PQI-3401 – Engenharia de Reações Químicas II
São Paulo, SP, janeiro/2021

Kinetics of Heterogeneous Catalytic Reactions

Reinaldo Giudici

UNIVERSIDADE DE SÃO PAULO
ESCOLA POLITÉCNICA
DEPARTAMENTO DE ENGENHARIA QUÍMICA

KINETICS OF HETEROGENEOUS CATALYTIC REACTIONS

Catalyst

Reaction Mechanism is a **set of elementary reaction steps** that **explains how the reactants are converted into the products**.

Besides the reactants and products, the reaction mechanism includes formation and consumption of **active intermediates**

Typical characteristics of an active intermediate:

- **Highly reactive**
- **Very short lifetime (e.g. ~10^{-9} s)**
- **Difficult to measure, very low concentrations**

Examples:

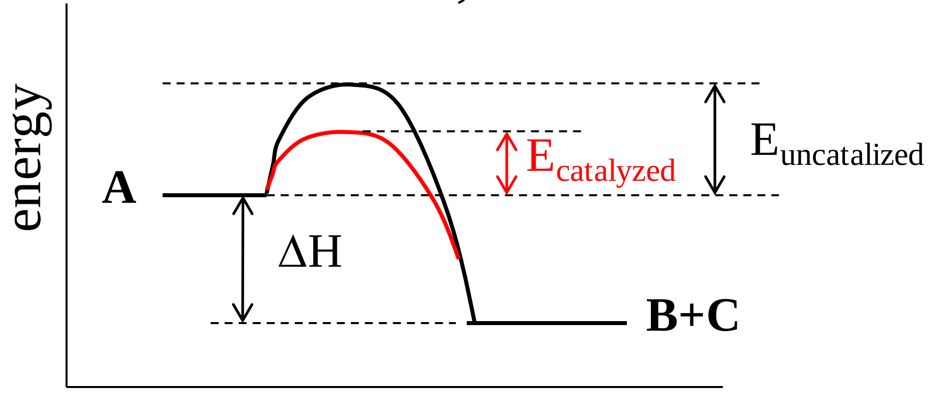
- activated complex
- transition state
- free radicals
- enzyme-substrate complex
- ions

...

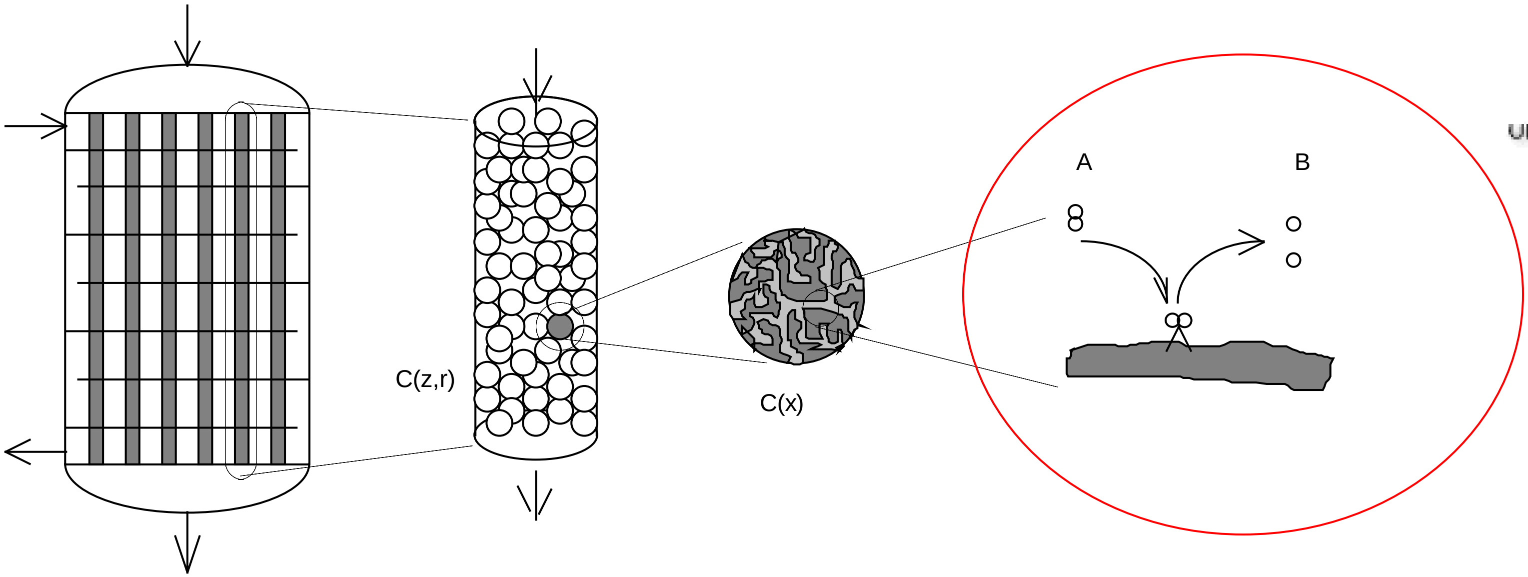
Catalysts

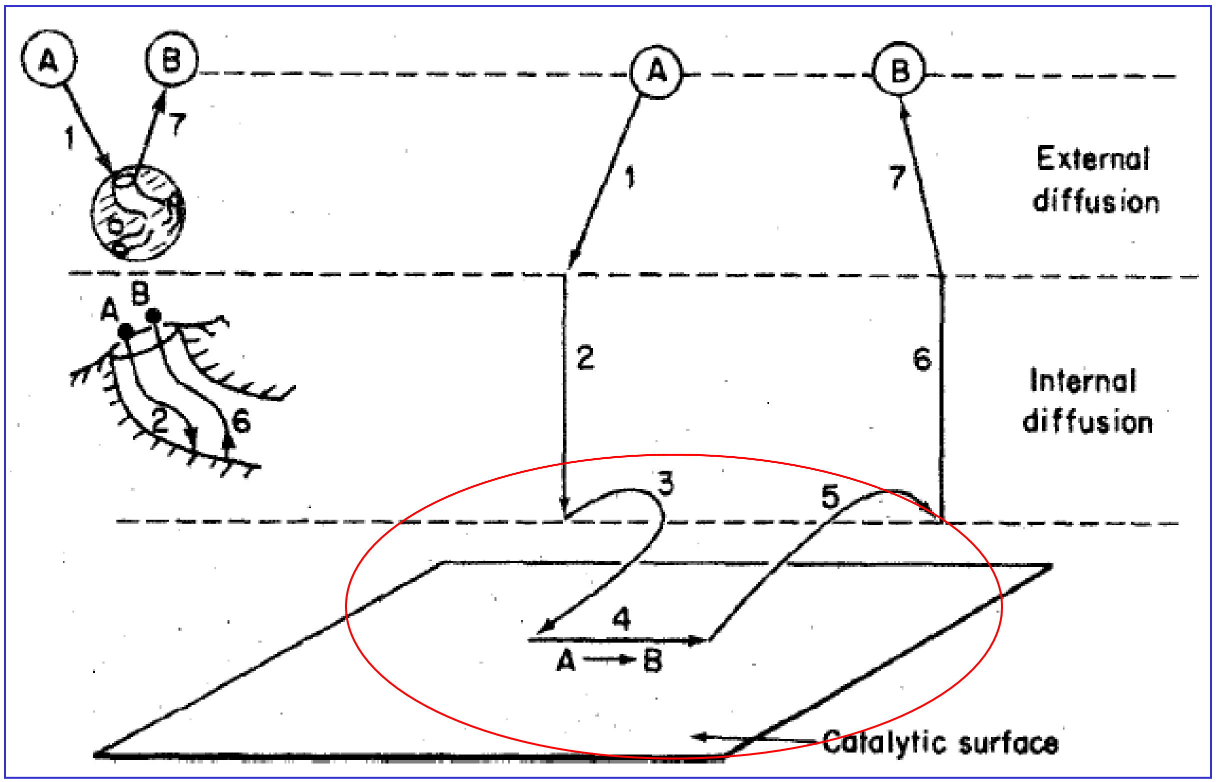
- Change (increase) the reaction rate
  - Reduce activation energy
  - Promote a new mechanism for the reaction
- Do not affect the reaction equilibrium
- Not consumed
- Can be selective for a given product
- Can be homogeneous or heterogeneous

A ⇆ B + C, exothermic



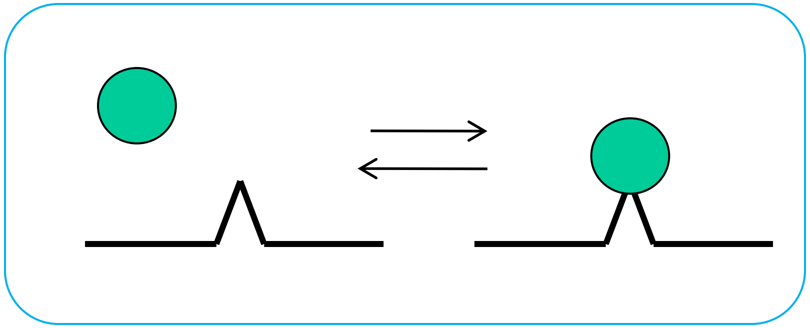
Catalyst
(different intermediate)
(different mechanism)
$E_{catalyzed} < E_{uncatalyzed}$


A
B
C(z,r)
C(x)


A
B
1
7
External diffusion
A
B
2
6
Internal diffusion
3
5
4
A → B
Catalytic surface

ADSORPTION EQUILIBRIUM
LANGMUIR ISOTHERM

Adsorption Isotherms



$$A_{(g)} + S \underset{des}{\overset{ads}{\rightleftarrows}} AS$$

rate of adsorption : $r_{ads} = k_A p_A C_v$

rate of desorption : $r_{des} = k_{-A} C_{AS}$

A = molecule A in gaseous phase

S = vacant site

AS = molecule A adsorbed on the site S

p_A = partial pressure of A in the gaseous phase (atm)

