)T} \right) dT \right]
\]

where: \(\Delta V\) means the relative amount of volatile components, which remained to be separated during the heating from \(T_{tot}\) to \(T\).

After transformation, an amount of volatile matter released in this range of temperature determines the relation:

\[
V = V^0 \left\{ 1 - \exp \left[ \frac{-1}{\beta} A \int_{T_{tot}}^{T} \exp \left( \frac{-E_a}{RT} \right) dT \right] \right\}
\]
Results of data fitting

\[ F_{x1}(z, k_{01}, E_1, V_{daf1}, m_1) \]
\[ Y_{11} \]

Given
\[ \text{resid1}(k_0x, Ex) = 0 \]

Parameters for best fit:
\[ \begin{bmatrix} k_{01} \\ E_1 \end{bmatrix} = \text{Minerr}(k_0x, Ex) \]
\[ \begin{bmatrix} k_{01} \\ E_1 \end{bmatrix} = \begin{bmatrix} 4.284 \times 10^{-3} \\ 2.136 \times 10^4 \end{bmatrix} \]
Direct differential method

• This method uses the differential form of the nonisothermal rate law (Eq. (8)) by numerically calculating the differential

\[
\left( \frac{d \alpha}{dT} \approx \frac{\Delta \alpha}{\Delta T} \right)
\]

• Taking the logarithm of the nonisothermal rate law, gives:

\[
\ln \frac{d \alpha/d T}{f(\alpha)} = \ln \frac{A}{\beta} - \frac{E_a}{RT}
\]
• Plotting the left-hand side (including the model $f(\alpha)$) versus $1/T$ gives the activation energy ($E_a$) and frequency factor ($A$) from the slope and intercept, respectively.

• The model that gives the best linear fit is usually chosen as the model.
Results
Coats-Redfern method

- This method uses the integral form of the nonisothermal rate law (Eq. (9)). Coats and Redfern utilized the asymptotic series expansion for approximating the temperature integral $p(x)$, producing:

\[
\ln \frac{g(\alpha)}{T^2} = \ln \left( \frac{AR}{\beta E_a} \left[ 1 - \left( \frac{2RT_{\text{exp}}}{E_a} \right) \right] \right) - \frac{E_a}{RT}
\]
• Where, $T_{\text{exp}}$ is the mean experimental temperature.

• Plotting the left-hand side (including the model, \(g(\alpha)\) versus \(1/T\) gives the activation energy \((E_a)\) and frequency factor \((A)\) from the slope and intercept, respectively. The model that gives us the best linear fit is chosen as the model.

• The Coats-Redfern equation was originally derived assuming a first-order model \((g(\alpha) = -\ln(1-\alpha))\) but has been generalized to other reaction models.
Model-free/isoconversional methods

• Model-free methods calculate the reaction activation energy ($E_a$) without modelistic assumptions, which is usually done by grouping terms such as the frequency factor (A) and model into the intercept of a linear equation and using the slope of that equation to calculate the activation energy ($E_a$).

• The frequency factor (A) can be calculated from the intercept of the linear equation but requires modelistic assumptions for such a determination. Therefore, model-free methods usually report only activation energies.
• Isoconversional methods are model-free methods that evaluate kinetic parameters, namely the activation energy ($E_a$) at progressive conversion values ($\alpha$). These methods require several kinetic curves to perform the analysis and have therefore been called, “multi-curve” methods.

• Calculations from several curves at different heating rates are performed on the same value of conversion ($\alpha$), thus, the name isoconversional. As a result, these methods calculate the activation energy for each conversion point ($E_a, \alpha$), resulting in an isoconversional plot ($E_a$ vs. $\alpha$).
• The terms, “model-free” and “isoconversional” are sometimes used interchangeably, however, not all model-free methods are isoconversional (Kissinger method).

• Isoconversional approaches can be used to analyze both isothermal and nonisothermal data, as described below.
Isoconversional methods for evaluating solid-state kinetics

Isthermal  Nonisothermal
Isothermal isoconversional methods

• These methods utilize the isothermal rate law (Eq. (6)) and include the standard and Friedman’s isoconversional methods.
Standard isoconversional method

• This method can be derived by taking the logarithm of the isothermal rate law to give:

\[ \ln g(\alpha) = \ln A - \frac{E_a}{RT} + \ln t \]  \hspace{1cm} (18)

• Which can be rearranged to give:

\[ -\ln t = \ln \left( \frac{A}{g(\alpha)} \right) - \frac{E_a}{RT} \]  \hspace{1cm} (19)
• A plot of \(-\ln t\) versus \(1/T\) for each \(a\) gives \(E_a\) from the slope for that \(a\) regardless of the model according to:

\[
-\ln t_\alpha = \ln\left(\frac{A}{g(\alpha)}\right)_\alpha - \frac{E_{a\alpha}}{RT_\alpha}
\]
Nonisothermal isoconversional methods

