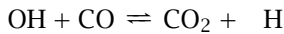
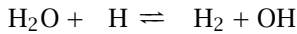
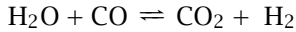


# Chemical Kinetics and Reactor Design Course Review

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## 1 Stoichiometry



$A_1 = \text{H}, A_2 = \text{H}_2, A_3 = \text{OH}, A_4 = \text{H}_2\text{O}, A_5 = \text{CO}, A_6 = \text{CO}_2$ .

$$\sum_{j=1}^{n_s} \nu_{ij} A_j = 0, \quad i = 1, \dots, n_r$$

$\nu_{ij} > 0$ , for  $A_j$  product;  $\nu_{ij} < 0$ , for  $A_j$  reactant.

$$\mathbf{vA} = 0, \quad \mathbf{v} = \begin{bmatrix} 0 & 1 & 0 & -1 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix}$$

$r_i$ : reaction rate for reaction  $i$ .

$R_j$ : production rate for species  $j$ .

$$R_j = \sum_{i=1}^{n_r} \nu_{ij} r_i, \quad j = 1, \dots, n_s$$

$$\mathbf{R} = \mathbf{v}^T \mathbf{r}$$

Extent of reaction:  $dn_j = \sum_{i=1}^{n_r} \nu_{ij} d\varepsilon_i, \quad j = 1, \dots, n_s$ .

## 2 Thermodynamics

At equilibrium, for a given  $T$  and  $P$ , the Gibbs free energy is a minimum.

### Chemical Equilibrium

$$dG = -SdT + VdP + \sum_{j=1}^{n_s} \mu_j dn_j$$

$\mu_j$ : chemical potential for species  $j$ .

$$\left( \frac{\partial G}{\partial \varepsilon_i} \right)_{T,P} = \sum_{j=1}^{n_s} \nu_{ij} \mu_j = 0, \quad i = 1, \dots, n_r$$

$$\mu_j = G_j^\circ + RT \ln a_j, \quad a_j = f_j / f_j^\circ$$

$$K_i = \prod_{j=1}^{n_s} a_j^{\nu_{ij}} \quad \Delta G_i^\circ = -RT \ln K_i$$

Standard state: pure species  $j$  at 1 atm and system temperature.

### Phase Equilibrium

$$f_j^\alpha = f_j^\beta, \quad j = 1, \dots, n_s, \quad \text{all phases } \alpha \text{ and } \beta$$

Know how to evaluate fugacities for ideal gases, ideal solutions, and Raoult and Henry law approximations.

### Temperature Dependence of $K$

$$\frac{\partial \ln K_i}{\partial T} = \frac{\Delta H_i^\circ}{RT^2} \quad (\text{van 't Hoff Equation})$$

$$\ln \left( \frac{K_{i2}}{K_{i1}} \right) = -\frac{\Delta H_i^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (\text{assumption?})$$

How does raising temperature affect the equilibrium extent for exothermic and endothermic reactions?

## 3 Reaction-Rate Expressions

$$r = k(T) f(c_j\text{'s})$$

Arrhenius expression for  $k$ :  $k(T) = k_0 e^{-E_a/RT}$ ,  $E_a$  is the activation energy, always positive. How does raising temperature affect reaction rate? What is  $f(c_j\text{'s})$  for a sequence of *elementary* steps. What is the difference between a mechanism and an overall stoichiometry. Quasi-steady-state assumption, equilibrium assumption and rate limiting step.

## Langmuir Isotherms (chemisorption)

$$A + X \rightleftharpoons A \cdot X \quad \bar{c}_A = \frac{K_A c_A \bar{c}_m}{1 + K_A c_A}$$

**Hougen-Watson rate expressions** Deciding which mechanism best explains rate data.

## 4 Material and Energy Balances

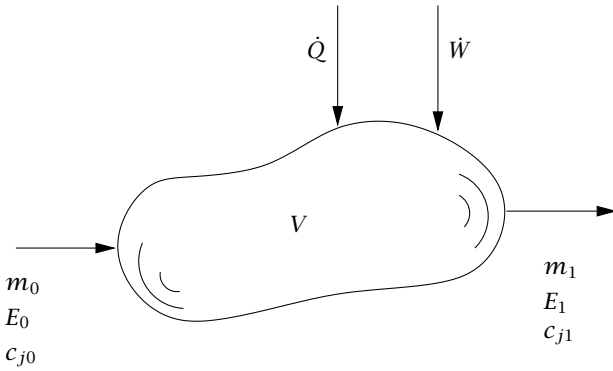


Figure 1: Reactor volume element.

