Catalytic Reaction Kinetics

- Why Catalytic Reaction Kinetics?
- Derivation rate expressions
- Simplifications
  - Rate determining step
  - Initial reaction rate
- Limiting cases
  - Temperature dependency
  - Pressure dependency
- Examples

Rate expression

How much detail?

A + B ⇌ C + D

A + B ⇌ [intermediates] ⇌ C + D

A + B + * ⇌ AB* ⇌ * + C + D

etc.

overall rate expression?

\[ r = f(p, T, \mu, K_{\text{eq}}, \text{catalyst}, ...) \]

rate constant(s)

thermodynamics

Reactors design equation - Packed bed

\[ \frac{dF_i}{dW} = V_i \cdot \eta \cdot \eta_i \]

Molar flow \( i \)

stoichiometric coefficient \( i \)

'bed coordinate'

catalyst effectiveness

Dimension of rate?

Rate expression - Gas phase reaction

forward rate

backward chance to success

amount of A \times\ \text{chance to meet} \ B

\[ r = k \cdot c_A \cdot c_B - k \cdot c_C^2 \]
### Role of catalyst?

- Concentrating reactants
  - adsorption/complexation
  - affect rate
- Providing alternative reaction path
  - catalyst selectivity
  - rate constant
  - other activation energy barrier
- But:
  - other components adsorb, too
  - block ‘active sites’
  - affect rate
  - fixed number of ‘active sites’
  - affect rate

*other form rate expression expected*

### Rate vs. pressure/concentration?

- rate
  - mol/s g_{cat}
- pressure / kPa

- fixed number of active sites
- mono & bimolecular reactions

### Rate expression – Catalysed reaction

\[
\begin{align*}
\text{rate} &= k \cdot c_{A}^{m} \cdot \text{ads} \cdot \theta_{A} - K \cdot c_{B}^{n} \cdot \text{ads} \\
\text{where} & \text{ } \theta &= \text{amount of A adsorbed} \\
& \text{chance of adjacent B adsorbed}
\end{align*}
\]

Note:
- c_{gas} and c_{ads} differ
- ratios components differ

### Kinetics

- Rate expressions *in principle* crucial for
  - design
  - process start-up and control
  - process development and improvement
  - selection reaction model
- Often used in catalysis
  - power rate models
  - models based on elementary processes
  - extrapolation more reliable
  - intellectually process better understood

\[
\begin{align*}
r &= k \cdot p_{A}^{m} \\
r &= \frac{\alpha N \cdot k \cdot K_{p} \cdot [p_{A} - p_{A}^{eq}]}{1 + k \cdot p_{A}^{eq} \cdot K_{p}}
\end{align*}
\]
Simple example: reversible reaction

A $\rightleftharpoons$ B

monomolecular

\[ \text{e.g. isomerization} \]

('Elementary processes'

\[ \text{Langmuir adsorption} \]

Elementary processes

- Rate expression follows from rate equation

\[ r = r_1 - r_{-1} = k_1 p_A N_T \theta_A - k_{-1} N_T \theta_A \]

\[ r = r_2 - r_{-2} = k_2 N_T \theta_A - k_{-2} N_T \theta_B \]

\[ r = r_3 - r_{-3} = k_3 N_T \theta_B - k_{-3} p_B N_T \theta_A \]

Eliminate unknown surface occupancies

Elementary processes contd.

Algebraic eqs.

- Site balance:

\[ 1 = \theta_A + \theta_B \] (3.5)

- Steady state assumption:

\[ \frac{d\theta_A}{dt} = 0 \] (3.6-7)

\[ \frac{d\theta_B}{dt} = 0 \]

- Rate expression:

\[ r = N_r k_r k_A (p_A - p_0 / K_{eq}) \]

\[ \frac{(\cdots) + (\cdots) p_A + (\cdots) p_0}{(\cdots)} \]

with:

\[ K_{eq} = K_K K_3 \]

Microkinetics

Michaelis-Menten

Quasi-equilibrium / rate determining step

\[ r = r_2 - r_{-2} \]

rate determining

'quasi-equilibrium'
Rate expression - r.d.s.

Rate determining step:
\[ r = r_2 - r_2 = k_2 N_1 \theta_2 - k_2 N_2 \theta_2 \]

Eliminate unknown occupancies

Quasi-equilibrium:
\[ r_2 = r_2 = k_1 p_2 N_2 \theta_2 = k_1 N_2 \theta_2 \]

So:
\[ \theta_A = k_1 p_2 \theta_2 \]
\[ \theta_A = k_1 p_2 \theta_2 \]

\[ \theta_A = \frac{p_1}{K_1} \theta_2 \]

\[ \theta_A = \frac{p_1}{K_1} \theta_2 \]

Rate expression, contd.