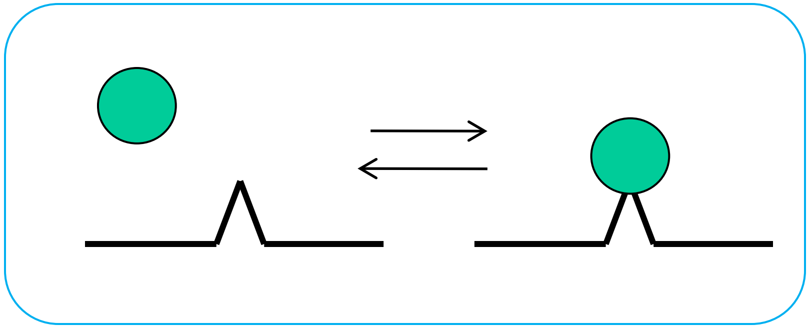
C_v = surface concentration of sites occupied by species A (mol A/g cat)

C_{AS} = surface concentration of vacant (mol of vacant sites/g cat)

C_t = total surface concentration of sites (mol of sites/g cat)

SITE BALANCE : $C_t = C_v + C_{AS}$

Adsorption Isotherms



$$A_{(g)} + S \underset{des}{\overset{ads}{\rightleftarrows}} AS$$

rate of adsorption : $r_{ads} = k_A p_A C_v$

rate of desorption : $r_{des} = k_{-A} C_{AS}$

at the equilibrium $r_{ads} = r_{des} \Rightarrow k_A p_{A,eq} C_{v,eq} = k_{-A} C_{AS,eq}$

$$\frac{k_A}{k_{-A}} = \frac{C_{AS,eq}}{p_{A,eq} C_{v,eq}} = K_A = \left(\begin{array}{c} \text{adsorption} \\ \text{equilibrium} \\ \text{constant for A} \end{array} \right)$$

$K_A p_{A,eq} C_{v,eq} = C_{AS,eq}$ and $C_t = C_{v,eq} + C_{AS,eq}$

$$K_A p_{A,eq} \left(C_t - C_{AS,eq} \right) = C_{AS,eq} \Rightarrow C_{AS,eq} = C_t \frac{K_A p_{A,eq}}{1 + K_A p_{A,eq}}$$

$$\boxed{\Theta_A = \frac{C_{AS,eq}}{C_t} = \frac{K_A p_{A,eq}}{1 + K_A p_{A,eq}}}$$ (LANGMUIR ADSORPTION ISOTHERM)

Adsorption Isotherms

UNIVERSIDADE DE SÃO PAULO

competitive adsorption of A and B

$$A + S \underset{des}{\overset{ads}{\rightleftarrows}} AS$$

$$B + S \underset{des}{\overset{ads}{\rightleftarrows}} BS$$

$$r_A = k_A p_{A,eq} C_{v,eq} - k_{-A} C_{AS,eq} = 0$$

$$r_B = k_B p_{B,eq} C_{v,eq} - k_{-B} C_{BS,eq} = 0$$

site balance :

$$C_t = C_{v,eq} + C_{AS,eq} + C_{BS,eq}$$

Show that :

$$\Theta_A = \frac{C_{AS,eq}}{C_t} = \frac{K_A p_{A,eq}}{1 + K_A p_{A,eq} + K_B p_{B,eq}}$$

$$\Theta_B = \frac{C_{BS,eq}}{C_t} = \frac{K_B p_{B,eq}}{1 + K_A p_{A,eq} + K_B p_{B,eq}}$$

adsorption of A_2 with dissociation

$$A_2 + 2S \underset{des}{\overset{ads}{\rightleftarrows}} 2AS$$

$$r_{A2} = k_A p_{A2,eq} C_{v,eq}^2 - k_{-A} C_{AS,eq}^2 = 0$$

site balance :

$$C_t = C_{v,eq} + C_{AS,eq}$$

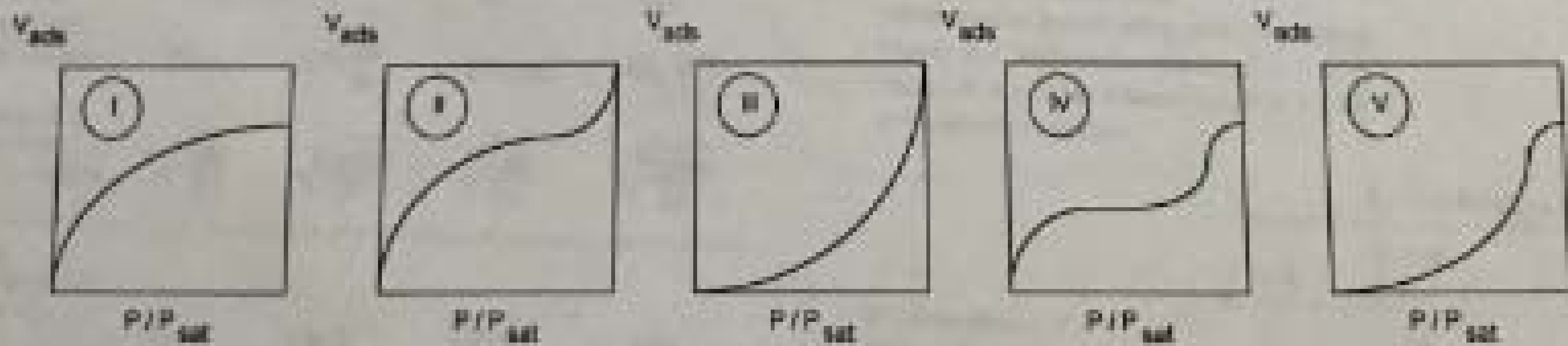
Show that :

$$\Theta_A = \frac{C_{AS,eq}}{C_t} = \frac{\sqrt{K_A p_{A2,eq}}}{1 + \sqrt{K_A p_{A2,eq}}}$$

Adsorção

	adsorção física	adsorção química
forças de ligação/ interação	intermoleculares (forças de Van der Waals, dipolo permanente, dipolo induzido)	intramoleculares (ligações químicas covalentes)
semelhança, analogia	análogo à condensação/ liquefação de gases	análogo à reação química
adsorvente	todos os sólidos	alguns sólidos quimicamente reativos
adsorvato	todos os gases abaixo da temperatura crítica	gases/vapores quimicamente reativos
cobertura	pode ocorrer multicamada	monocamada (no máx.)
reversibilidade	reversível	pode ser reversível ou irreversível
velocidade de adsorção	rápida (não requer energia de ativação), pode ser limitada por difusão	pode ser rápida ou lenta, dependendo da temperatura (e energia de ativação)
entalpia de adsorção	pequena, similar à entalpia de liquefação (2 a 6 kcal/mol), sempre exotérmica	maiores, similar à entalpia de reação (20 a 150 kcal/mol), quase sempre exotérmica
faixa de T p/ ocorrência	T próximas à T_{eb} na pressão de operação	T muito acima de T_{eb}
dependência da temperatura	diminui com o aumento da temperatura	pode ser complexa
especificidade	não específica, ocorre em qualquer ponto da superfície	específica, pode só ocorrer em alguns pontos da superfície
aplicação	determinação da área específica e de distribuição de tamanho de poros	determinação de área da superfície cataliticamente ativa e elucidação da cinética da reação

Isotermas de BET



trecho inicial:

I, II e IV	formação da monocamada
III e V	sistemas onde interação gás-camada > gás-superficie ($\Delta H_{ads} < \Delta H_{liq}$)

trecho final:

I	monocamada
II e III	multicamada
IV e V	"condensação capilar" (poros pequenos, de volume limitado, impedem o aumento do n° de camadas).

LHHW kinetic model
for heterogeneous catalytic reactions

LHHW = Langmuir-Hinshelwood-Hougen-Watson

LHHW mechanism / kinetic model

Hypotheses:

(1) in the surface reaction step, **all reactants** are adsorbed and **all products** formed are **adsorbed** on the catalytic sites

(2) **PSSH** applies for the reaction **intermediates**

(3) **A rate-limiting step** is assumed (i.e., one of the reaction steps is rate-limiting)

LHHW mechanism/kinetic model

global reaction ... $A \rightleftarrows C + D$ .... $(-r_A) = r_C = r_D = f(p_A, p_C, p_D)$

Mechanism (elementary steps)

(1) $A + S \underset{}{\overset{1}{\rightleftarrows}} AS$ $\quad R_1 = k_1\left(p_A C_v - \dfrac{C_{AS}}{K_1}\right)$

(2) $AS + S \overset{2}{\rightleftarrows} CS + DS$ $\quad R_2 = k_2\left(C_{AS} C_v - \dfrac{C_{CS} C_{DS}}{K_2}\right)$

(3) $CS \overset{3}{\rightleftarrows} C + S$ $\quad R_3 = k_3\left(C_{CS} - \dfrac{p_C C_v}{K_3}\right)$

(4) $DS \overset{4}{\rightleftarrows} D + S$ $\quad R_4 = k_4\left(C_{DS} - \dfrac{p_D C_v}{K_4}\right)$

LHHW mechanism/kinetic model

global reaction ... $A \rightleftarrows C + D$ .... $(-r_A) = r_C = r_D = f(p_A, p_C, p_D)$

Mechanism (elementary steps)

(1) $A + S \underset{}{\overset{1}{\rightleftarrows}} AS$ $\quad R_1 = k_1\left(p_A C_v - \dfrac{C_{AS}}{K_1}\right) = k_A\left(p_A C_v - \dfrac{C_{AS}}{K_A}\right)$

(2) $AS + S \underset{}{\overset{2}{\rightleftarrows}} CS + DS$ $\quad R_2 = k_2\left(C_{AS} C_v - \dfrac{C_{CS} C_{DS}}{K_2}\right) = k_{sr}\left(C_{AS} C_v - \dfrac{C_{CS} C_{DS}}{K_{sr}}\right)$

