Catalytic Kinetics: Cycles and the LHHW Formalism

"A Catalyst is by definition a substance that increases the rate of approach to equilibrium of a chemical reaction without being substantially consumed in the reaction; a catalyst works by forming chemical bonds to one or more reactants and thereby facilitating their conversion. A catalyst does not significantly affect the reaction equilibrium."

"The definition of a catalyst rests on the idea of reaction rate and therefore the subject of reaction kinetics is central, providing the quantitative framework."

Common theme: Catalysis = Kinetics

Reaction Chemistry:  
The Practice of Catalysis

Reaction:  \[ A \rightarrow B + C \]

Thermodynamics:  \[ \Delta H_R^o = \Delta H_{fB}^o + \Delta H_{fC}^o - \Delta H_{fA}^o \]

Role of Catalyst:  Increase the rate

Implications:  Smaller vessels  
Better selectivities (relative rates)
Reaction Coordinate Diagram
Motivates and Explains Catalysis

$$\Delta H_R = E_B + E_C - E_A$$ is independent of catalyst
Kinetics of Heterogeneous Catalytic Reactions

External Transport

Adsorption/Desorption

Internal Transport

Surface Reaction
Series and Parallel Events in Catalytic Reactions

Steps 1, 3, 4, 5, 7 in series
Steps 2, 3, 4, 5, 6 in parallel
SITES AND ACTIVE CENTERS

"|" USED TO INDICATE A CATALYTIC SITE

Single Site

\[ A \rightleftharpoons R = S \]

\[ A_I \rightleftharpoons R_I \rightleftharpoons S_I \]

Dual Site

\[ A \rightleftharpoons R \rightleftharpoons S \]

\[ A_{I_1} = R_{I_1} \quad R_{I_2} \rightleftharpoons S_{I_2} \]

Surface Intermediates, Active Centers
## Adsorption

<table>
<thead>
<tr>
<th>Physical adsorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adsorbent</strong></td>
<td>All solids</td>
</tr>
<tr>
<td><strong>Adsorbate</strong></td>
<td>All gases below critical point</td>
</tr>
<tr>
<td><strong>Temperature range</strong></td>
<td>Low $T$</td>
</tr>
<tr>
<td><strong>Heat of adsorption</strong></td>
<td>Low, $\sim \Delta H_{\text{liq}}$</td>
</tr>
<tr>
<td><strong>Rate and activation energy</strong></td>
<td>Very rapid, low $E$</td>
</tr>
<tr>
<td><strong>Coverage</strong></td>
<td>Multilayer</td>
</tr>
<tr>
<td><strong>Reversibility</strong></td>
<td>Highly reversible</td>
</tr>
<tr>
<td><strong>Importance</strong></td>
<td>For determination of surface area and pore size</td>
</tr>
</tbody>
</table>

Adsorption Isotherms

Langmuir Model:

Homogeneous solid surface
Energetics independent of coverage
Adsorbed species don't interact

Mass Action Steps:

\[ A + l = Al \]

\[ r_a = k_a C_A C_l \]
\[ r_d = k_d C_{Al} \]
Adsorption Isotherms

The Equilibrium Isotherm:

\[ r_a = r_d \quad k_a C_A C_I = k_d C_{Al} \]

or, with

\[ C_t = \text{constant} = C_I + C_{Al} \]

\[ \Theta_A = \frac{C_{Al}}{C_t} = \frac{K_A C_A}{1 + K_A C_A} \]

---

Graph showing:
- 0 order
- 1st order

\[ \Theta_A \]

\[ 0 \quad \text{to} \quad 1 \]

\[ C_A / C_{ASAT} \]

\[ 0 \quad \text{to} \quad 1 \]

Reactions
Extensions of Basic Idea

1. Multicomponent Systems

$$\Theta_i = C_{i\|}/C_t = K_i C_i/(1 + \Sigma K_j C_j)$$

2. Dissociative Adsorption of "A"

$$\Theta_A = (K_A P_A)^{1/2}/(1 + (K_A P_A)^{1/2} + \Sigma K_j P_j)$$
Heterogeneous Rate Laws