Substitution:
\[ r = r_2 - r_3 = k_3 N_2 \theta_2 - k_3 N_2 \theta_2 \]
\[ r = k_1 N_1 \theta_1 \{ p_1 \theta_1 - k_2 p_2 \theta_2 \} \]

where:
\[ K_w = K_1 K_2 K_3 = \frac{[p_1]}{[p_2]}_{eq} \]

Unknown still \( \theta \).

Rate expression, contd.

Site balance:
\[ 1 - \theta_A + \theta_A + \theta_B = 1 \cdot \{1 + K_1 p_2 + p_3 / K_1 \} \]
\[ \theta_A = \frac{1}{1 + K_1 p_2 + p_3 / K_1} \]

Finally:
\[ r = \frac{k_3 N_2 \{ p_1 - p_2 / K_w \}}{1 + K_1 p_2 + p_3 / K_1} \]

Surface occupancies

Empty sites
\[ \theta_A = \frac{1}{1 + K_1 p_2 + p_3 / K_1} \]

Occupied by A
\[ \theta_A = \frac{K_1 p_2}{1 + K_1 p_2 + p_3 / K_1} \]

Occupied by B
\[ \theta_B = \frac{p_2 / K_1}{1 + K_1 p_2 + p_3 / K_1} \]
Other steps rate determining

Adsorption r.d.s.
\[ r = k_r N_A \left( p_A - p_{\text{eq}} / K_a \right) / \left( 1 + K_A \right) \]

Surface reaction r.d.s.
\[ r = k_s N_r K_r \left( p_A - p_{\text{eq}} / K_r \right) / \left( 1 + K_A \right) \]

Desorption r.d.s.
\[ r = k_d N_d K_d \left( p_A - p_{\text{eq}} / K_d \right) / \left( 1 + K_A \right) \]

Rule of thumb: Generally surface reaction r.d.s.

Langmuir adsorption

- Uniform surface (no heterogeneity)
- Discrete number of sites
- No interaction between adsorbed species

\[ A + * \rightleftharpoons A^* \]

\[ \theta_A = \frac{K_A p_A}{1 + K_A p_A} \]

\[ \theta_A \quad 0.1 \]

\[ 0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 \]

\[ p_A / \text{bar} \quad 0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 \]

Multicomponent adsorption / inhibition

\[ \theta_A = \frac{K_A p_A}{1 + K_A p_A + \sum K_i p_i} \]

Inhibitors

Thermodynamics

Equilibrium constant
\[ \text{Reaction entropy} \]

\[ RT \ln K_{eq} = \Delta G^\circ(T) = \Delta H^\circ(T) - T \Delta S^\circ \]

Adsorption constant

\[ \ln K_A = \frac{\Delta S^\circ}{R} \quad \frac{\Delta H^\circ}{RT} \]

Data sources: Handbooks, API, JANAF, Chemsage, HSC
Langmuir adsorption model

- Generally used
  - although nonlinear, mathematically simple
  - simple physical interpretation
  - rather broadly applicable
    - multicomponent adsorption
    - non-uniform surfaces
      - 'compensation effect'
      - very weak and strong sites do not contribute much to the rate
    - for microporous media (activated carbons) often not satisfactory

Dissociative adsorption

\[ H_2 + 2* \rightleftharpoons 2H^* \]

\[ \theta_h = \left( \frac{K_{p,h}p_h}{1 + K_{p,h}p_h} \right)^{0.5} \]

Two adjacent sites needed

Initial rate expressions

- Forward rates
- Product terms negligible

\[ r = k' \theta_0 \]

\[ r = \frac{k'p_{2A}}{1 + K_A p_{2A}} \]

\[ r = k' \]

Dual site reaction:

\[ A + B \rightleftharpoons C \]

\[ \begin{align*}
  &1. A + * \leftrightarrow A^* \\
  &2. B + * \leftrightarrow B^* \\
  &3. A^* + B^* \leftrightarrow C^* + * \quad \text{(r.d.s.)} \\
  &4. C^* \leftrightarrow C + * \\
\end{align*} \]
Dual site reaction, contd.

\[ r = r_1 - r_2 = s \cdot N_s \left[ k_1 \theta_1 \theta_2 - k_2 \theta_1 \theta_2 \right] \]

