

CHEM E 465 Reactor Design

Rate Law

| Equilibrium constant

Description	Equations
Equilibrium constant and concentration	$K_c = \prod_i C_i^{\nu_i}$
Equilibrium constant and rate constant	$K_i = \frac{k_i}{k_{-i}}$
van't Hoff equation ★ $\Delta h_{\text{rxn}}^\circ \neq f(T)$	$\frac{d \ln K}{dT} = \frac{\Delta h_{\text{rxn}}^\circ}{RT^2}$
T dependence of equilibrium constant	$\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta h_{\text{rxn}}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

| Rate constant

Description	Equations
General reaction	$a A + b B \xrightarrow{k} c C + d D$
Relative reaction rates	$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{-r_C}{c} = \frac{-r_D}{d}$
Power law	$r_A = -k C_A^a C_B^b$
Unit of rate constant	$k [=] \text{M}^{1-n}/\text{s}$
Arrhenius equation ★ $E_a \neq f(T)$	$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$
Arrhenius equation	$k = A \exp \left(-\frac{E_a}{RT} \right)$
T dependence of rate constant	$\ln \left(\frac{k_2}{k_1} \right) = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$
Arrhenius plot	$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}$
Note	Increase E_a , increase k 's sensitivity to T
Collision theory	$k \propto \sqrt{T} \exp \left(-\frac{E_0}{RT} \right)$
Transition state theory	$k \propto T \exp \left(-\frac{\Delta H^*}{RT} \right)$

Reactor Design and Sizing

1. Reactor design equation (mole balance): $r_i = f(n) = f(X)$
2. Rate law: $r_i = f(C_i)$
3. Stoichiometry: $C_i = f(X)$
4. Combine: $r_i = f(X)$

	Description	Equations
	General mole balance	$\text{in} - \text{out} + \text{generation} = \text{accumulation}$ $\dot{n}_{i0} - \dot{n}_i + G_i = \frac{dn_i}{dt}$
	General generation term	$G_i = \int r_i dV$
	Spatially uniform generation term	$G_i = r_i V$
	Conversion	$X_i \equiv X = \frac{n_{i0} - n_i}{n_{i0}} = \frac{\dot{n}_{i0} - \dot{n}_i}{\dot{n}_{i0}}$
	Mole/flow rate in terms of conversion	$n_i = n_{i0}(1 - X)$ $\dot{n}_i = \dot{n}_{i0}(1 - X)$
	Heterogeneous reaction rate	$r_i = \rho_b r'_i$

Reactor	Design Equations	Integral Form
Batch ★ Perfectly mixed	$r_i V = \frac{dn_i}{dt} = -n_{i0} \frac{dX}{dt}$	$t = \int_{n_{i1}}^{n_{i0}} \frac{dn_i}{-r_i V} = n_{i0} \int_0^X \frac{dX}{-r_i V}$
CSTR ★ Perfectly mixed, steady-state	$V = \frac{\dot{n}_{i0} - \dot{n}_i}{-r_i} = \frac{\dot{n}_{i0} X}{-r_i}$	-
PFR ★ Steady state ★ Plug flow, no radial dependence	$r_i = \frac{d\dot{n}_i}{dV} = -\dot{n}_{i0} \frac{dX}{dV}$	$V = \int_{\dot{n}_i}^{\dot{n}_{i0}} \frac{d\dot{n}_i}{-r_i} = \dot{n}_{i0} \int_0^X \frac{dX}{-r_i}$
PBR ★ Steady state	$r'_i = \frac{d\dot{n}_i}{dm} = -\dot{n}_{i0} \frac{dX}{dm}$	$m = \int_{\dot{n}_i}^{\dot{n}_{i0}} \frac{d\dot{n}_i}{-r'_i} = \dot{n}_{i0} \int_0^X \frac{dX}{-r'_i}$
Semi-batch reactor	$r_i = \frac{\frac{dn_i}{dt} - \dot{n}_{i0}}{V(t)}$	-

| Levenspiel plot

	Description	Equations
	Levenspiel plot	$\frac{\dot{n}_{i0}}{-r_i}$ vs. X
	CSTR volume	$V = \frac{\dot{n}_{i0} X}{-r_i} = \text{Area of rectangle}$
	PFR volume	$V = \dot{n}_{i0} \int_0^X \frac{dX}{-r_i} = \text{Area under Levenspiel plot}$
	Reaction of order > 0	$V_{\text{CSTR}} > V_{\text{PFR}}$ (Choose PFR)
	Reaction of order < 0	$V_{\text{CSTR}} < V_{\text{PFR}}$ (Choose CSTR)

| Reactor choice

Reactor Type	Advantage	Disadvantage
Batch	- High conversion	- High labor cost and downtime - Difficult to scale up - Batch-to-batch variability