(3) $CS \underset{}{\overset{3}{\rightleftarrows}} C + S$ $\quad R_3 = k_3\left(C_{CS} - \dfrac{p_C C_v}{K_3}\right) = k_C\left(\dfrac{C_{CS}}{K_C} - p_C C_v\right)$

(4) $DS \underset{}{\overset{4}{\rightleftarrows}} D + S$ $\quad R_4 = k_4\left(C_{DS} - \dfrac{p_D C_v}{K_4}\right) = k_D\left(\dfrac{C_{DS}}{K_D} - p_D C_v\right)$

$$k_1 = k_{ads,A} = k_A$$

$$K_1 = K_{ads,A} = K_A$$

$$k_2 = k_{sr}$$

$$K_2 = K_{sr}$$

$$K_3 = \frac{k_3}{k_{-3}} = \frac{k_{des,C}}{k_{ads,C}} = \frac{1}{K_C} \qquad k_3 = k_{des,C} = \frac{k_{ads,C}}{K_C} = \frac{k_C}{K_C}$$

$$K_4 = \frac{k_4}{k_{-4}} = \frac{k_{des,D}}{k_{ads,D}} = \frac{1}{K_D} \qquad k_4 = k_{des,D} = \frac{k_{ads,D}}{K_D} = \frac{k_D}{K_D}$$

LHHW mechanism/kinetic model

global reaction ... $A \rightleftarrows C + D$ .... $(-r_A) = r_C = r_D = f(p_A, p_C, p_D)$

Mechanism (elementary steps)

(1) $A + S \overset{1}{\rightleftarrows} AS$ $\quad R_1 = k_1\left(p_A C_v - \dfrac{C_{AS}}{K_1}\right) = k_A\left(p_A C_v - \dfrac{C_{AS}}{K_A}\right)$

(2) $AS + S \overset{2}{\rightleftarrows} CS + DS$ $\quad R_2 = k_2\left(C_{AS} C_v - \dfrac{C_{CS} C_{DS}}{K_2}\right) = k_{sr}\left(C_{AS} C_v - \dfrac{C_{CS} C_{DS}}{K_{sr}}\right)$

(3) $CS \overset{3}{\rightleftarrows} C + S$ $\quad R_3 = k_3\left(C_{CS} - \dfrac{p_C C_v}{K_3}\right) = k_C\left(\dfrac{C_{CS}}{K_C} - p_C C_v\right)$

(4) $DS \overset{4}{\rightleftarrows} D + S$ $\quad R_4 = k_4\left(C_{DS} - \dfrac{p_D C_v}{K_4}\right) = k_D\left(\dfrac{C_{DS}}{K_D} - p_D C_v\right)$

$r_A = -R_1$

$r_C = +R_3$

$r_D = +R_4$

$r_{AS} = +R_1 - R_2 = 0$ (PSSH)

$r_{CS} = +R_2 - R_3 = 0$ (PSSH)

$r_{DS} = +R_2 - R_4 = 0$ (PSSH)

$\cancel{r_S = -R_1 - R_2 + R_3 + R_4 = 0 \text{ (PSSH)}}$

$C_{AS} = ?$

$C_{CS} = ?$

$C_{DS} = ?$

$C_v = ?$

LHHW mechanism/kinetic model

global reaction ... $A \underset{}{\overset{}{\rightleftarrows}} C + D$ .... $(-r_A) = r_C = r_D = f(p_A, p_C, p_D)$

Mechanism (elementary steps)

(1) $A + S \overset{1}{\rightleftarrows} AS$ $\qquad R_1 = k_1\left(p_A C_v - \dfrac{C_{AS}}{K_1}\right) = k_A\left(p_A C_v - \dfrac{C_{AS}}{K_A}\right)$

(2) $AS + S \overset{2}{\rightleftarrows} CS + DS$ $\qquad R_2 = k_2\left(C_{AS} C_v - \dfrac{C_{CS} C_{DS}}{K_2}\right) = k_{sr}\left(C_{AS} C_v - \dfrac{C_{CS} C_{DS}}{K_{sr}}\right)$

(3) $CS \overset{3}{\rightleftarrows} C + S$ $\qquad R_3 = k_3\left(C_{CS} - \dfrac{p_C C_v}{K_3}\right) = k_C\left(\dfrac{C_{CS}}{K_C} - p_C C_v\right)$

(4) $DS \overset{4}{\rightleftarrows} D + S$ $\qquad R_4 = k_4\left(C_{DS} - \dfrac{p_D C_v}{K_4}\right) = k_D\left(\dfrac{C_{DS}}{K_D} - p_D C_v\right)$

$r_A = -R_1$

$r_C = +R_3$

$r_D = +R_4$

$$\left.\begin{aligned} r_{AS} &= +R_1 - R_2 = 0 \quad \text{(PSSH)} \\ r_{CS} &= +R_2 - R_3 = 0 \quad \text{(PSSH)} \\ r_{DS} &= +R_2 - R_4 = 0 \quad \text{(PSSH)} \end{aligned}\right\} \quad R_1 = R_2 = R_3 = R_4$$

$\cancel{r_S = -R_1 - R_2 + R_3 + R_4 = 0 \quad \text{(PSSH)}}$

site balance

$C_t = C_v + C_{AS} + C_{CS} + C_{DS}$

global reaction ... $A \rightleftarrows C + D$

$$A + S \overset{1}{\rightleftarrows} AS \qquad R_1 = k_A\left(p_A C_v - \frac{C_{AS}}{K_A}\right) \rightarrow\rightarrow\rightarrow\rightarrow\rightarrow C_{AS} = K_A p_A C_v$$

$$\boxed{AS + S \overset{2}{\rightleftarrows} CS + DS,} \quad R_2 = k_{sr}\left(C_{AS} C_v - \frac{C_{CS} C_{DS}}{K_{sr}}\right) \rightarrow \boxed{\begin{matrix}\text{rate}\\ \text{limiting}\\ \text{step}\end{matrix} \rightarrow R_{global} = R_2}$$

$$CS \overset{3}{\rightleftarrows} C + S \qquad R_3 = k_C\left(\frac{C_{CS}}{K_C} - p_C C_v\right) \rightarrow\rightarrow\rightarrow\rightarrow\rightarrow C_{CS} = K_C p_C C_v$$

$$DS \overset{4}{\rightleftarrows} D + S \qquad R_4 = k_D\left(\frac{C_{DS}}{K_D} - p_D C_v\right) \rightarrow\rightarrow\rightarrow\rightarrow\rightarrow C_{DS} = K_D p_D C_v$$

$$R_{global} = R_2 = k_{sr}\left(K_A p_A C_v\, C_v - \frac{K_C p_C C_v K_D p_D C_v}{K_{sr}}\right) = k_{sr} K_A C_v^2 \left(p_A - \frac{K_C K_D p_C p_D}{K_A K_{sr}}\right) =$$

$$R_{global} = k_{sr} K_A C_v^2 \left(p_A - \frac{p_C p_D}{K}\right)$$

$$\frac{K_C K_D}{K_A K_{sr}} = \frac{\left(\frac{C_{CS}}{p_C C_v}\right)_{eq}\left(\frac{C_{DS}}{p_D C_v}\right)_{eq}}{\left(\frac{C_{AS}}{p_A C_v}\right)_{eq}\left(\frac{C_{CS} C_{DS}}{C_{AS} C_v}\right)_{eq}} = \left(\frac{p_A}{p_C p_D}\right)_{eq} = \frac{1}{K}$$

$$K = \left(\begin{matrix}\text{equilibrium}\\ \text{constant}\\ \text{of the global}\\ \text{reaction}\end{matrix}\right)$$

global reaction ... $A \rightleftarrows C + D$

$$A + S \underset{}{\overset{1}{\rightleftarrows}} AS \qquad R_1 = k_A\left(p_A C_v - \frac{C_{AS}}{K_A}\right) \rightarrow\rightarrow\rightarrow\rightarrow\rightarrow C_{AS} = K_A p_A C_v$$

$$\boxed{AS + S \overset{2}{\rightleftarrows} CS + DS,} \quad R_2 = k_{sr}\left(C_{AS} C_v - \frac{C_{CS} C_{DS}}{K_{sr}}\right) \rightarrow \boxed{\text{rate limiting step} \rightarrow R_{global} = R_2}$$

$$CS \overset{3}{\rightleftarrows} C + S \qquad R_3 = k_C\left(\frac{C_{CS}}{K_C} - p_C C_v\right) \rightarrow\rightarrow\rightarrow\rightarrow\rightarrow C_{CS} = K_C p_C C_v$$

$$DS \overset{4}{\rightleftarrows} D + S \qquad R_4 = k_D\left(\frac{C_{DS}}{K_D} - p_D C_v\right) \rightarrow\rightarrow\rightarrow\rightarrow\rightarrow C_{DS} = K_D p_D C_v$$

$$R_{global} = k_{sr} K_A C_v^2 \left(p_A - \frac{p_C p_D}{K}\right)$$

$$C_t = C_v + C_{AS} + C_{CS} + C_{DS} = C_v + K_A p_A C_v + K_C p_C C_v + K_D p_D C_v$$

$$C_t = C_v (1 + K_A p_A + K_C p_C + K_D p_D)$$

$$\boxed{R_{global} = R_2 = \frac{k_{sr} K_A C_t^2 \left(p_A - \frac{p_C p_D}{K}\right)}{(1 + K_A p_A + K_C p_C + K_D p_D)^2}}$$

global reaction ... $A \rightleftarrows C + D$

$\boxed{A + S \overset{1}{\rightleftarrows} AS}$ $\quad R_1 = k_A\left(p_A C_v - \dfrac{C_{AS}}{K_A}\right) \rightarrow\rightarrow\rightarrow\rightarrow$ $\boxed{\text{rate limiting step} \rightarrow R_{global} = R_1}$