$$\frac{d}{dt} \int_V c_j dV = Q_0 c_{j0} - Q_1 c_{j1} + \int_V R_j dV, \quad j = 1, \dots, n_s$$

$$\frac{dU}{dt} = m_0 \hat{H}_0 - m_1 \hat{H}_1 + \dot{Q} + \dot{W}_s + \dot{W}_b$$

## 5 Fixed-Bed Catalytic Reactors

### Steps in a Catalytic Reactor

1. convection of reactant in the bulk fluid
2. mass transfer from bulk fluid to catalyst
3. diffusion of reactant in the pores (molecular and Knudsen diffusion)
4. adsorption of reactant on the active sites
5. reaction of adsorbed reactants to adsorbed products (surface reaction)
6. desorption of adsorbed products
7. diffusion out of pores
8. mass transfer from catalyst to bulk fluid
9. convection of product in the bulk fluid

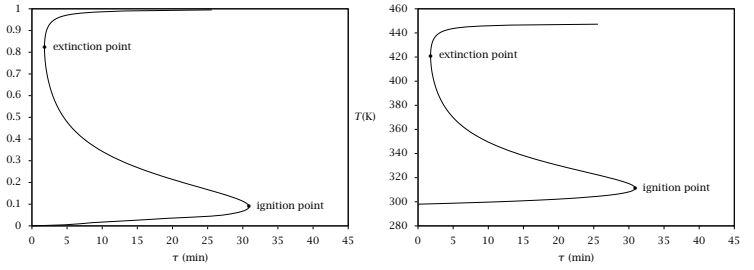


Figure 2: CSTR steady-state multiplicity, stable and unstable steady states, ignition, extinction, hysteresis.

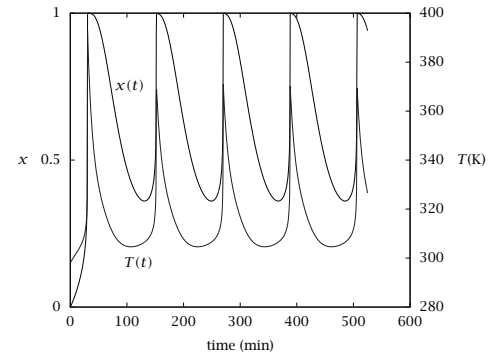


Figure 3: CSTR oscillations.

BATCH	$\frac{d(c_j V_R)}{dt} = R_j V_R$
constant volume	$\frac{dc_j}{dt} = R_j$
SEMI-BATCH	$\frac{d(c_j V_R)}{dt} = Q_f c_{jf} + R_j V_R$
CSTR	$\frac{d(c_j V_R)}{dt} = Q_f c_{jf} - Q c_j + R_j V_R$
constant volume	$\frac{dc_j}{dt} = \frac{1}{\tau} (c_{jf} - c_j) + R_j$
steady state	$c_j = c_{jf} + R_j \tau$
PFR	$\frac{\partial c_j}{\partial t} = -\frac{\partial(c_j Q)}{\partial V} + R_j$
steady-state	$\frac{d(c_j Q)}{dV} = R_j$
constant density	$\frac{dc_j}{d\tau} = R_j$

BATCH	$V_R \rho \hat{C}_P \frac{dT}{dt} = - \sum_i \Delta H_{Ri} r_i V_R + \dot{Q}$
CSTR	$V_R \rho \hat{C}_P \frac{dT}{dt} = - \sum_i \Delta H_{Ri} r_i V_R + \dot{Q} + \sum_j c_{jf} Q_f (\bar{H}_{jf} - \bar{H}_j)$
PFR (steady state)	$Q \rho \hat{C}_P \frac{dT}{dV} = - \sum_i \Delta H_{Ri} r_i + \dot{q}$

Table 1: Summary of Material and Energy Balances for Several Ideal Reactors.

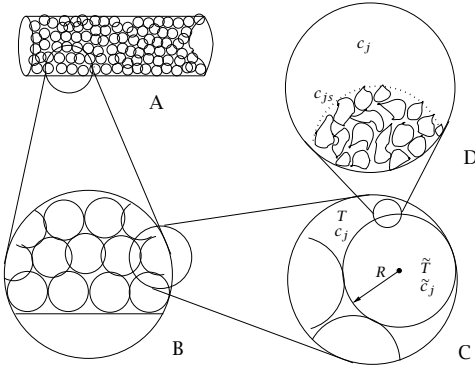


Figure 4: Expanded views of a fixed-bed reactor.