Reactor Type	Advantage	Disadvantage
CSTR	- Good T control	- Hard to get high conversion
PFR	- Easy maintenance - High conversion per unit volume	- Difficult for T control

Stoichiometry

| Stoichiometric table

Species	Initial	Change	Remaining
A	n_{A0}	$-n_{A0}X$	$n_A = n_{A0}(1 - X)$
B	n_{B0}	$-\frac{b}{a}n_{A0}X$	$n_B = n_{A0}(\Theta_B - \frac{b}{a}X)$
C	n_{C0}	$\frac{c}{a}n_{A0}X$	$n_C = n_{A0}(\Theta_C + \frac{c}{a}X)$
D	n_{D0}	$\frac{d}{a}n_{A0}X$	$n_D = n_{A0}(\Theta_D + \frac{d}{a}X)$
I	n_{I0}	0	$n_I = n_{I0}$
Total	n_{T0}	$\delta n_{A0}X$	$n_T = n_{T0} + \delta n_{A0}X$

Description	Equations
Sample reaction	$A + \frac{b}{a} B \longrightarrow \frac{c}{a} C + \frac{d}{a} D$
$\frac{\text{total mol change}}{\text{mol A reacted}}$	$\delta = \sum \nu_i = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$
$\frac{\text{mol Z initially}}{\text{mol A initially}}$	$\Theta_Z = \frac{n_{Z0}}{n_{A0}} = \frac{\dot{n}_{Z0}}{\dot{n}_{A0}} = \frac{y_{Z0}}{y_{A0}} = \frac{C_{Z0}}{C_{A0}}$
$\frac{\text{total mol change for } X = 1}{\text{mol feed}}$	$\varepsilon = y_{A0}\delta = \frac{\dot{n}_{Tf} - \dot{n}_{T0}}{\dot{n}_{T0}}$
Concentration	$C_i = \frac{n_i}{V} = \frac{\dot{n}_i}{\dot{V}}$
Molar fraction	$y_i = \frac{\dot{n}_i}{\dot{n}_T}$
Pressure ratio	$p = \frac{P}{P_0}$

Description	Equations
Molar flow rate	$\dot{n}_i = \dot{n}_{A0}(\Theta_i - \nu_i X)$
Concentration ★ Constant PVT	$C_i = C_{A0}(\Theta_i - \nu_i X)$
Volumetric flow rate	$\dot{V} = \dot{V}_0 \left(\frac{\dot{n}_T}{\dot{n}_{T0}} \right) \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right)$ $= \dot{V}_0(1 + \varepsilon X) \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right)$

Description	Equations
Concentration	$C_i = \frac{\dot{n}_i}{\dot{V}}$
	$= C_{A0} \left(\frac{\dot{n}_i}{\dot{n}_T} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$
	$= C_{A0} y_{ip} \left(\frac{T_0}{T} \right)$
	$= \frac{C_{A0}(\Theta_i + \nu_i X)}{1 + \varepsilon X} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$

Isothermal Reactor Design

| Batch reactor

Description	Equations
Characteristic reaction time (1st order)	$t_R = \frac{1}{k} \ln \left(\frac{1}{1 - X} \right)$
Characteristic reaction time (2nd order)	$t_R = \frac{1}{k C_{A0}} \frac{X}{1 - X}$
Total time	Total = Fill + Heat + Reaction + Clean

| CSTR

Description	Equations
Space time	$\tau = \frac{V}{\dot{V}} = \frac{C_{A0} X}{-r_A}$
Damkohler number	$\text{Da} = \frac{-r_{A0} V}{\dot{n}_{A0}}$ $= \frac{\text{rate at entrance}}{\text{molar flow at entrance}}$ $= \frac{\text{reaction rate}}{\text{convective mass transport rate}}$
Damkohler number and conversion	$\text{Da} < 0.1, X < 0.1$ $\text{Da} > 10, X > 0.9$