Number of neighbouring sites (here: 6)

More than one reactant

- **One-site models**
  - single site reaction
    \[ r = kN_s \theta_1 - kN_s \theta_1 \theta_2 \]
  - dual site reaction
    \[ r = kN_s \theta_1 \theta_2 - kN_s \theta_1 \theta_2 \]

- **Two-site models**
  - different sites
    \[ r = kN_s \theta_1 \theta_2 - kN_s \theta_1 \theta_2 \]

- Number of sites conditions dependent
  \[ N_s = \frac{N_s \left( k_s \rho_s \right)^n}{\left( 1 + k_s \rho_s \right)^n} \]

Langmuir-Hinshelwood/Hougen-Watson models (LHHW)

\[ r = \frac{(\text{kinetic factor}) \cdot (\text{driving force})}{(\text{adsorption term})^n} \]

- includes \( N_s, k\text{(rds)} \)
- includes \( \rho_1, \rho_2, \rho_3 / K_{eq} \)
- molecular: \( K_p \rho_s \)
- dissociative: \( (K_p \rho_s)^n \)

\[ n = 0, 1, 2, \ldots \]

What about observed: reaction order activation energy?

**Determination:**

- Reaction order
  \[ \text{slope} = \text{order} n \]
  \[ \ln r = \ln p_1 \]

- Activation energy
  \[ \text{slope} = -\frac{E_{\text{act}}}{R} \cdot \frac{\partial \ln r}{\partial \frac{1}{T}} \]

- LHHW models
  \[ r = \frac{k_1 N_s k_s \rho_s}{\left( 1 + k_s \rho_s + K_p \rho_s \right)} \]
**Reaction order - Activation energy**

**Rate expression**

\[ r = \frac{k_1 N_1 K_p A}{(1 + K_p A_p + K_p B_p)} \]

Reaction order

\[ n_a = 1 - \theta_a \]
\[ n_b = -\theta_b \]

Activation energy

\[ E_a^{\text{act}} = E_{a^0} + (1 - \theta_a) \Delta H_a - \theta_b \Delta H_b \]

- depend strongly on occupancy!
- vary during reaction

**Limiting cases?**

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**Limiting cases - forward rates**

**Surface reaction r.d.s.**

\[ r = \frac{k_1 N_1 K_p A}{(1 + K_p A_p + K_p B_p)} \]

1. **Strong adsorption A**

\[ r = k_1 N_1 \]

\[ E_a^{\text{act}} = E_{a^0} \]

---

2. **Weak adsorption**

\[ r = k_1 N_1 K_p A \]

\[ E_a^{\text{act}} = E_{a^0} + \Delta H_a \]

---

3. **Strong adsorption B**

\[ r = \frac{k_1 N_1 K_p A}{K_p B_p} \]

\[ E_a^{\text{act}} = E_{a^0} + \Delta H_a - \Delta H_B \]
Catalysis Engineering - Kinetics

Cracking of \(n\)-alkanes over ZSM-5

J. Wei I&EC Res. 33(1994)2467

\[ r_c = k_c K_c \rho_c \]

\[ E_{a2}^a = E_{a2} + \Delta H_{a2} \]

\[ negative!? \]

\[ E_{a2}^o = E_{a2} + \Delta H_{a2} \]

\[ \text{kJ/mol} \]

\[ 0 \]

\[ 100 \]

\[ 200 \]

\[ 5 \]

\[ 10 \]

\[ 15 \]

\[ 20 \]

\[ \text{Carbon number} \]

\[ E_a \]

\[ E_{a2} \]

\[ \Delta H_{a2} \]

\[ A + * \]

\[ \Delta H_{a2} \]

\[ E_{a2} \]

\[ A^* \]

\[ B^*, C^* \]

\[ \text{Adsorbed state} \]

\[ \text{Energy diagram} \]

\[ \text{Energy diagram} \]

\[ \text{Energy diagram} \]

n-Alkanes cracking

Observed temperature behaviour

- \(T\) higher → coverage lower
- Highest \(E_a\) most favoured

\[ \ln r_{\text{obs}} \]

\[ 1/T \]

\[ \text{Adsorption r.d.s.} \]

\[ \text{Desorption r.d.s.} \]

Change in r.d.s.