$AS + S \overset{2}{\rightleftarrows} CS + DS, \quad R_2 = k_{sr}\left(C_{AS} C_v - \dfrac{C_{CS} C_{DS}}{K_{sr}}\right) \rightarrow C_{AS} = \dfrac{C_{CS} C_{DS}}{C_v K_{sr}} = \dfrac{K_C K_D}{K_{sr}} p_C p_D C_v$

$CS \overset{3}{\rightleftarrows} C + S \quad R_3 = k_C\left(\dfrac{C_{CS}}{K_C} - p_C C_v\right) \rightarrow\rightarrow\rightarrow C_{CS} = K_C p_C C_v$

$DS \overset{4}{\rightleftarrows} D + S \quad R_4 = k_D\left(\dfrac{C_{DS}}{K_D} - p_D C_v\right) \rightarrow\rightarrow\rightarrow C_{DS} = K_D p_D C_v$

$$R_{global} = R_1 = k_A\left(p_A C_v - \frac{K_C K_D}{K_A K_{sr}} p_C p_D C_v\right) = k_A C_v\left(p_A - \frac{p_C p_D}{K}\right)$$

$$C_t = C_v + C_{AS} + C_{CS} + C_{DS} = C_v\left(1 + \frac{K_C K_D}{K_{sr}} p_C p_D + K_C p_C + K_D p_D\right)$$

$$\boxed{R_{global} = R_1 = \frac{k_A C_t\left(p_A - \dfrac{p_C p_D}{K}\right)}{1 + \dfrac{K_A}{K} p_C p_D + K_C p_C + K_D p_D}}$$

global reaction ... $A \rightleftarrows C + D$

$$A + S \underset{}{\overset{1}{\rightleftarrows}} AS \qquad R_1 = k_A\left(p_A C_v - \frac{C_{AS}}{K_A}\right) \rightarrow\rightarrow\rightarrow C_{AS} = K_A p_A C_v$$

$$AS + S \overset{2}{\rightleftarrows} CS + DS, \quad R_2 = k_{sr}\left(C_{AS} C_v - \frac{C_{CS} C_{DS}}{K_{sr}}\right) \rightarrow\rightarrow C_{CS} = \frac{K_{sr} C_{AS} C_v}{C_{DS}} = \frac{K_{sr} K_A p_A}{K_D p_D} C_v$$

$$\boxed{CS \overset{3}{\rightleftarrows} C + S} \qquad R_3 = k_C\left(\frac{C_{CS}}{K_C} - p_C C_v\right) \rightarrow\rightarrow\rightarrow \boxed{\begin{array}{c}\text{rate}\\ \text{limiting}\\ \text{step}\end{array} \rightarrow R_{global} = R_3}$$

$$DS \overset{4}{\rightleftarrows} D + S \qquad R_4 = k_D\left(\frac{C_{DS}}{K_D} - p_D C_v\right) \rightarrow\rightarrow\rightarrow\rightarrow C_{DS} = K_D p_D C_v$$

$$R_{global} = R_3 = k_C\left(\frac{K_{sr} K_A}{K_C K_D} \frac{p_A}{p_D} C_v - p_C C_v\right) = k_C C_v \frac{K}{p_D}\left(p_A - \frac{p_C p_D}{K}\right)$$

$$C_t = C_v + C_{AS} + C_{CS} + C_{DS} = C_v\left(1 + K_A p_A + \frac{K_{sr} K_A}{K_D} \frac{p_A}{p_D} + K_D p_D\right)$$

$$\boxed{R_{global} = R_3 = \frac{k_C C_t K\left(p_A - \dfrac{p_C p_D}{K}\right)}{p_D\left(1 + K_A p_A + K_C K \dfrac{p_A}{p_D} + K_D p_D\right)}}$$

global reaction ... $A \rightleftarrows C + D$

$$A + S \underset{}{\overset{1}{\rightleftarrows}} AS \qquad R_1 = k_A\left(p_A C_v - \frac{C_{AS}}{K_A}\right) \rightarrow\rightarrow\rightarrow C_{AS} = K_A p_A C_v$$

$$AS + S \underset{}{\overset{2}{\rightleftarrows}} CS + DS, \quad R_2 = k_{sr}\left(C_{AS} C_v - \frac{C_{CS} C_{DS}}{K_{sr}}\right) \rightarrow\rightarrow C_{DS} = \frac{K_{sr} C_{AS} C_v}{C_{CS}} = \frac{K_{sr} K_A p_A}{K_C p_C} C_v$$

$$CS \underset{}{\overset{3}{\rightleftarrows}} C + S \qquad R_3 = k_C\left(\frac{C_{CS}}{K_C} - p_C C_v\right) \rightarrow\rightarrow\rightarrow\rightarrow C_{CS} = K_C p_C C_v$$

$$\boxed{DS \underset{}{\overset{4}{\rightleftarrows}} D + S} \qquad R_4 = k_D\left(\frac{C_{DS}}{K_D} - p_D C_v\right) \rightarrow\rightarrow\rightarrow \boxed{\text{rate limiting step} \rightarrow R_{global} = R_4}$$

$$R_{global} = R_4 = k_D\left(\frac{K_{sr} K_A}{K_C K_D} \frac{p_A}{p_C} C_v - p_D C_v\right) = k_D C_v \frac{K}{p_C}\left(p_A - \frac{p_C p_D}{K}\right)$$

$$C_t = C_v + C_{AS} + C_{CS} + C_{DS} = C_v\left(1 + K_A p_A + K_C p_C + \frac{K_{sr} K_A}{K_C} \frac{p_A}{p_C}\right)$$

$$\boxed{R_{global} = R_4 = \frac{k_D C_t K\left(p_A - \dfrac{p_C p_D}{K}\right)}{p_C\left(1 + K_A p_A + K_C p_C + K_D K \dfrac{p_A}{p_C} + \right)}}$$

Results for LHHW (depending on the rate-limiting step Chosen)

global reaction

$$A \rightleftharpoons C + D$$

mechanism LHHW

$$A + S \underset{}{\overset{1}{\rightleftharpoons}} AS$$

$$AS + S \underset{}{\overset{2}{\rightleftharpoons}} CS + DS$$

$$CS \underset{}{\overset{3}{\rightleftharpoons}} C + S$$

$$DS \underset{}{\overset{4}{\rightleftharpoons}} D + S$$

$$R_{global} = R_1 = \frac{k_A C_t \left(p_A - \dfrac{p_C p_D}{K} \right)}{1 + \dfrac{K_A}{K} p_C p_D + K_C p_C + K_D p_D}$$

$$R_{global} = R_2 = \frac{k_{sr} K_A C_t^2 \left(p_A - \dfrac{p_C p_D}{K} \right)}{(1 + K_A p_A + K_C p_C + K_D p_D)^2}$$

$$R_{global} = R_3 = \frac{k_C C_t K \left(p_A - \dfrac{p_C p_D}{K} \right)}{p_D \left(1 + K_A p_A + K_C K \dfrac{p_A}{p_D} + K_D p_D \right)}$$

$$R_{global} = R_4 = \frac{k_D C_t K \left(p_A - \dfrac{p_C p_D}{K} \right)}{p_C \left(1 + K_A p_A + K_C p_C + K_D K \dfrac{p_A}{p_C} + \right)}$$

LHHW mechanism / kinetic model

Other reactions

$$A \underset{}{\overset{\cdot}{\rightleftarrows}} C$$

$$A \underset{}{\overset{\cdot}{\rightleftarrows}} C + D$$

$$A + B \underset{}{\overset{\cdot}{\rightleftarrows}} C$$

$$A + B \underset{}{\overset{\cdot}{\rightleftarrows}} C + D$$

etc

LHHW mechanism / kinetic model

$$\text{overall rate} = \frac{(\text{kinetic factor})(\text{driving\_force group})}{(\text{adsorption group})}$$

LHHW kinetic model

Driving-Force Groups

Reaction	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
Adsorption of A controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A - \frac{p_R}{K p_B}$	$p_A - \frac{p_R p_S}{K p_B}$
Adsorption of B controlling	0	0	$p_B - \frac{p_R}{K p_A}$	$p_B - \frac{p_R p_S}{K p_A}$
Desorption of R controlling	$p_A - \frac{p_R}{K}$	$\frac{p_A}{p_S} - \frac{p_R}{K}$	$p_A p_B - \frac{p_R}{K}$	$\frac{p_A p_B}{p_S} - \frac{p_R}{K}$
Surface reaction controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$
Impact of A controlling (A not adsorbed)	0	0	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$
Homogeneous reaction controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$

Froment & Bischoff, Chemical Reactor Analysis and Design, 2nd ed., Wiley, 1990

Replacements in the General Adsorption Groups
$(1 + K_A p_A + K_B p_B + K_R p_R + K_S p_S + K_I p_I)^n$

Reaction	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
Where adsorption of A is rate controlling, replace $K_A p_A$ by	$\frac{K_A p_R}{K}$	$\frac{K_A p_R p_S}{K}$	$\frac{K_A p_R}{K p_B}$	$\frac{K_A p_R p_S}{K p_B}$
Where adsorption of B is rate controlling, replace $K_B p_B$ by	0	0	$\frac{K_B p_R}{K p_A}$	$\frac{K_B p_R p_S}{K p_A}$
Where desorption of R is rate controlling, replace $K_R p_R$ by	$K K_R p_A$	$K K_R \frac{p_A}{p_S}$	$K K_R p_S p_B$	$K K_R \frac{p_A p_B}{p_S}$
Where adsorption of A is rate controlling with dissociation of A, replace $K_A p_A$ by	$\sqrt{\frac{K_A p_R}{K}}$	$\sqrt{\frac{K_A p_R p_S}{K}}$	$\sqrt{\frac{K_A p_R}{K p_B}}$	$\sqrt{\frac{K_A p_R p_S}{K p_B}}$
Where equilibrium adsorption of A takes place with dissociation of A, replace $K_A p_A$ by and similarly for other components adsorbed with dissociation	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$
Where A is not adsorbed, replace $K_A p_A$ by and similarly for other components that are not adsorbed	0	0	0	0

Froment & Bischoff, Chemical Reactor Analysis and Design, 2nd ed., Wiley, 1990

LHHW kinetic model

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			
	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
No dissociation of A	1	2	2	2
Dissociation of A	2	2	3	3
Dissociation of A (B not adsorbed)	2	2	2	2
No dissociation of A (B not adsorbed)	1	2	1	2

From Yang and Hougen [33].