Premises

Homogeneous Principles Valid

Surface Concentrations Relevant

Three Different Classes of (Equal) Rates
Heterogeneous Rate Laws

1. Adsorption \[ A + l = Al \]
   \[ r_a = k_A (C_{Al} - C_{Al}/K_A) \]

2. Surface Reaction \[ Al = Rl \]
   \[ r_{sr} = k_{sr} (C_{Al} - C_{Rl}/K_{sr}) \]

3. Desorption \[ Rl = R + l \]
   \[ r_d = k_R (C_{Rl}/K_R - C_{RCl}) \]

\[ K_i = \text{Adsorption Equilibrium Constant} \]
(used by convention)

Site Balance: \[ C_t = C_l + C_A + C_B + ... \]
Steady State Solution

This General Rate Expression Reduced for Various Rate Controlling Steps

Which May:
Not Exist
Change with T
Change with P
Rate Determining Step

1. The Usual Procedure

2. Requires that all other steps be in virtual equilibrium

Two Common Cases:

1. Surface Reaction Controls

2. Adsorption/Desorption Controls
Surface Reaction Controlling

\[ A \rightleftharpoons R \]

\[ r = k_{sr}(C_{Al} - C_{Rl}/K_{sr}) \]

\[ \Theta_i = C_{il}/C_t = K_iC_i/(1 + \sum K_jC_j) \]

\[ r = k_{sr}C_tK_A(C_A-C_R/K)/(1 + K_AC_A + K_RC_R) \]

\[ K = K_{sr}K_A/K_R \]
Bimolecular Reactions

\[ A + B \rightleftharpoons R + S \]

\[ r = k_{sr}C_tK_AK_B(C_AC_B-C_RC_S/K)/(1 + \Sigma K_JC_J)^2 \]
Additional Examples

Two-Site Mechanisms

\[ A_{l1} + B_{l2} \rightarrow R_{l1} + S_{l2} \]

\[ r = k_{sr}C_{Al1}C_{Bl2} = \]

\[ k_{sr}C_{t}K_{A}K_{B}C_{A}C_{B}/(1 + \Sigma K_{i1}C_{i})(1 + \Sigma K_{i2}C_{i2}) \]
Rideal Mechanism

\[ \text{Al} + \text{B} \quad \text{(g)} \rightarrow \text{RI} + \text{S} \quad \text{(g)} \]

\[ r = k_{sr} C_t K_A C_A C_B / (1 + \Sigma K_i C_i) \]
Additional Examples

Mole Change

\[ \text{I} + \text{Al} \rightleftharpoons \text{Bl} + \text{Cl} \]

\[ r = k_{sr}C_tK_A(C_A - C_BC_C/K)/(1 + \Sigma K_iC_i)^2 \]
Kinetic Groups

Adsorption of A controlling $k_A$
Adsorption of B controlling $k_B$
Desorption of R controlling $k_R K$
Adsorption of A controlling with dissociation $k_A$
Impact of A controlling $k_A K_B$
Homogeneous reaction controlling $k$

Surface Reaction Controlling

\[
\begin{array}{cccc}
A & \rightleftharpoons & R & \\
A & \rightleftharpoons & R + S & \\
A + B & \rightleftharpoons & R & \\
A + B & \rightleftharpoons & R + S & \\
\end{array}
\]

Without dissociation $k_s K_A$
With dissociation of A $k_s K_A$
B not adsorbed $k_s K_A$
B not adsorbed, A dissociated $k_s K_A$

Yang/Hougen tables from Froment, G. F. and K. B. Bischoff, Chemical Reactor Analysis and Design, Wiley
Exponents of Adsorption Groups

Adsorption of A controlling without dissociation \( n = 1 \)
Desorption of R controlling \( n = 1 \)
Adsorption of A controlling with dissociation \( n = 2 \)
Impact of A without dissociation \( A + B \rightleftharpoons R \) \( n = 1 \)
Impact of A without dissociation \( A + B \rightleftharpoons R + S \) \( n = 2 \)
Homogeneous reaction \( n = 0 \)

Surface Reaction Controlling

\[
\begin{array}{cccc}
A & R & A & R + S \\
\text{No dissociation of A} & 1 & 2 & 2 & 2 \\
\text{Dissociation of A} & 2 & 2 & 3 & 3 \\
\text{Dissociation of A} & 2 & 2 & 2 & 2 \\
\text{(B not adsorbed)} & & & & \\
\text{No dissociation of A} & 1 & 2 & 1 & 2 \\
\text{(B not adsorbed)} & & & & \\
\end{array}
\]