Catalytic reaction kinetics, summary

- Langmuir adsorption
  - uniform sites, no interaction adsorbed species, finite number of sites, multicomponent
- Rate expression derivation
  - series of elementary steps
  - steady state assumption, site balance
  - quasi-equilibrium / rate determining step(s)
  - initial rates (model selection)
- LHHW models
  - inhibition, variable reaction order, activation energy

\[ \text{mechanism} \xRightarrow{\chi} \text{kinetics} \]
Hydrodesulphurization kinetics

Example: HDS vacuum gasoil
- Apparent second order behaviour
- \( \text{H}_2\text{S} \) inhibits strongly

Composition oil fractions

Sulphur compounds
- Thioethers
- Thiophene
- Benzothiophene
- Dibenzothiophene
- Substituted dibenzothiophene

Complex mixtures different reactivities ⇒ lumping

Simulated profiles - HDS reactivity lumping

Simulated model data:
- 2\textsuperscript{nd} order:
  \( k=10 \text{ m}^3/\text{mol.s} \)
  \( c_0=2 \text{ mol/m}^3 \)
- Three lump model:
  - 1\textsuperscript{st} orders:
    \( k_1=36.1 \text{ s}^{-1} \)
    \( c_{01}=1.23 \)
    \( k_2=16.0 \text{ s}^{-1} \)
    \( c_{02}=0.59 \)
    \( k_3=7.5 \text{ s}^{-1} \)
    \( c_{03}=0.18 \)

Three lump model: first order reactions

- Sum:
- 1
- 2
- 3

Three lump model adequate
Inhibition through LHHW models

Kinetic coupling between catalytic cycles

Bifunctional catalysis: Reforming

Isomerization \( n\text{-C}_5 \rightarrow i\text{-C}_5 \)
- Pt function:
  - \( n\text{-C}_5 \rightarrow n\text{-C}_5^* \)
  - Surface diffusion
- Acid function:
  - \( n\text{-C}_5^* \rightarrow i\text{-C}_5 \)
  - Surface diffusion
- \( i\text{-C}_5^* \rightarrow i\text{-C}_5 \)

Coupled catalytic cycles on different sites

See tutorial
**Initial rates - CO hydrogenation over Rh**

Van Santen et al.

Kinetic model
1. \( \text{CO} * + * \rightarrow \text{CO}^* \) 
2. \( \text{CO}^* + * \rightarrow \text{C}^* + \text{O}^* \) (r.d.s.)

Initial rate
\[
\frac{\text{d}N}{\text{d}t} = sN_0 \eta_0 \theta_0 \cdot \theta_0
\]

\[
I_r = \frac{s \eta_0 k_0 N_0 (\theta_0)}{1 + k_0 N_0 \theta_0}
\]

**Catalysed N\textsubscript{2}O decomposition over oxides**

Winter, Cimino

Rate expressions:
- \( r = k_{\text{cat}} \cdot p_{\text{N}_2\text{O}} \)  \( \text{1st order} \)
- \( r = k_{\text{cat}} \cdot \frac{p_{\text{N}_2\text{O}}}{(p_{\text{O}_2})} \)  \( \text{strong O}_2 \text{ inhibition} \)
- \( r = k_{\text{cat}} \cdot \frac{p_{\text{N}_2\text{O}}}{(1+(p_{\text{O}_2}/k^*)^\text{m})} \)  \( \text{moderate inhibition} \)

Also:
- orders 0.5-1
- water inhibition

**N\textsubscript{2}O decomposition over Mn\textsubscript{2}O\textsubscript{3}**


\( 2 \text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2 \)

Kinetic model
1. \( \text{N}_2\text{O} + * \leftrightarrow \text{N}_2\text{O}^* \)
2. \( \text{N}_2\text{O}^* \rightarrow \text{N}_2 + \text{O}^* \)
3. \( 2\text{O}^* \leftrightarrow 2^* + \text{O}_2 \)

Rate expression
\[
r = \frac{k_{\text{cat}} N_0 K_p \theta_0}{1 + K_p \theta_0 + (p_{\text{O}_2}/k^*)^\text{m}}
\]
**N₂O decomposition over Mn₂O₃**  
Vannice et al. 1996

**Oxygen inhibition**

order N₂O ~0.78  

$$E_{a} = 96 \text{kJ/mol}$$

**Values**  

\(\Delta H = -29 \text{kJ/mol}\)  
\(\Delta S = -38 \text{J/mol K}\)

**Rate expression**

$$r = \frac{k_{p}}{[N_{2}O][O]}$$

**Thermodynamically consistent**

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**Ethanol dehydrogenation**  
Franckaerts & Froment