### Simultaneous Reaction and Diffusion

$$\frac{\partial c_j}{\partial t} = D_j \nabla^2 c_j + R_j$$

1st order reaction, spherical pellet, steady state:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) - \Phi^2 c = 0$$

$$c = 1, \quad r = 3$$

$$\frac{\partial c}{\partial r} = 0, \quad r = 0$$

Solution:  $c(r) = \frac{3 \sinh \Phi r}{r \sinh 3\Phi}$

Thiele modulus:  $\Phi = a \left( \frac{n+1}{2} \frac{k C_{As}^{n-1}}{D_A} \right)^{1/2}$       $a = \frac{V_p}{S_p}$

Effectiveness factor:  
 $\eta = \frac{\text{actual rate in pellet}}{\text{rate without diffusional limitations}}$

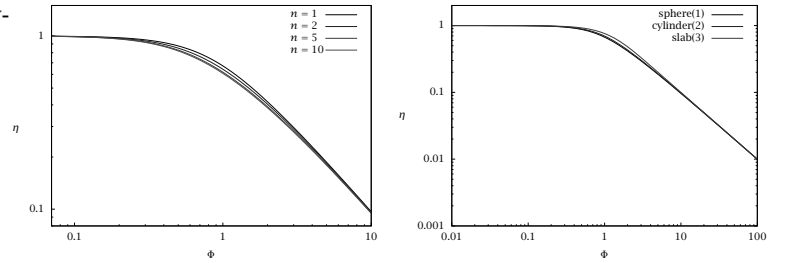
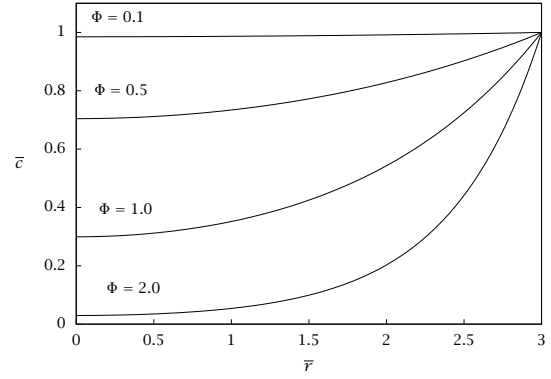


Figure 5: Effectiveness Factor Versus Thiele Modulus: Effect of Geometry and Reaction Order.

$$\frac{dN_j}{dV} = R_j$$

$$Q \rho \hat{C}_p \frac{dT}{dV} = - \sum_i \Delta H_{Ri} r_i + \frac{2}{R} U^o (T_a - T)$$

$$\frac{dP}{dV} = - \frac{(1 - \epsilon_B) Q}{D_p \epsilon_B^3 A_c^2} \left[ 150 \frac{(1 - \epsilon_B) \mu_f}{D_p} + \frac{7 \rho Q}{4 A_c} \right]$$

$$R_j = (1 - \epsilon_B) \tilde{R}_{jp} \quad (\text{use of } \eta \text{ to evaluate } \tilde{R}_{jp})$$

$$\sum_i \Delta H_{Ri} r_i = (1 - \epsilon_B) \sum_i \Delta H_{Ri} \tilde{r}_{ip}$$

$$\epsilon_B = 1 - \rho_B / \rho_p, \quad Q = \sum_j N_j / c(P, T)$$

$$\text{Biot number: } B = k_m a / D_A \quad \eta = R_{Ap} / R_{As}$$

Sphere	$\eta = \frac{1}{\Phi} \left[ \frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi} \right]$ (1)
Cylinder	$\eta = \frac{1}{\Phi} \frac{I_1(2\Phi)}{I_0(2\Phi)}$ (2)
Slab	$\eta = \frac{\tanh \Phi}{\Phi}$ (3)

Table 2: Effectiveness factor versus Thiele modulus for the sphere, semi-infinite cylinder, and semi-infinite slab.

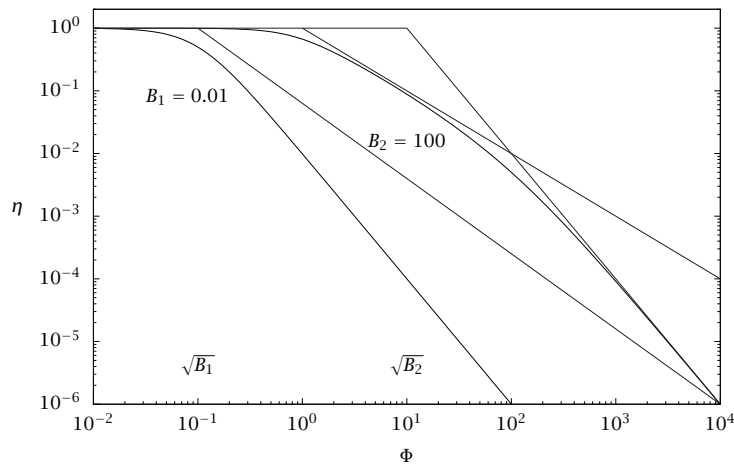


Figure 6: Effectiveness factor versus Thiele modulus for different values of the Biot number; first-order reaction in a spherical pellet.