• Unlike isothermal data, nonisothermal data involve the use of the temperature integral (Eq. (9)). Therefore, two common approximations of the temperature integral have been widely used:
  – A linear approximation (less accurate) utilizing the Doyle approximation has been used in the Ozawa and Flynn-Wall methods.
  – A non-linear approximation (more accurate) utilizing the Senum-Yang approximation has been used in the Vyazovkin method.
Ozawa, Flynn and Wall (OFW) method

- Ozawa and Flynn-Wall independently developed an isoconversional calculation method for nonisothermal data which is commonly referred to as the OFW method. Taking the common logarithm of the nonisothermal rate law (Eq. (9)) gives the following,

\[
\log g(\alpha) = \log \frac{AE^a}{\beta R} + \log p(x)
\]  

(20)
• Substituting Doyle’s approximation in Eq. (20) gives,

\[
\log g(\alpha) = \log \frac{AE_a}{\beta R} - 2.315 - 0.457x
\]  

(21)

• Substituting \( E_a / RT \) for \( x \) and rearranging gives,

\[
\log \beta = \log \frac{AE_a}{g(\alpha)R} - 2.315 - 0.457 \frac{E_a}{RT}
\]  

(22)
A plot of ln b versus 1/T at each a yields Ea from the slope for that a regardless of the model according to:

$$\log \beta = \log \left( \frac{A_\alpha E_{a\alpha}}{g(\alpha)R} \right) - 2.315 - 0.457 \frac{E_{a\alpha}}{RT_\alpha}$$
Heating rate vs. temperature inverse
Activation energy, kJ/kmol
The Vyazovkin (VYZ) method

• The temperature integral $p(x)$ in the nonisothermal rate law is a function of $E_a$ and temperature. Therefore Eq. (9) can be written as,

$$g(\alpha) = \frac{AE_a}{\beta R} I(E_a, T)$$  \hspace{1cm} (23)
Where, \( I(E_a, T) = p(x) \). The general assumption used in Vyazovkin’s method (or any other isoconversional method) is that the reaction model is independent of the heating rate (i.e., \( g(\alpha) \) will be the same for any heating rate). Therefore, for a conversion value \((\alpha)\), the relationship below could be defined if two heating rates are applied:

\[
g(\alpha) = \frac{A_\alpha E_{a\alpha}}{\beta_1 R} \cdot I(E_{a\alpha}, T_{\alpha_1}) = \frac{A_\alpha E_{a\alpha}}{\beta_2 R} \cdot I(E_{a\alpha}, T_{\alpha_2})
\]
• Where, $\beta_1$ is the first heating rate, $\beta_2$ is the second heating rate, $T_{a_1}$ is the temperature for a particular $a$ using the first heating rate, $T_{a_2}$ is the temperature at the same $a$ using the second heating rate, $E_{a_\alpha}$ is the activation energy at that $\alpha$ and $A_{a_\alpha}$ is the frequency factor at that $\alpha$. For an experiment having “n” heating rates, the relationship would be,

$$\frac{A_{a_\alpha}E_{a_\alpha}}{\beta_1 R} I(E_{a_\alpha}, T_{a_1}) = \frac{A_{a_\alpha}E_{a_\alpha}}{\beta_2 R} I(E_{a_\alpha}, T_{a_2}) = \ldots = \frac{A_{a_\alpha}E_{a_\alpha}}{\beta_n R} I(E_{a_\alpha}, T_{a_n})$$
• which reduces to:

\[ \frac{I(E_{a\alpha}, T_{\alpha 1})}{\beta_1} = \frac{I(E_{a\alpha}, T_{\alpha 2})}{\beta_2} = \ldots = \frac{I(E_{a\alpha}, T_{\alpha n})}{\beta_n} = \sigma \]

• where, \( \sigma \) is a constant.
• For “n” heating rates, Eqs. can be generalized as,

\[
\sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{\beta_j I(E_{a\alpha}, T_{\alpha_i})}{\beta_i I(E_{a\alpha}, T_{\alpha_j})} = n(n-1)
\]

or

\[
\left( n(n-1) - \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{\beta_j I(E_{a\alpha}, T_{\alpha_i})}{\beta_i I(E_{a\alpha}, T_{\alpha_j})} \right) = 0
\] (24)
• For experimental data, Eq. (24) might not converge to 0, but an $E_{a\alpha}$ which minimizes the left-hand side can be found if the following form is used:

\[
\left| n(n - 1) - \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{\beta_j I(E_{a\alpha}, T_{\alpha_i})}{\beta_i I(E_{a\alpha}, T_{\alpha_j})} \right| = \Omega
\]
• Minimizing Eq. (25) is equivalent to minimizing the following function,

\[ \Omega = \left| \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{\beta_j I(E_{a\alpha}, T_{\alpha_i})}{\beta_i I(E_{a\alpha}, T_{\alpha_j})} \right| \]
Results of calculation