Reaction, Reactor	Damkohler number Da_i	Space time τ	Conversion X	Concentration C_i
1st order, single CSTR	$\tau k = \frac{X}{1 - X}$	$\frac{X}{k(1 - X)}$	$\frac{\tau k}{1 + \tau k}$	$\frac{C_{A0}}{1 + \tau k}$
2nd order, single CSTR	$\tau k C_{A0}$	$\frac{X}{k C_{A0} (1 - X)^2}$	$\frac{1 + 2\text{Da}_2 - \sqrt{1 + 4\text{Da}_2}}{2\text{Da}_2}$	$C_{A0} \frac{-1 + \sqrt{1 + 4\text{Da}_2}}{2\text{Da}_2}$
1st order, CSTR series	-	-	$1 - \frac{1}{(1 + \text{Da}_1)^n}$	$\frac{C_{A0}}{(1 + \text{Da}_1)^n}$

| PFR

Description	Equations
Reactor volume for 2nd order gas phase rxn	$V = \frac{\dot{V}_{A0}}{kC_{A0}} \left[2\varepsilon(1 + \varepsilon) \ln(1 - X) + \varepsilon^2 X + \frac{(1 + \varepsilon)^2 X}{1 - X} \right]$
Ergun equation	$\frac{dP}{dz} = \frac{G}{\rho g_c D_P} \left(\frac{1 - \phi}{\phi^3} \right) \left[\frac{150(1 - \phi)\mu}{D_P} + 1.75G \right]$
Porosity (void fraction)	$\phi = \frac{\text{void volume}}{\text{total bed volume}}$
PBR pressure drop	$\frac{dP}{dz} = -\beta_0 \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) \left(\frac{\dot{n}_T}{\dot{n}_{T0}} \right)$
Packed bed property	$\beta_0 = \frac{G(1 - \phi)}{\rho_0 g_c D_P \phi^3} \left[\frac{150(1 - \phi)\mu}{D_P} + 1.75G \right] [=] \frac{\text{Pa}}{\text{m}}$
Bulk density of catalyst	$\rho_b = \rho_c(1 - \phi)$
Catalyst mass	$m = (1 - \phi)A_c z \rho_c = A_c z \rho_b$
Ergun equation for packed bed (multiple reaction)	$\frac{dp}{dm} = -\frac{\alpha}{2p} \frac{T}{T_0} \frac{\dot{n}_T}{\dot{n}_{T0}}$
	$\alpha = \frac{2\beta_0}{A_c \rho_c (1 - \phi) P_0} [=] \text{kg}^{-1}$
Ergun equation for packed bed (single reaction)	$\frac{dp}{dm} = -\frac{\alpha}{2p} (1 + \varepsilon X) \frac{T}{T_0}$
System of pressure and conversion ODEs	$\begin{cases} \frac{dX}{dm} = F_1(X, p) & \text{Reactor design} \\ \frac{dp}{dm} = F_2(X, p) & \text{Ergun equation} \end{cases}$
Pressure ratio ★ $\varepsilon = 0$ or $\varepsilon X \ll 1$, isothermal	$p = \sqrt{1 - \alpha m} = \sqrt{1 - \frac{2\beta_0}{P_0} z}$
Pressure drop in pipes	$p = \sqrt{1 - \alpha_p V}$
Pipe factor	$\alpha_p = \frac{4fG^2}{A_c \rho_0 P_0 D}$

Rate law determination by data

| Batch reactors

Description	Equations
Power law	$r_A = -kC_A^\alpha C_B^\beta$
Integral method	$\frac{dC_A}{dt} = -kC_A^\alpha$
0th order rxn	$C_A = C_{A0} - kt$
1st order rxn	$\ln \frac{C_{A0}}{C_A} = kt$ $\ln C_A = \ln C_{A0} - kt$
2nd order rxn	$\frac{1}{C_A} = kt + \frac{1}{C_{A0}}$
Differential method	$\ln \left(-\frac{dC_A}{dt} \right) = \ln k_A + \alpha \ln C_A$

| Differential reactors (PBR)

Description	Equations
	$-r'_A = \frac{\dot{V}_0 C_{A0} - \dot{V} C_{AP}}{\Delta m} = \frac{\dot{V}_{A0} X}{\Delta m} = \frac{\dot{V}_P}{\Delta m}$

Multiple reactions

| Batch reactors

Description	Equations
Parallel (competing) reactions	$A \xrightarrow{k_1} B$ $A \xrightarrow{k_2} C$
Series (consecutive) reactions	$A \xrightarrow{k_1} B \xrightarrow{k_2} C$
Independent reactions	$A \longrightarrow B + C$ $D \longrightarrow E + F$
Complex reactions	$A + B \longrightarrow C + D$ $A + C \longrightarrow E$ $E \longrightarrow G$