Yang/Hougen tables from Froment, G. F. and K. B. Bischoff, Chemical Reactor Analysis and Design, Wiley
Driving-Force Groups

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A ⇌ R</th>
<th>A ⇌ R + S</th>
<th>A + B ⇌ R</th>
<th>A + B ⇌ R + S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption of A controlling</td>
<td>$p_A - \frac{p_R}{K}$</td>
<td>$p_A - \frac{p_R p_S}{K}$</td>
<td>$p_A - \frac{p_R}{K_{pB}}$</td>
<td>$p_A - \frac{p_R p_S}{K_{pB}}$</td>
</tr>
<tr>
<td>Adsorption of B controlling</td>
<td>0</td>
<td>0</td>
<td>$p_B - \frac{p_R}{K_{pA}}$</td>
<td>$p_B - \frac{p_R p_S}{K_{pA}}$</td>
</tr>
<tr>
<td>Desorption of R controlling</td>
<td>$p_A - \frac{p_R}{K}$</td>
<td>$p_A - \frac{p_R p_S}{p_s}$</td>
<td>$p_A p_B - \frac{p_R}{K}$</td>
<td>$p_A p_B - \frac{p_R p_S}{K}$</td>
</tr>
<tr>
<td>Surface reaction controlling</td>
<td>$p_A - \frac{p_R}{K}$</td>
<td>$p_A - \frac{p_R p_S}{K}$</td>
<td>$p_A p_B - \frac{p_R}{K}$</td>
<td>$p_A p_B - \frac{p_R p_S}{K}$</td>
</tr>
<tr>
<td>Impact of controlling</td>
<td>0</td>
<td>0</td>
<td>$p_A p_B - \frac{p_R}{K}$</td>
<td>$p_A p_B - \frac{p_R p_S}{K}$</td>
</tr>
<tr>
<td>(A not adsorbed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Yang/Hougen tables from Froment, G. F. and K. B. Bischoff, Chemical Reactor Analysis and Design, Wiley
## Replacement in the General Adsorption Groups

\[ (1 + K_{A_{pA}} + K_{B_{pB}} + K_{S_{pS}} + K_{R_{pR}} + K_{I_{pI}}) \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( A \leftrightarrow R )</th>
<th>( A \leftrightarrow R + S )</th>
<th>( A + B \leftrightarrow R )</th>
<th>( A + B \leftrightarrow R + S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Where adsorption of A is rate controlling, replace ( K_{A_{pA}} ) by</td>
<td>( \frac{K_{A_{pR}}}{K} )</td>
<td>( \frac{K_{A_{pR}pS}}{K} )</td>
<td>( \frac{K_{A_{pR}}}{K_{pB}} )</td>
<td>( \frac{K_{A_{pR}pS}}{K_{pB}} )</td>
</tr>
<tr>
<td>Where adsorption of B is rate controlling, replace ( K_{S_{pS}} ) by</td>
<td>0</td>
<td>0</td>
<td>( \frac{K_{B_{pR}}}{K_{pA}} )</td>
<td>( \frac{K_{B_{pR}pS}}{K_{pA}} )</td>
</tr>
<tr>
<td>Where desorption of A is rate controlling, replace ( K_{A_{pA}} ) by</td>
<td>( K K_{R_{pA}} )</td>
<td>( K K_{R_{pA}pS} )</td>
<td>( K K_{R_{pA}pS} )</td>
<td>( K K_{R_{pA}pS} )</td>
</tr>
<tr>
<td>Where adsorption of A is rate controlling with dissociation of A, replace ( K_{A_{pA}} ) by</td>
<td>( \sqrt{K_{A_{pR}}} )</td>
<td>( \sqrt{K_{A_{pR}pS}} )</td>
<td>( \sqrt{K_{A_{pR}}} )</td>
<td>( \sqrt{K_{A_{pR}pS}} )</td>
</tr>
</tbody>
</table>