Froment & Bischoff, Chemical Reactor Analysis and Design, 2nd ed., Wiley, 1990

LHHW kinetic model

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

	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
Without dissociation	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A K_B$	$k_{sr} K_A K_B$
With dissociation of A	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A K_B$	$k_{sr} K_A K_B$
B not adsorbed	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$
B not adsorbed, A dissociated	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$

Froment & Bischoff, Chemical Reactor Analysis and Design, 2nd ed., Wiley, 1990

LHHW mechanism / kinetic model

$$A \rightleftarrows C$$

$$A + B \rightleftarrows C$$

$$A + B \rightleftarrows C + D$$

ASSIGNMENT:
- choose one of these reactions;
- write the steps of the LHHW mechanism;
- choose one of the steps as rate-limiting;
- derive the corresponding rate equation;
- obtain the rate equation from the tables (kinetic factor, driving-force group, adsorption group) and compare with the per-you-derived rate equation

Eley-Rideal mechanism

Similar to LHHW, except that in the surface reaction step, not all reactants (or not all the products) are adsorbed (i.e., hypothesis (1) of LHHW is not adopted).

$$\text{global reaction} \ldots \quad A \rightleftarrows C + D$$

$$\text{Eley - Rideal Mechanism (elementary steps)}$$

$$(1) \quad A + S \underset{}{\overset{1}{\rightleftarrows}} AS \qquad R_1 = k_1\left(p_A C_v - \frac{C_{AS}}{K_1}\right)$$

$$(2) \quad AS \overset{2}{\rightleftarrows} CS + D \qquad R_2 = k_2\left(C_{AS} - \frac{C_{CS}\, p_D}{K_2}\right)$$

$$(3) \quad CS \overset{3}{\rightleftarrows} C + S \qquad R_3 = k_3\left(C_{CS} - \frac{p_C C_v}{K_3}\right)$$

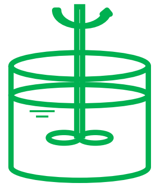
Design Equations for Ideal Reactors

(mole balance for component A – limiting reagent)

one reaction & isothermal reactor

- Batch reactor

$$\frac{dN_A}{dt} = r_A V$$

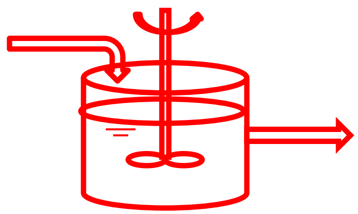


$$\boxed{N_{Ao}\frac{dX_A}{dt} = (-r_A)V}$$

$$\boxed{t = N_{Ao}\int_{X_{A0}}^{X_A}\frac{dX_A}{(-r_A)V}}$$

- CSTR

$$V = \frac{F_{A0} - F_A}{(-r_A)}$$



$$\boxed{V = F_{A0}\frac{X_A - X_{Ao}}{(-r_A)}}$$

- PFR

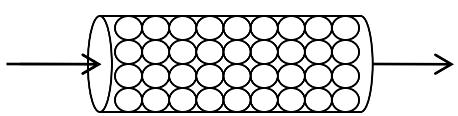
$$\frac{dF_A}{dV} = r_A$$

$$\boxed{F_{A0}\frac{dX_A}{dV} = (-r_A)}$$

$$\boxed{V = F_{Ao}\int_{X_{A0}}^{X_A}\frac{dX_A}{(-r_A)}}$$

- PBR

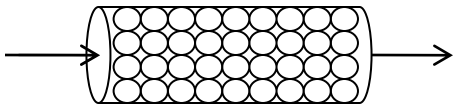
$$\frac{dF_A}{dW} = r'_A$$



$$\boxed{F_{A0}\frac{dX_A}{dW} = (-r'_A)}$$

$$\boxed{W = F_{Ao}\int_{X_{A0}}^{X_A}\frac{dX_A}{(-r'_A)}}$$

Use of LHHW kinetic model in reactor design



$$F_{A0}\frac{dX_A}{dW} = (-r'_A)$$

$$W = F_{Ao}\int_{X_{A0}}^{X_A}\frac{dX_A}{(-r'_A)}$$

$$(-r'_A) = \frac{k_{sr}K_A C_t^2\left(p_A - \dfrac{p_C p_D}{K}\right)}{(1 + K_A p_A + K_C p_C + K_D p_D)^2}$$

$$\varepsilon_A = \delta . y_{A0} = \\ = (+1)\left(\frac{F_{Ao}}{F_{Ao} + F_{Co} + F_{Do} + F_{Io}}\right)$$

$$p_A = C_A RT = C_{Ao}RT\frac{(1 - X_A)}{(1 + \varepsilon_A X_A)}\left(\frac{T_o P}{TP_o}\right) = y_{Ao}P\frac{(1 - X_A)}{(1 + \varepsilon_A X_A)}\left(\frac{T_o P}{TP_o}\right)$$

$$p_C = C_C RT = C_{Ao}RT\frac{\left(\dfrac{F_{Co}}{F_{Ao}} + X_A\right)}{(1 + \varepsilon_A X_A)}\left(\frac{T_o P}{TP_o}\right) = y_{Ao}P\frac{\left(\dfrac{F_{Co}}{F_{Ao}} + X_A\right)}{(1 + \varepsilon_A X_A)}\left(\frac{T_o P}{TP_o}\right)$$

$$p_D = C_D RT = C_{Ao}RT\frac{\left(\dfrac{F_{Do}}{F_{Ao}} + X_A\right)}{(1 + \varepsilon_A X_A)}\left(\frac{T_o P}{TP_o}\right) = y_{Ao}P\frac{\left(\dfrac{F_{Do}}{F_{Ao}} + X_A\right)}{(1 + \varepsilon_A X_A)}\left(\frac{T_o P}{TP_o}\right)$$

Discrimination of kinetic models using initial rates ($p_C=p_D=0$)

$$A \rightleftharpoons C + D$$

$$R_{global} = R_1 = \frac{k_A C_v \left(p_A - \dfrac{p_C p_D}{K} \right)}{1 + \dfrac{K_A}{K} p_C p_D + K_C p_C + K_D p_D}$$

$$R_{global} = R_1 = k_A p_A$$

$$R_{global} = R_2 = \frac{k_{sr} K_A C_t^2 \left(p_A - \dfrac{p_C p_D}{K} \right)}{(1 + K_A p_A + K_C p_C + K_D p_D)^2}$$

$$R_{global} = R_2 = \frac{k_{sr} K_A p_A}{(1 + K_A p_A)^2}$$

$$R_{global} = R_3 = \frac{k_C C_t K \left(p_A - \dfrac{p_C p_D}{K} \right)}{p_D \left(1 + K_A p_A + K_C K \dfrac{p_A}{p_D} + K_D p_D \right)}$$

$$R_{global} = R_3 = \frac{k_C}{K_C}$$

$$R_{global} = R_4 = \frac{k_D C_t K \left(p_A - \dfrac{p_C p_D}{K} \right)}{p_C \left(1 + K_A p_A + K_C p_C + K_D K \dfrac{p_A}{p_C} + \right)}$$

$$R_{global} = R_4 = \frac{k_D}{K_D}$$

Analysis of the rate equation

Nonlinear regression
(using the original rate equation)

$$(-r_A) = \frac{kC_A C_B}{\left(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D\right)^2}$$

$$\underbrace{\left(\frac{C_A C_B}{-r_A}\right)^{1/2}}_{Y} = \frac{1}{\sqrt{k}} + \frac{K_A}{\sqrt{k}}\underbrace{C_A}_{X_1} + \frac{K_B}{\sqrt{k}}\underbrace{C_B}_{X_2} + \frac{K_C}{\sqrt{k}}\underbrace{C_C}_{X_3} + \frac{K_D}{\sqrt{k}}\underbrace{C_D}_{X_4}$$

Linear regression
(using the linearized-transformed equation)

LHHW mechanism / kinetic model

Recommended Exercises
(Fogler Chapter 10)

P-10-5 (3^a. Ed.) = P-10-6 (4^a. Ed.)

P-10-8 (3^a. Ed.) = P-10-9 (4^a. Ed.)

P-10-9 (3^a. Ed.) = P-10-10 (4^a. Ed.)

P-10-10 (3^a. Ed.) = P-10-11 (4^a. Ed.)

P10-5$_B$ The dehydration of n-butyl alcohol (butanol) over an alumina-silica catalyst was investigated by J. F. Maurer (Ph.D. thesis, University of Michigan)). The data in Figure P10-5 were obtained at 750°F in a modified differential reactor. The feed consisted of pure butanol.

(a) Suggest a mechanism and rate-controlling step that is consistent with the experimental data.

(b) Evaluate the rate law parameters.

(c) At the point where the initial rate is a maximum, what is the fraction of vacant sites? What is the fraction of occupied sites by both **A** and B?