Description	Equations
Instantaneous selectivity based on rate	$S_{D/U} = \frac{r_D}{r_U} = \frac{\text{rate of formation of D}}{\text{rate of formation of U}}$
Overall selectivity based on flow rate	$\tilde{S}_{D/U} = \frac{\dot{n}_D}{\dot{n}_U} = \frac{n_D}{n_U} = \frac{\text{exit molar flow rate of D}}{\text{exit molar flow rate of U}}$
Selectivity of CSTR	$S_{D/U} = \tilde{S}_{D/U}$
Instantaneous yield based on rate	$Y_D = -\frac{r_D}{r_A}$
Overall yield based on flow rate	$\tilde{Y}_D = \frac{\dot{n}_D}{\dot{n}_{A0} - \dot{n}_A} = \frac{n_D}{n_{A0} - n_A}$
Conversion of batch and flow reactor	$X_A = \frac{\dot{n}_{A0} - \dot{n}_A}{\dot{n}_{A0}}$
Conversion of semi-batch reactor	$X_A = \frac{C_{A0}V_0 - C_A V}{C_{A0}V}$
Conversion of semi-batch reactor	$X_B = \frac{\dot{n}_{B0}t - C_B V}{\dot{n}_{B0}t}$

| Parallel reactions

Description	Equations
Concentration dependence of instantaneous selectivity	$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$
$\alpha_1 > \alpha_2$	$\uparrow C_A, \uparrow S_{D/U}$
$\alpha_1 < \alpha_2$	$\downarrow C_A, \uparrow S_{D/U}$
Temperature dependence of instantaneous selectivity	$S_{D/U} = \frac{r_D}{r_U} \frac{k_D}{k_U} = \frac{A_D}{A_U} \exp\left(-\frac{E_D - E_U}{RT}\right)$
$E_D > E_U$	$\uparrow T, \uparrow S_{D/U}$

	Description	Equations
	$E_D < E_U$	$\downarrow T, \uparrow S_{D/U}$

Enzymatic Reactions

	Description	Equations
	Pseudo-steady-state hypothesis	$r_{A*} = \sum r_{i,A*} = 0$

| Mechanism development

	Rate law	Mechanism (rule of thumb)
	Species concentration in denominator	Species collision with active intermediate
	Constant in denominator	Reaction of spontaneous decomposition of active intermediate
	Species concentration in numerator	Species produce active intermediate

| Michaelis-Menten kinetics

	Description	Equations
	Overall reaction	$E + S \longrightarrow E + P$
	Reaction mechanism	$S + E \xrightleftharpoons[k_{-1}]{k_1} ES$ $ES + W \xrightarrow{k_2} P + E$
	Enzyme balance	$[E_T] = [E] + [ES]$ $[E] = [E_T] - [ES]$
	Pseudo-steady-state approximation	$r_{ES} = k_1[S][E] - k_{-1}[ES] - k_2[ES][W] = 0$ $r_{ES} = k_1[S]([E_T] - [ES]) - k_{-1}[ES] - k_2[ES][W] = 0$ $[ES] = \frac{k_1[S][E_T]}{k_1[S] + k_{-1} + k_2[W]}$
	Turnover number (# substrates converted to product per unit time on one enzyme at saturation)	$k_{cat} = k_2[W]$
	Michaelis-Menten constant (attraction of enzyme of its substrate, [Substrate] which rate of rxn is 1/2 max)	$K_M = \frac{k_{cat} + k_{-1}}{k_1}$
	Maximum rate	$V_{max} = k_{cat}[E_T]$
	Michaelis-Menten equation Rate of reaction	$r_P = k_2[ES][W]$ $= \frac{k_1 k_2 [S][E_T][W]}{k_1[S] + k_{-1} + k_2[W]}$ $= \frac{k_{cat}[S][E_T]}{K_M + [S]}$ $= \frac{V_{max}[S]}{K_M + [S]}$
	Lineweaver-Burk equation	$\frac{1}{r_P} = \frac{K_M}{V_{max}} \frac{1}{[S]} + \frac{1}{V_{max}}$
	Eadie-Hofstee equation	$r_P = V_{max} - K_M \frac{r_P}{[S]}$