Where equilibrium adsorption of A takes place with dissociation of A, replace \( K_{A_{pA}} \) by and similarly for other components adsorbed with dissociation:

| \( \sqrt{K_{A_{pA}}} \) | \( \sqrt{K_{A_{pA}}} \) | \( \sqrt{K_{A_{pA}}} \) | \( \sqrt{K_{A_{pA}}} \) |

Where A is not adsorbed replace \( K_{A_{pA}} \) by and similarly for other components that are not adsorbed:

| 0 | 0 | 0 | 0 | 0 |
ADSORPTION/DESORPTION CONTROLLING

- SURFACE REACTION IN VIRTUAL EQUILIBRIUM

\[ K_{SR} = \Pi_i C_{il}^{\nu il} \]

1. \( \text{Al} + \text{Bl} \rightleftharpoons \text{Rl} + \text{Sl} \) with Adsorption of "A" controlling

\[
r = k_A C_A C_I - k_d A C_{Al} = k_A (C_A C_I - C_{Al}/K_A) \\
C_{Bl} = K_B C_B C_I \\
C_{Rl} = K_R C_R C_I \\
C_{SI} = K_S C_S C_I \\
C_{Al} = C_{Rl} C_{SI}/(C_{Bl} K_{SR}) \]

4 eqn, 4 unknowns

Used instead of final adsorption isotherm

\[
r = \frac{k_A C_t (C_A - C_{RCS}/C_B K)}{\left(1 + \frac{C_{RCS}}{C_B} \frac{K_A}{K} + K_B C_B + K_R C_R + K_S C_S\right)}
\]
Some Criteria for Parameter Estimation

1. Adsorption and Rate Constants be Statistically non-negative

2. $E^* > 0 \quad \ln k \downarrow \text{ with } 1/ T \uparrow$ (Arrhenius)

3. Exothermic adsorption $\ln k \uparrow \text{ with } 1/T \uparrow$

Confidence intervals may make negative-value containing models acceptable.
Linearization of Model

\[
\begin{align*}
    r_A &= \frac{k_r \ K_A(p_A - p_R \ p_S/K)}{(1+ K_A p_A + K_R p_R + K_S p_S)^2} \quad \rightarrow \quad y = a + b p_A + c p_R + d p_S \\
    y &= \sqrt{\frac{p_A - p_R p_S/K}{r_A}} \\
    a &= \frac{1}{\sqrt{k K_A}} \\
    b &= \frac{K_A}{\sqrt{k K_A}} \\
    c &= \frac{K_R}{\sqrt{k K_A}} \\
    d &= \frac{K_S}{\sqrt{k K_A}}
\end{align*}
\]

This allows linear regression. However, this suffers from lack of statistical rigor--y not truly dependent variable.
Catalysis in Series

$$A_1 \xrightarrow{r_1} A_2 \xrightarrow{r_2} A_3$$

$A_1$ strongly held, $A_2$ weak, $A_3$ not at all

Independent Rates:

$$r_1 = \frac{k_1 K_1 A_1}{1+ K_1 A_1} \approx k_1$$

$$r_2 = \frac{k_2 K_2 A_2}{1+ K_2 A_2} \approx k_2 K_2 A_2$$

@ Max of $A_2$  

$$0 = r_1 - r_2 \Rightarrow k_1 = k_2 K_2 A_2$$

or $$A_2|_{\text{Max}} = \frac{k_1}{k_2 K_2}$$
Coupled Rates

In reality, with coupling,

\[ r_2 = \frac{k_2K_2A_2}{1 + K_2A_2 + K_1A_1} \approx \frac{k_2K_2}{K_1} \frac{A_2}{A_1} \]

\[ A_{2,\text{MAX}} = \left(\frac{k_1}{k_2}\right) \left(\frac{K_1}{K_2}\right) A_1 \]

or

\[ \frac{A_{2,\text{MAX}}^c}{A_{2,\text{MAX}}^l} = K_1A_1 >> 1 \]

- Gain in selectivity due to coupling
- This is thermodynamic in nature
Analytical Rate Laws Derived from Mechanism BEFORE Use In Reactor Model