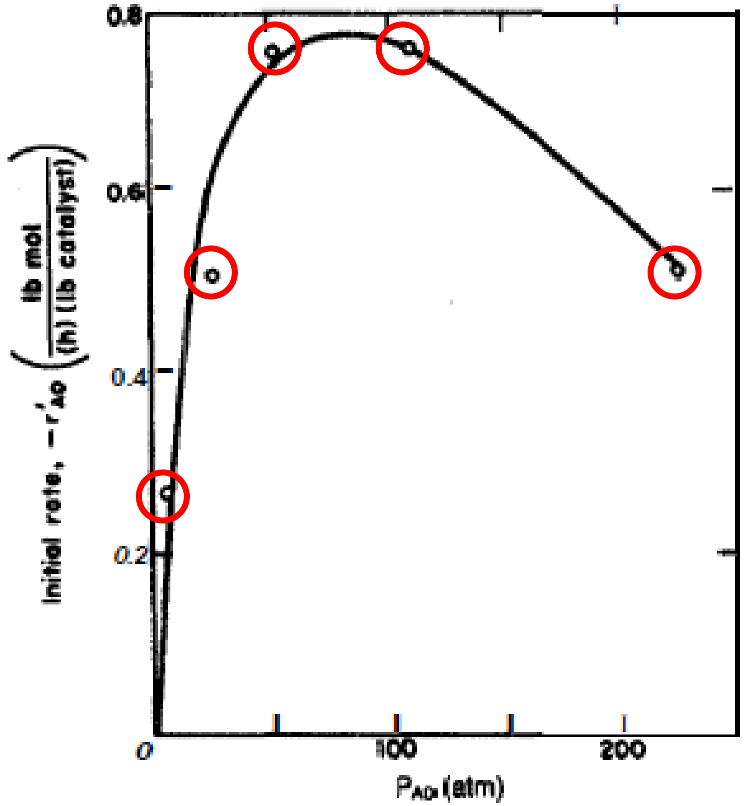


Figure P10-5

Discrimination of kinetic models using initial rates ($p_C=p_D=0$)

$$A \rightleftarrows C + D$$

$$R_{global} = R_1 = \frac{k_A C_t\left(p_A - \frac{p_C p_D}{K}\right)}{1 + \frac{K_A}{K} p_C p_D + K_C p_C + K_D p_D} \xrightarrow{p_C=p_D=0} R_{global} = R_1 = k_A p_A$$

$$R_{global} = R_2 = \frac{k_{sr} K_A C_t^2\left(p_A - \frac{p_C p_D}{K}\right)}{(1 + K_A p_A + K_C p_C + K_D p_D)^2} \xrightarrow{p_C=p_D=0} R_{global} = R_2 = \frac{k_{sr} K_A p_A}{(1 + K_A p_A)^2}$$

$$R_{global} = R_3 = \frac{k_C C_t K\left(p_A - \frac{p_C p_D}{K}\right)}{p_D\left(1 + K_A p_A + K_C K \frac{p_A}{p_D} + K_D p_D\right)} \xrightarrow{p_C=p_D=0} R_{global} = R_3 = \frac{k_C}{K_C}$$

$$R_{global} = R_4 = \frac{k_D C_t K\left(p_A - \frac{p_C p_D}{K}\right)}{p_C\left(1 + K_A p_A + K_C p_C + K_D K \frac{p_A}{p_C} + \right)} \xrightarrow{p_C=p_D=0} R_{global} = R_4 = \frac{k_D}{K_D}$$

Discrimination of kinetic models using initial rates ($p_C=p_D=0$)

$$A \rightleftarrows C + D$$

Adsorption of A

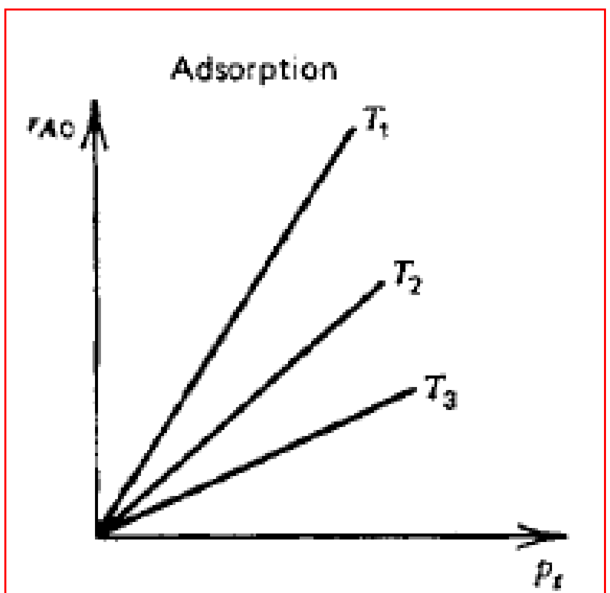
Surface reaction

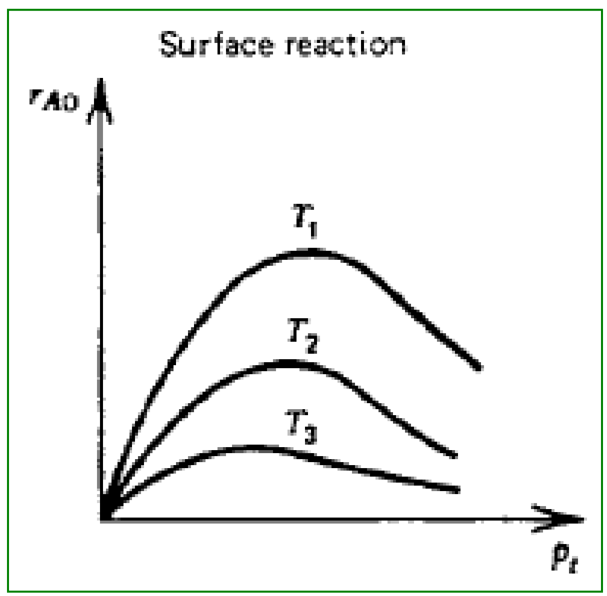
Desorption of C

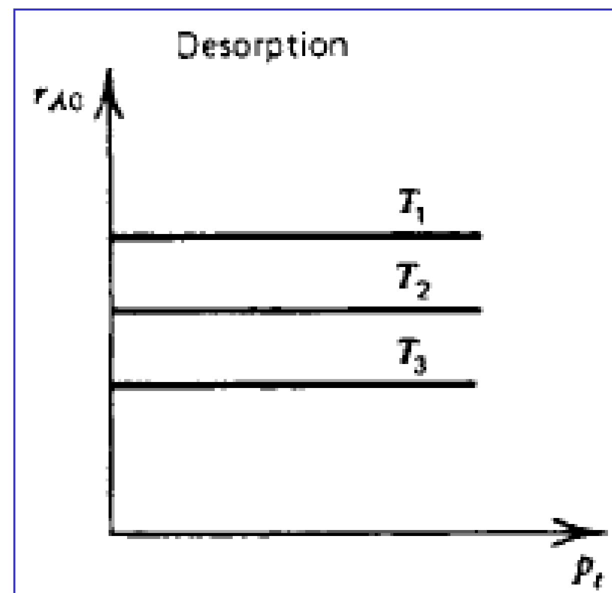
$$R_{initial} = k_A p_A$$

$$R_{initial} = \frac{k_{sr} K_A p_A}{(1 + K_A p_A)^2}$$

$$R_{initial} = \frac{k_C}{K_C}$$







Discrimination of kinetic models using initial rates ($p_C = p_D = 0$)

$$A \rightleftarrows C + D$$

Surface reaction

$$R_{initial} = \frac{k_{sr} K_A p_A}{(1 + K_A p_A)^2}$$

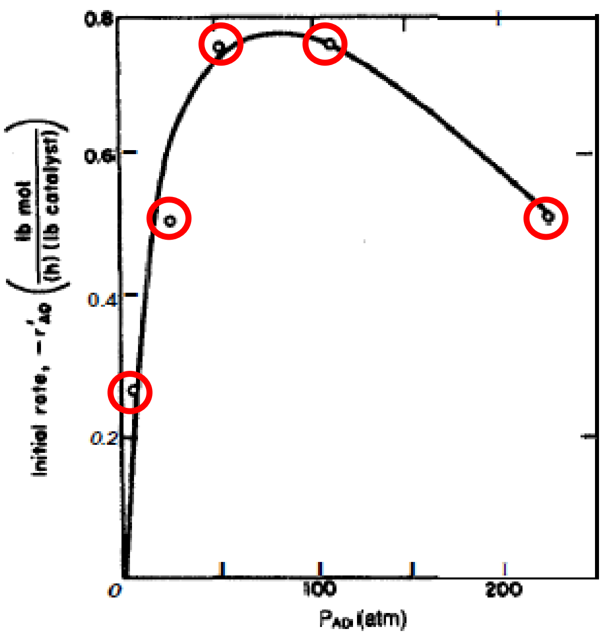
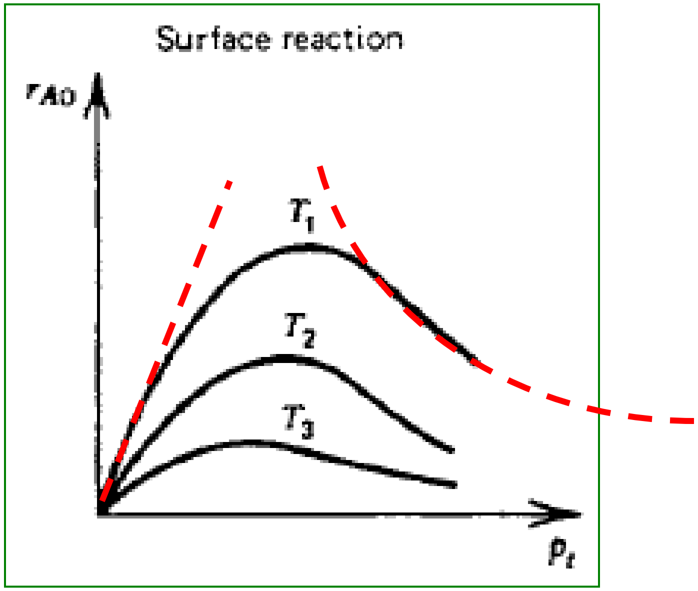