![Graph showing the relationship between energy of activation (Ea, kJ/kmol) and TSI^5 vs. extend of reaction (α)].
Controversies in solid-state kinetics

• Varying activation energy in solid-state kinetics
  – Solid-state kinetics was developed from reaction kinetics in homogenous systems (i.e. gases and liquids). The Arrhenius equation relates the rate constant of a simple one-step reaction to the temperature through the activation energy ($E_a$) and preexponential factor ($A$).
  – It has been generally assumed that activation energy ($E_a$) and frequency factor ($A$) remain constant, however, it’s been shown in solid-state reactions these kinetic parameters may vary with the reaction progress ($\alpha$).
  – This variation can be detected by isoconversional methods. While this variation appears to be in conflict with basic chemical kinetic principles, in reality, it may not be.
Effect of physical processes

- Nucleation and growth – the energy barrier for nucleation could be relatively large compared to growth. Once a nucleus is established, the rate of interface advance can be much lower than that for nucleation. There is no sharp demarcation where nucleation stops and growth starts, since the two are interdependent. The contribution of nucleation may diminish as the reaction progresses, leading to an effective activation energy that varies with the reaction progress.
- Imperfection distribution – different samples of the same material may have different imperfection distributions. Therefore, no two solid samples are identical, although they may be similar. This could change the degradation kinetic profiles of each sample.
- Sublimation occurring simultaneously with other reaction processes.
- Surface adsorption-desorption processes on the reactants/products.
- Diffusion of a gaseous product through the sample.
- Rate of growth may vary along each crystallographic axis of a nucleus
- Particle size – if a solid-state reaction occurs at surfaces or defect points, larger particles, which have a lower specific surface area, will be less reactive than smaller particles. Various particle sizes could have different kinetic behavior, therefore a variable particle-sized sample could show complex reaction behavior.
- Particle or solid morphology – degradation kinetics of a spherical particle or compact could differ from that of a cylindrical one. A non-homogenous sample that contains several solid shapes may show complex reaction behavior.
- Localized melting – melt degradation rates usually differ from that of the solid producing variable reactivity throughout the sample [76].
Kinetic Compensation Effect

• A kinetic compensation effect (KCE), is a relationship between the activation energy \( (E_a) \) and frequency factor \( (A) \) according to:

\[
\ln A = bE_a + c
\]

• Where, \( b \) and \( c \) are constants. This relationship is called a “compensation” because a change in the activation energy \( (E_a) \) is partially or completely compensated by a change in the frequency factor \( (A) \).
Kinetic compensation effect and isokinetic relationship
Summary

• Most solid-state kinetic principles were derived from those for homogenous phases in the past century. Rate laws describing pyrolysis are more complex than those in homogenous phases.

• Solid-state kinetic reactions can be mechanistically classified as nucleation, geometrical contraction, diffusion and reaction order models.

• Experimentally, solid-state kinetics are studied either isothermally or nonisothermally.

• Many mathematical methods have been developed to interpret experimental data for both heating protocols.

• These methods generally fall into one of two categories: model-fitting and model-free.
Historically, model-fitting methods were widely used because of their ability to directly determine the kinetic triplet (i.e., frequency factor \( A \), activation energy \( E_a \) and model).

However, these methods suffer from several problems among which is their inability to uniquely determine the reaction model.

This has led to the decline of these methods in favor of isoconverisonal (model-free) methods that evaluate kinetics without modelistic assumptions.

However, isoconverisonal methods do not compute a frequency factor nor determine a reaction model which are needed for a complete and accurate kinetic analysis.

A new approach has to be proposed that combines the power of isoconverisonal methods with model-fitting methods.
• Iso-conversional methods rise controversies with regard to interpreting solid-state kinetic results which include variable activation energy, calculation methods and kinetic compensation effects.

• The concept of variable activation energy in solid-state reaction kinetics has caused considerable debate because this behavior has been viewed by some as a violation of basic chemical kinetic principles.

• Activation energy variation has been detected by isoconversional or “model-free” calculation methods which generate activation energy as a function of reaction progress.
• Variable activation energy in simple reactions could be an artifact resulting from the use of isoconversational methods; this artifactual behavior can be seen in both isothermal and nonisothermal kinetic experiments.

• Therefore, care should be taken when interpreting kinetic results from isoconversational methods. If the variation in activation energy is artifactual, this variation can lead to a false mechanistic conclusion about a reaction being complex while, in fact, it is not.

• Artifactual variation can be reduced by careful experimental design and control of experimental variables in addition to experimental replication, so that averaged kinetic parameters and their confidence intervals can be estimated.