**Model:**

1. \(A + * \leftrightarrow A^{*}\)
2. \(A^{*} + S \leftrightarrow R^{*} + S^{*}\) (r.d.s.)
3. \(R^{*} \leftrightarrow R + *\)
4. \(S^{*} \leftrightarrow S + *\)

**Derive rate expression**

$$r_{i} = \frac{k_{i} N_{A} K_{p_{i}}}{[1 + K_{p_{A}} + K_{p_{A}} + K_{p_{S}}]}$$

After rearrangement

$$\frac{[P_{A}]}{r_{i}} = \frac{1}{k_{p_{A}}} + K_{p_{A}} K_{A} \rho_{A}$$

**Linear form:**

$$y = \beta + \alpha x$$

(linear least squares fit trends, positive parameters)
**Kinetic studies**

Differential reactor:
- plug flow, low conversion
- CSTR

\[
\frac{dx}{d\left(\frac{W}{F_0}\right)} = -V_i \cdot r \quad \Rightarrow \quad r = -\frac{x_i}{V_i \cdot \left(\frac{W}{F_0}\right)}
\]

Integral reactor

= model selection =
= rate parameters =

**Model selection**

- Mechanistic information
- Initial rate measurements
- Fit data on rate expressions (non-linear least squares)
- Best model:
  - low SSR (sum of squares of residuals)
  - no trending in residuals
  - parameters significant
  - parameters obey thermodynamics
  - 'linearization'

**Data fitting - Parameter estimation**

- Linear least squares - straightforward
- Nonlinear least squares methods:
  - Simplex / Powell etc. (iterative)
  - Levenberg-Marquardt (gradient)

\[
O.F. = \text{Min} \sum (x_{\text{calc}} - x_{\text{obs}})^2
\]

with:
\[
x_{\text{calc}} = f(...k_i...)
\]

= initial parameters values needed =

**Model selection**

- Divergence rival models
- Experimental design (sequential)
**N$_2$O decomposition over ZSM-5 (Co,Cu,Fe)

Kapteijn et al. 11th ICC, 1996**

$$2 \text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$$

Kinetic model

1. $\text{N}_2\text{O} + * \rightarrow \text{N}_2 + \text{O}^*$
2. $\text{N}_2\text{O} + \text{O}^* \rightarrow \text{N}_2 + \text{O}_2 + ^*$

Rate expression

$$r = \frac{k_1 N_o P_{\text{N}_2\text{O}}}{(1 + k_1/k_2 + K_P_{\text{O}_2})}$$

*no oxygen inhibition*

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**Effect of CO on N$_2$O decomposition**

CO + $O^*$ → CO$_2$ + *

CO + * ↔ CO$^*$ (Cu$^*$)

CO removes oxygen from surface
so ‘enhances’ step 2, oxygen removal

now observed: rate of step 1

$$r_1 = k_1 N_o P_{\text{N}_2\text{O}}$$

increase: ~2, >3, >100
Effect of CO on N$_2$O decomposition

rate without CO \hspace{1cm} \text{rate with CO}

\[ r = \frac{k_1 N_I p_{N_2O}}{1 + k_1/k_2} \hspace{1cm} r = k_1 N_I p_{N_2O} \]

\[ \text{ratio} = 1 + \frac{k_1}{k_2} \hspace{1cm} \theta = \frac{k_1}{k_2} \]

So \( k_1/k_2 = \) Co \( >2 \) Cu \( >100 \) Fe

\[ \theta = 0.7 \quad >0.9 \quad >0.99 \]

Apparent activation energies N$_2$O decomposition

CO/ N$_2$O = 0

\[ r = \frac{k_1 N_I p_{N_2O}}{1 + k_1/k_2} \]

\[ E_{\text{obs}}^{a1} = \text{mix}(E_{a1}, E_{a2}) \]

CO/ N$_2$O = 2

\[ r = \frac{k_1 N_I p_{N_2O}}{(1 + k_1/k_2 + k_{CO}p_{CO})} \]

\[ E_{\text{obs}}^{a1} = E_{a1} + \Delta H_{CO} \]

Hydrogenation: butyne -> butene -\> butane

A1 A2 A3

- butyne and butene compete for the same sites
- but: \( K_1 > K_2 \)
- resulting high selectivity for butene (desired) possible even when \( k_2 > k_1 \)
- since:

\[ S_2 = \frac{k_2}{k_1} \]

Meyer and Burwell (JACS 85(1963)2877) mo\%:

- 2-butyne: 22.0
- cis-2-butene: 77.2
- trans-2-butene: 0.7
- 1-butene: 0.0
- butane: 0.1