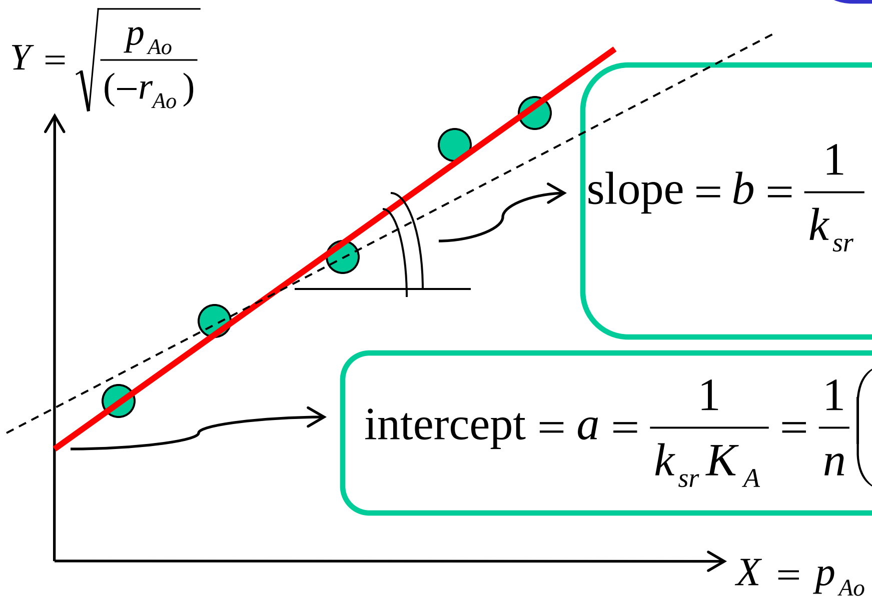
Figure P10-5



Linearization of the model equation

$$(-r_{Ao}) = \frac{k_{sr} K_A p_{Ao}}{(1 + K_A p_{Ao})^2}$$

$$\underbrace{\sqrt{\frac{p_{Ao}}{(-r_{Ao})}}}_{Y} = \underbrace{\frac{1}{k_{sr} K_A}}_{a} + \underbrace{\frac{1}{k_{sr}}}_{b} \underbrace{p_{Ao}}_{X} \Leftrightarrow Y = a + bX$$



$$\text{slope} = b = \frac{1}{k_{sr}} = \frac{\sum_{i=1}^{n} y_i x_i - \frac{1}{n} \sum_{i=1}^{n} y_i \sum_{i=1}^{n} x_i}{\sum_{i=1}^{n} x_i^2 - \frac{1}{n} \left(\sum_{i=1}^{n} x_i \right)^2}$$

$$\text{intercept} = a = \frac{1}{k_{sr} K_A} = \frac{1}{n} \left(\sum_{i=1}^{n} y_i - b \sum_{i=1}^{n} x_i \right)$$

$$\left\{ \begin{array}{l} k_{sr} = \dfrac{1}{\text{slope}} = \dfrac{1}{b} \\[2ex] K_A = \dfrac{\text{slope}}{\text{intercept}} = \dfrac{b}{a} \end{array} \right.$$

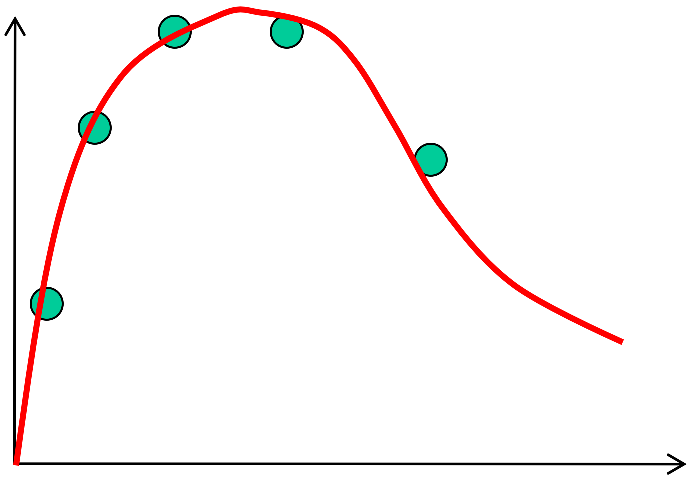
$$\min F(a,b) = \sum_{i=1}^{5} \left[Y_{i,\exp} - Y_{i,calc} \right]^2 \Leftrightarrow \min F(a,b) = \sum_{i=1}^{5} \left[\left(\sqrt{\frac{p_{Ao}}{(-r_{Ao})}} \right)_{i,\exp} - \left(\sqrt{\frac{p_{Ao}}{(-r_{Ao})}} \right)_{i,calc} \right]^2$$

Linear Regression (fit of the linearized equation to the transformed variables Y and X)

$$(-r_{Ao}) = \frac{k_{sr} K_A p_{Ao}}{(1 + K_A p_{Ao})^2}$$

Fit of the original (nonlinear) equation to the original (non-transformed) data

$$Y = (-r_{Ao})$$



$$X = p_{Ao}$$

$$\min F(k_{sr}, K_A) = \sum_{i=1}^{5} \left[(-r_{Ao})_{i,\exp} - (-r_{Ao})_{i,calc} \right]^2$$

Matlab
Octave
Scilab
Polymath
Excel ("solve")
etc.

Nonlinear Regression (fit of the nonlinear equation to the original data)

Try the two methods and compare

- Linear regression using the linerized equation and transformed variables

- Nonlinear regression using the original equation and the original variables

Which of the two methods above is the easiest one?

Which of the two methods above is the best one?

Parameter Estimation

UNIVERSIDADE DE SÃO PAULO

- Model: $\hat{y} = f(x, \beta)$

- Experimental data: n measurements (y_i, x_i)

- General criterion:

  max likelihood function

$$\max_{\beta} L(\beta | y, x) = \prod_{i=1}^{n} p(y_i | x_i, \beta)$$

Least Squares Criterion

Assumptions:

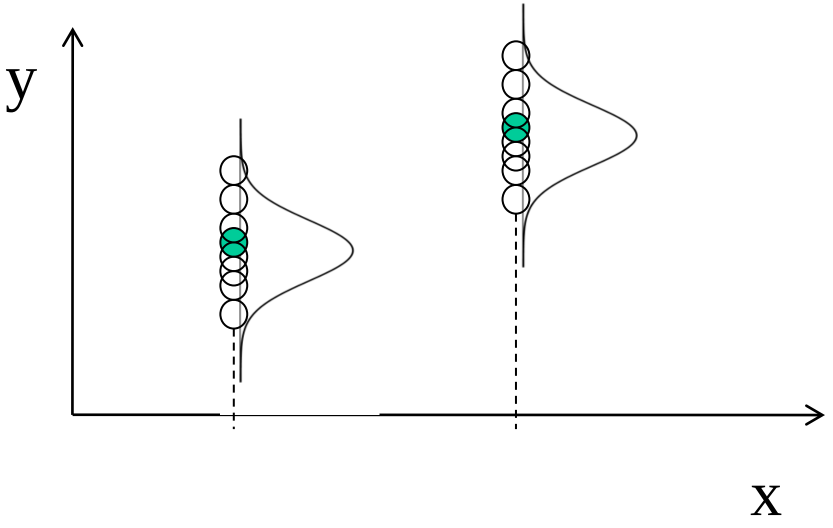
(1) Errors on variable x are zero

(i.e., x are “perfect” measurements, with no error)

(2) Errors on the variable y is distributed according to a normal (Gaussian) distribution with mean=zero and

(3) variance σ^2 = constant

$$p\left(y_i \middle| x_i, \beta\right) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[\frac{-\left(y_i - \hat{y}_i\right)^2}{2\sigma^2}\right]$$



Least Squares Criterion

Assumptions:

(1) Errors on variable x are zero

(i.e., x are "perfect" measurements, with no error)

(2) Errors on the variable y is distributed according to a normal (Gaussian) distribution with mean=zero and

(3) variance σ^2 = constant

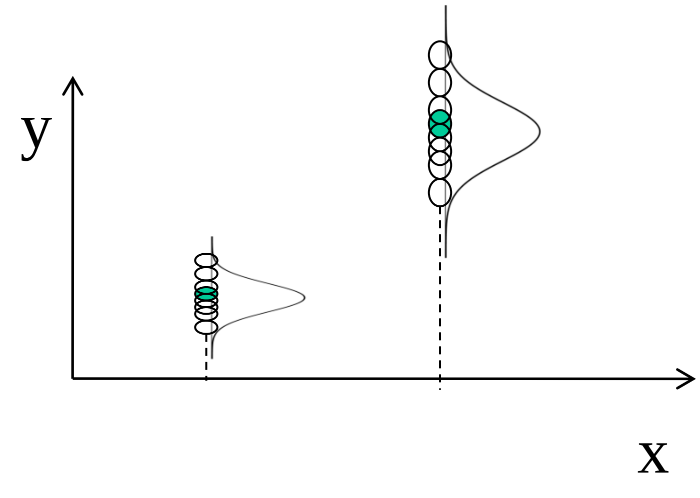
$$p\left(y_i \middle| x_i, \beta\right) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[\frac{-\left(y_i - \hat{y}_i\right)^2}{2\sigma^2}\right]$$

$$L(\beta | y, x) = \prod_{i=1}^{n} p\left(y_i \middle| x_i, \beta\right) = \prod_{i=1}^{n} \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[\frac{-\left(y_i - \hat{y}_i\right)^2}{2\sigma^2}\right]$$

$$\max(L) \Rightarrow \max(\ln(L)) \Rightarrow \max\left(\underbrace{\ln\left(\frac{1}{\sqrt{2\pi\sigma^2}}\right)^n}_{\text{constant}} - \frac{1}{2\sigma^2}\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2\right) \Rightarrow \min\left(\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2\right)$$