## 6 Mixing in Chemical Reactors

Residence-time distribution

$p(\theta)d\theta$ , probability that a feed molecule spends time  $\theta$  to  $\theta + d\theta$  in the reactor  
 $P(\theta)$ , probability that a feed molecule spends time zero to  $\theta$  in the reactor

$$c_e(t) = \int_0^t c_f(t')p(t-t')dt', \quad c_f(t) = 0, t \leq 0$$

Step response, impulse response for CSTR, PFR,  $n$  CSTRs, PFR with dispersion. Effect of mixing on rates of convex and concave rate expressions. Simple mixing models.

## 7 Parameter Estimation

**Probability review.** Normal distribution, mean, variance.

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{1}{2} \frac{(x-m)^2}{\sigma^2}\right)$$

$$p(\mathbf{x}) = \frac{1}{(2\pi)^{n_p/2} |\mathbf{P}|^{1/2}} \exp\left[-\frac{1}{2}(\mathbf{x}-\mathbf{m})^T \mathbf{P}^{-1}(\mathbf{x}-\mathbf{m})\right]$$

**Least squares.** Let  $y$  be measured as a function of  $x$

$$y_i = mx_i + b, \quad i = 1, \dots, n$$

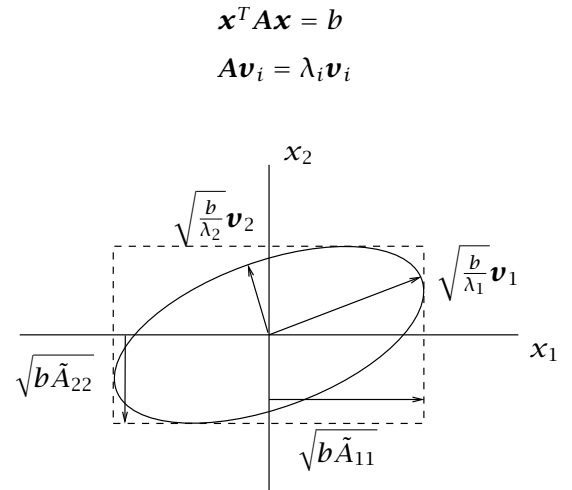


Figure 7: The geometry of quadratic form  $\mathbf{x}^T \mathbf{A} \mathbf{x} = b$ .  $\tilde{A}_{ii} = (i, i)$  element of  $\mathbf{A}^{-1}$ .

$$\mathbf{y} = \mathbf{X}\boldsymbol{\theta} + \mathbf{e}, \quad \mathbf{e} \sim N(\mathbf{0}, \sigma^2 \mathbf{I})$$

The best estimate of  $\boldsymbol{\theta}$  in a least squares sense is given by

$$\hat{\boldsymbol{\theta}} = (\mathbf{X}^T \mathbf{X})^{-1} \mathbf{X}^T \mathbf{y}$$

$$\hat{\boldsymbol{\theta}} \sim N(\boldsymbol{\theta}, \mathbf{P}), \quad \mathbf{P} = \sigma^2 (\mathbf{X}^T \mathbf{X})^{-1}$$

Confidence interval.  $\alpha$ -level confidence region for estimating  $n_p$  parameters is given

$$\frac{(\boldsymbol{\theta} - \hat{\boldsymbol{\theta}})^T \mathbf{X}^T \mathbf{X} (\boldsymbol{\theta} - \hat{\boldsymbol{\theta}})}{\sigma^2} \leq \chi^2(n_p, \alpha)$$

$$\frac{(\boldsymbol{\theta} - \hat{\boldsymbol{\theta}})^T \mathbf{X}^T \mathbf{X} (\boldsymbol{\theta} - \hat{\boldsymbol{\theta}})}{s^2} \leq n_p F(n_p, n_d - n_p, \alpha)$$

$$s^2 = \frac{1}{n_d - n_p} (\mathbf{y} - \mathbf{X}\hat{\boldsymbol{\theta}})^T (\mathbf{y} - \mathbf{X}\hat{\boldsymbol{\theta}})$$

## 8 Notes

Gas constant:  $R = 82.06 \text{ cm}^3 \cdot \text{atm/mol} \cdot \text{K}$ ;  $R = 1.987 \text{ cal/mol} \cdot \text{K}$