Description	Equations
Hanes-Woolf equation	$\frac{[S]}{r_P} = \frac{K_M}{V_{\max}} + \frac{1}{V_{\max}}[S]$

| Product-enzyme complex

Description	Equations
Overall reaction	$E + S \longrightarrow E + P$
Reaction mechanism	$S + E \rightleftharpoons ES \rightleftharpoons PE \rightleftharpoons P + E$
Briggs-Haldane equation	$r_P = \frac{V_{\max}([S] - [P]/K_C)}{[S] + K_{\max} + K_P[P]}$

| Batch enzymatic reactor

Description	Equations
Time	$t = \frac{K_M}{V_{\max}} \ln \left(\frac{[A]_0}{[A]} \right) + \frac{[A]_0 - [A]}{V_{\max}}$ $= \frac{K_M}{V_{\max}} \ln \left(\frac{1}{1 - X} \right) + \frac{[A]_0 X}{V_{\max}}$
Linearized form	$\frac{1}{t} \ln \left(\frac{[A]_0}{[A]} \right) = \frac{V_{\max}}{K_M} - \frac{[A]_0 - [A]}{K_M t}$

| Enzymatic inhibition

| Competitive inhibition

Description	Equations
Reaction mechanism	$E + S \rightleftharpoons ES$ $ES \longrightarrow E + P$ $E + I \rightleftharpoons EI \text{ (inactive)}$
Reaction rate	$r_P = \frac{V_{\max}[S]}{[S] + K_M \left[1 + \frac{[I]}{K_I} \right]}$
Lineweaver-Burk form ↑ K_I , ↑ slope	$\frac{1}{r_P} = \frac{1}{[S]} \left[\frac{K_M}{V_{\max}} \left[1 + \frac{[I]}{K_I} \right] \right] + \frac{1}{V_{\max}}$

| Uncompetitive inhibition

Description	Equations
Reaction mechanism	$E + S \rightleftharpoons ES$ $ES \longrightarrow E + P$ $ES + I \rightleftharpoons ESI \text{ (inactive)}$
Reaction rate	$r_P = \frac{V_{\max}[S]}{K_M + [S] \left[1 + \frac{[I]}{K_I} \right]}$

Description	Equations
Lineweaver-Burk form ↑ K_I , ↑ intercept	$\frac{1}{r_P} = \frac{1}{[S]} \frac{K_M}{V_{\max}} + \frac{1}{V_{\max}} \left[1 + \frac{[I]}{K_I} \right]$

| Noncompetitive (mixed) inhibition

Description	Equations
Reaction mechanism	$E + S \rightleftharpoons ES$
	$ES \longrightarrow E + P$
	$E + I \rightleftharpoons EI \text{ (inactive)}$
	$ES + I \rightleftharpoons ESI \text{ (inactive)}$
	$S + EI \rightleftharpoons ESI \text{ (inactive)}$
Reaction rate	$r_P = \frac{V_{\max} [S]}{([S] + K_M) \left[1 + \frac{[I]}{K_I} \right]}$
Lineweaver-Burk form ↑ K_I , ↑ slope, ↑ intercept	$\frac{1}{r_P} = \frac{1}{[S]} \frac{K_M}{V_{\max}} \left[1 + \frac{[I]}{K_I} \right] + \frac{1}{V_{\max}} \left[1 + \frac{[I]}{K_I} \right]$

Catalytic Reactions

| Reaction mechanisms

Reaction	Mechanism	Rate Law
Adsorption	$A + * \rightleftharpoons A^*$	$r_A = k_A \left[P_A[*] - \frac{[A^*]}{K_A} \right]$
Desorption	$A^* \rightleftharpoons A + *$	$r_D = k_D \left[[A^*] - \frac{P_A[*]}{K_D} \right]$
Single site surface rxn	$A^* \xrightleftharpoons[k_{-S}]{k_S} B^*$	$r_S = k_S \left[[A^*] - \frac{[B^*]}{K_S} \right]$
Dual site (I) surface rxn	$A^* + * \xrightleftharpoons[k_{-S}]{k_S} B^* + *$	$r_S = k_S \left[[A^*][*] - \frac{[B^*][*]}{K_S} \right]$
Dual site (II) surface rxn	$A^* + B^* \xrightleftharpoons[k_{-S}]{k_S} C^* + D^*$	$r_S = k_S \left[[A^*][B^*] - \frac{[C^*][D^*]}{K_S} \right]$
Dual site (III) surface rxn	$A^* + B^{*'} \xrightleftharpoons[k_{-S}]{k_S} C^{*'} + D^*$	$r_S = k_S \left[[A^*][B^{*'}] - \frac{[C^{*'}][D^*]}{K_S} \right]$
Eley-Rideal surface rxn	$A^* + B(g) \xrightleftharpoons[k_{-S}]{k_S} C^*$	$r_S = k_S \left[[A^*]P_B - \frac{[C^*]}{K_S} \right]$