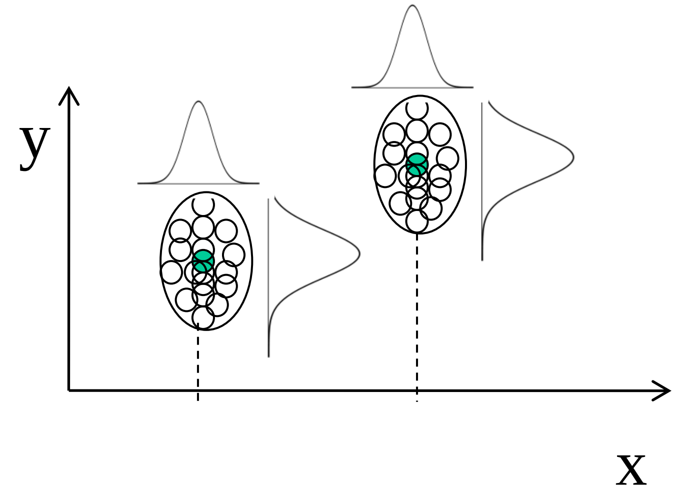
Other Criteria

(a) Error(x) = 0 and
Error(y) = N(mean=0, σ^2 **not constant**)
WEIGHTED LEAST SQUARES
(with weights proportional to
the inverse of the variance)



$$\min\left(\sum_{i=1}^{n} w_i\left(y_i - \hat{y}_i\right)^2\right) = \min\left(\sum_{i=1}^{n}\frac{1}{\sigma_i^2}\left(y_i - \hat{y}_i\right)^2\right)$$

(b) Error(x) = N(mean=0, $\sigma^2{}_x$) (**not zero**)
Error(y) =N(mean=0, $\sigma^2{}_y$)
ERROR-IN-VARIABLES



$$\min\left(\sum_{i=1}^{n}\frac{1}{\sigma_{yi}^2}\left(y_i - \hat{y}_i\right)^2 + \sum_{i=1}^{n}\frac{1}{\sigma_{xi}^2}\left(x_i - \hat{x}_i\right)^2\right)$$

Least Squares Criterion

Assumptions:

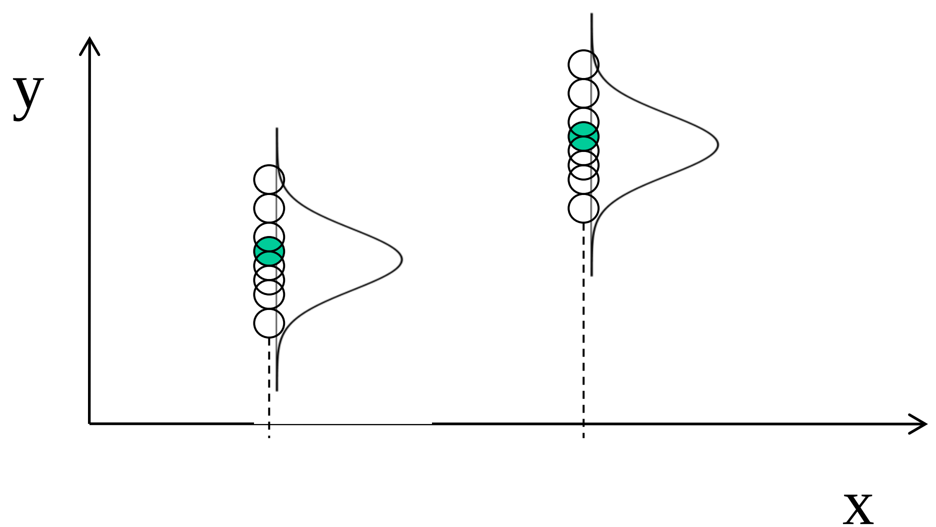
(1) Errors on variable x are zero

(i.e., x are "perfect" measurements, with no error)

(2) Errors on the variable y is distributed according to a normal (Gaussian) distribution with mean=zero and

$$p\left(y_i \middle| x_i, \beta\right) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[\frac{-\left(y_i - \hat{y}_i\right)^2}{2\sigma^2}\right]$$

(3) variance σ^2 = constant



Linearization of the equation by variable transformation

$y = a{x_1}^b {x_2}^c$	$\underbrace{\ln(y)}_{Y} = \underbrace{\ln(a)}_{\beta_0} + \underbrace{(b)}_{\beta_1}\underbrace{\ln(x_1)}_{X_1} + \underbrace{(c)}_{\beta_2}\underbrace{\ln(x_2)}_{X_2}$
$y = ae^{bx}$	$\underbrace{\ln(y)}_{Y} = \underbrace{\ln(a)}_{\beta_0} + \underbrace{(b)}_{\beta_1}\underbrace{(x)}_{X}$
$y = \dfrac{1}{a + bx}$	$\underbrace{(1/y)}_{Y} = \underbrace{(a)}_{\beta_0} + \underbrace{(b)}_{\beta_1}\underbrace{(x)}_{X}$
$y = a + \dfrac{b}{x}$	$\underbrace{(y)}_{Y} = \underbrace{(a)}_{\beta_0} + \underbrace{(b)}_{\beta_1}\underbrace{(1/x)}_{X}$
$y = \dfrac{ax}{b + x}$	$\underbrace{(1/y)}_{Y} = \underbrace{(1/a)}_{\beta_0} + \underbrace{(b/a)}_{\beta_1}\underbrace{(1/x)}_{X}$ $\underbrace{(x/y)}_{Y} = \underbrace{(b/a)}_{\beta_0} + \underbrace{(1/a)}_{\beta_1}\underbrace{(x)}_{X}$ $\underbrace{(y)}_{Y} = \underbrace{(a)}_{\beta_0} + \underbrace{(-b)}_{\beta_1}\underbrace{(y/x)}_{X}$

Linearization of the equation by variable transformation

Disadvantages

(1) If the values of x_1 are in a narrow range (less than one order of magnitude), $\ln(x_1)$ will be in an even narrower range. Because all elements of 1st column of matrix X are equal to 1, the matrix X^TX becomes quase-singular.

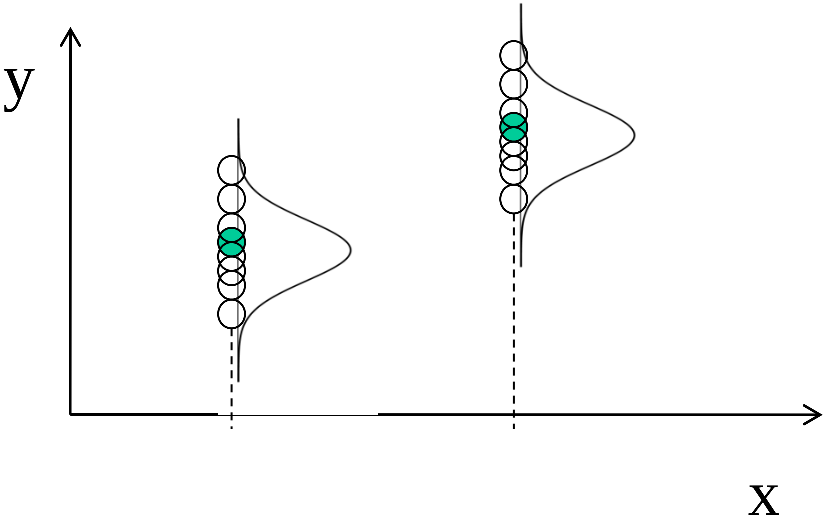
(2) Variable transformation may change the error structure (i.e., error on the transformed variable is not normally distributed), thus introducing bias in the parameter estimates.

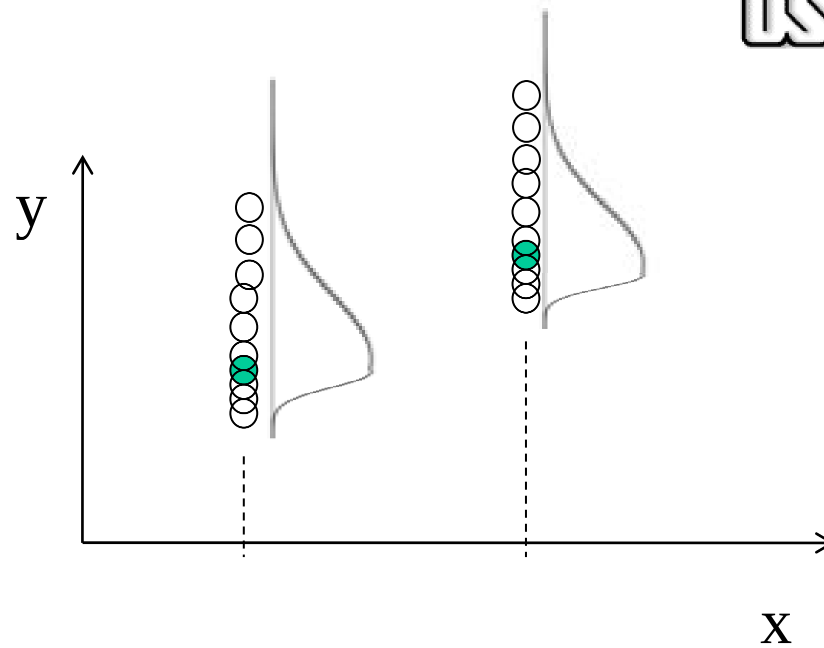
(3) In some transformations, y enters in the transformed "independent" variables (thus adding errors to the tranformed X)

Advantages

(a) Convert the original problem (nonlinear regression) into an easier problem (linear regression)

(b) Useful for obtaining the initial guesses of the parameters to be used in the nonlinear regression.





Symmetrical
error distribution

Non-symmetrical
error distribution

Variables transformation

Variable transformation changes the error distribution

$Y = 20 \pm 4$

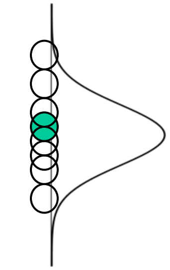
16

20

24

4

4



$\ln(Y) = 2.996 \pm ?$

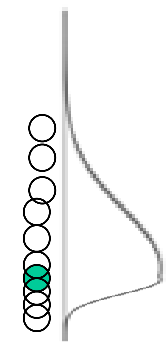
$\ln(16) = 2.773$

$\ln(20) = 2.996$

$\ln(24) = 3.178$

0.223

0.182



$1/Y = 0.05 \pm ?$

$1/16 = 0.0625$

$1/20 = 0.0500$

$1/24 = 0.0417$

0.0125

0.0083