A Heterogeneous Chemistry (A → B) Example

\[ A + l \Leftrightarrow Al \]
\[ Al \Leftrightarrow Bl \]
\[ Bl \Leftrightarrow B + l \]

\[ r_A = \frac{l_0(A - B / K)}{\left(\frac{1}{K_A k_{sr}} + \frac{1}{k_A} + \frac{1}{K k_B}\right) + \left(\frac{1}{K_A k_{sr}} + \frac{1 + K_{sr}}{K k_B}\right)} K_A A + \left(\frac{1}{K_A k_{sr}} + \frac{1 + K_{sr}}{K k_A}\right) K_B B \]

- Surface rxn control
- Adsorption control
- Desorption control

\[ r_A = \frac{l_0 k_A (A - B / K)}{1 + K_A A + K_B B} \]
\[ r_A = \frac{l_0 k_B K(A - B / K)}{1 + K_A A + K K_B A} \]
\[ r_A = \frac{l_0 k_A (A - B / K)}{1 + K_A B + K_B B} \]
Steady State Solution

\[ A = R \]
Derivation of Rate Laws: Useful Tools

The Steady State Approximation

\[ A \xrightarrow{k_1} B \xrightarrow{k_2} C \]

\[ \frac{A}{A_0} = e^{-k_1 t} \quad \frac{B}{B_0} = \frac{k_1}{k_2 - k_1} \left( e^{-k_1 t} - e^{k_2 t} \right) \]

For large \( k_1 \), after \( t = 0 \),

\[ \frac{B}{A_0} = \frac{k_1}{k_2} e^{-k_1 t} = \frac{k_1}{k_2} \frac{A}{A_0} = \lambda \frac{A}{A_0} \]

\[ \frac{dB}{dt} = k_1 A - k_2 B = k_1 A - k_1 A = 0! \]
Derivation of Rate Laws: Useful Tools

The Steady State Approximation

Relaxation Time

\[
\frac{A, B}{A_0}
\]

"exact" solution \( B_0 = 0 \), not \( A_0 / \lambda \)
The Steady State Approximation

Estimation of Relaxation Time

\[ \varepsilon = \frac{(B^*-B)}{B^*} \Rightarrow B = (1-e)B^* \]

\[ \frac{dB}{dt} = k_1A - k_2B \Rightarrow -B^* \frac{d\varepsilon}{dt} = k_1A - k_2B^* + k_2B^* \varepsilon \]

SSA: \[ k_1A = k_2B^* \]

\[ \frac{d\varepsilon}{dt} = -k_2t \Rightarrow \varepsilon = \varepsilon_0 e^{-k_2t} \]

\[ t_r = \frac{1}{k_2} \]
Summary of Relaxation Time Issues

The Steady State Approximation

\[ \frac{A, B}{A_0} \]

\[ B (\lambda = 10) \quad B (\lambda = 1) \quad B (\lambda = 100) \]

\[ t_r \sim \frac{1}{k_2} \]

\[ t_r = 0(10^{-5} \text{ to } 10^{-10} \text{ s}) \]
Closer Look at the Relaxation Time

The Steady State Approximation

- \( t < t_R \) Inner Solution
- \( t > t_R \) Outer Solution

Define

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

\[
\dot{y}_1 = \frac{A}{A_0}
\]

\[
\dot{y}_2 = \frac{\lambda B}{A_0}
\]

\[
\tau = k_1 t
\]

Then \( A \xrightarrow{1} B \xrightarrow{2} C \) becomes

\[
\frac{1}{\lambda} \frac{d\dot{y}_2}{d\tau} = \dot{y}_1 - \dot{y}_2
\]

\( \dot{y}_2(0) = 0 \)

The small coefficient usually small

\[
\dot{y}_2 = \frac{1}{(1 - \frac{1}{\lambda})} \left[ e^{-\tau} - e^{-\lambda \tau} \right]
\]
Closer Look at the Relaxation Time

The Steady State Approximation

Series solution of the form

\[ \hat{y}_2(\tau) = \sum_{m=0}^{\infty} \frac{(n)}{y_2(\tau)} / \lambda^n \]  \hspace{1cm} (I)

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

expansion parameter

\[ (n) \]

\[ y_2(\tau) = \text{perturbation function} \]

\[ \frac{1}{\lambda} \hat{y}_2 = y_1 - y_2 \]

Approach: substitute (I) into ODE, compare like powers of 1/\lambda
Closer Look at the Relaxation Time

*The Steady State Approximation*

\[
\frac{1}{\lambda} \frac{d}{d\tau} \left[ \frac{(0)}{y_2} + \frac{(1)}{\lambda} + \frac{(2)}{\lambda^2} + \frac{(3)}{\lambda^3} + \ldots \right] = \frac{\hat{y}_1}{\lambda} - \frac{(0)}{1} - \frac{(1)}{\lambda} - \frac{(2)}{\lambda^2} - \ldots
\]

From ODE
\[
\frac{1}{\lambda} \frac{d}{dt} y_2 = \frac{(1)}{\lambda} y_2 \Rightarrow \frac{d}{dt} \frac{(0)}{y_2} = -\frac{(1)}{y_2}
\]

\[
\hat{y}_1 = y_2 \rightarrow \text{SSA}
\]
Closer Look at the Relaxation Time

The Steady State Approximation

Coordinate Transform for Short Time (+ < \( t_R \)) region

Modify coordinates so that all terms same order of magnitude even for large \( \lambda \).

Stretch time

\[
\begin{align*}
  w &= \lambda \tau \quad \text{or} \quad \tau = w / \lambda \\
  w\sigma(1) &\quad \text{in region of interest}
\end{align*}
\]
Closer Look at the Relaxation Time

The Steady State Approximation

Then

\[ \dot{y}_1 = \exp(-\tau) = \exp(-w / \lambda) \]

\[ \frac{1}{\lambda} \frac{d \dot{y}_2}{dt} = \dot{y}_1 - \dot{y}_2 \Rightarrow \frac{dY_2}{dw} = \dot{y}_1 - Y_2 = \exp(-w / \lambda) - Y_2 \]

\[ Y_2 = Y_2(w) = \sum_{n=0}^{\infty} \frac{(n)}{\lambda^n} \]

We have “removed” leading $1/\lambda$ term

\[ \frac{d}{dw} \left[ \right] = \exp(-w / \lambda) - \]

Taylor series for $\exp(-w / \lambda) = 1 - w / \lambda + (w / \lambda)^2 / 2 - (w^3 / \lambda^3) / 3! + \cdots$

Now equate like powers of $1/\lambda$
Closer Look at the Relaxation Time

*The Steady State Approximation*

\[(0)\]
\[Y'_2 = 1 - Y_2^{(0)}\]

\[(1)\]
\[Y'_2 = -w - Y_2^{(1)}\]

\[(m)\]
\[Y'_2 = (-w)^n / n! - Y_2^{(n)}\]

Solve ODEs with \[Y(0) = 0\]

\[(0)\]
\[Y_2^{(0)} = 1 - \exp(-w)\]

\[(1)\]
\[Y_2^{(1)} = -(w - 1) - \exp(-w)\]

\[(2)\]
\[Y_2^{(2)} = \frac{w^2 - 2w + 2}{2} - \exp(-w)\]

\[Y_2(w) = 1 - \exp(-w) + \frac{1}{\lambda} \left[ -(w - 1) - \exp(-w) \right] + \frac{1}{2\lambda^2} \left[ w^2 - 2w + 2 - 2\exp(-w) \right] + O\left(\frac{1}{\lambda^3}\right)\]
Closer Look at the Relaxation Time

The Steady State Approximation

But $Y_2(w)$ and $-y_2(\tau)$ Different forms of same solution (exact)

$$y_2(\tau \to 0) = Y_2(w \to \infty)$$
required

$$y_2(\tau) = \left(1 - \tau + \frac{\tau^2}{2} - \frac{\tau^3}{3} + \ldots\right) \left(1 + \frac{1}{\lambda} + \frac{1}{\lambda^2} + \ldots\right)$$

$$\lim_{t \to 0} = 1 + \frac{1}{\lambda}(1-w) + \frac{1}{\lambda^2} \left[1 - w + \frac{w^2}{2}\right] + \frac{1}{\lambda^3} \left[\ldots\right] + \ldots$$
**Closer Look at the Relaxation Time**

*The Steady State Approximation*

\[
\begin{align*}
\tau &= k_1 T \\
\tau_R &= k_1 \cdot t_R = k_1 / k_2 = 1 / \lambda
\end{align*}
\]