

PHEN 612

SPRING 2008

WEEK 1

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Chapter 1*

1.1 Rate of reactions $-r_A$



Species A, B, and C

- We are interested in the rate of disappearance of A
- The rate of reaction, $-r_A$, is the number of moles of A reacting per unit time per unit volume (mole/s.m^3).

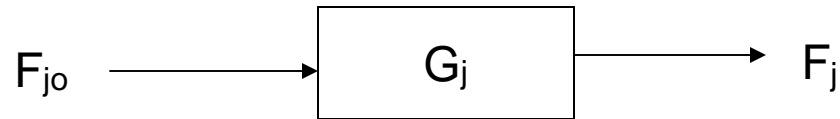
* Elements of Chemical Reaction Engineering – Fourth Edition
by H. Scott Fogler, Prentice Hall, 2006

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- For heterogeneous system, $-r_A$ [mole/s.g catalyst).
- The rate law for r_j is independent of the type of reactor used: $f(T, P, \text{type of catalyst, position})$
- The rate law is an algebraic expression (ex: $-r_A = k.C_A$) \rightarrow based on experiments.
- Convention: r_A : rate of formation or generation of A; $-r_A$: rate of disappearance of A

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1.2 The general mole balance equation



- Accumulation = input – output + generation

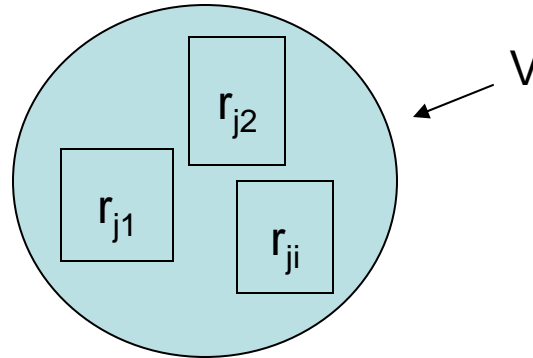
$$\frac{d(N_j)}{dt} = F_{j0} - F_j + G_j$$

If one assumes uniformity in the control volume: $G_j = r_j \cdot V$
(moles/time = moles/(time.volume).volume)

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- In general:

$$\Delta G_{ji} = r_{ji} \Delta V_i$$



Total rate of generation:
$$G_j = \sum_{i=1}^M \Delta G_{ji} = \sum_{i=1}^M r_{ji} \Delta V_i$$

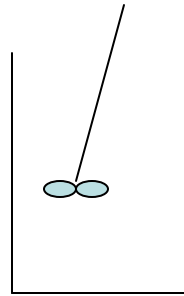
In the limit:
$$G_j = \int^V r_j dV \longrightarrow \frac{d(N_j)}{dt} = F_{jo} - F_j + G_j$$

$$\frac{d(N_j)}{dt} = F_{jo} - F_j + \int^V r_j dV$$

We need to estimate the time (batch) or reactor volume (continuous flow) necessary to convert a desired amount of reactants into product.

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1.3 Batch reactors:



Constant volume, no flow in, no flow out

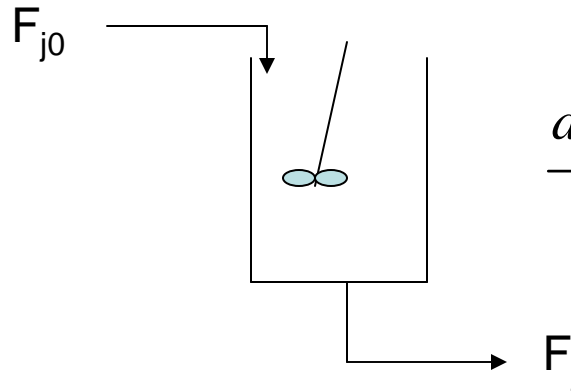
$$\frac{d(N_j)}{dt} = r_j V \quad t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$$

Time t_1 is the time necessary to reduce the # of moles from N_{A0} to N_{A1} .
Also the time to form N_{B1} moles of B

1.4 Continuous-flow reactors: CSTR; PFR; PBR

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1.4.1 Continuous stirred tank reactor (CSTR)



$$\frac{d(N_j)}{dt} = F_{j0} - F_j + \int_V r_j dV$$

Assuming steady-state operation: $d(N_j)/dt = 0$

No spatial variation in the reaction rate (i.e., perfect mixing):

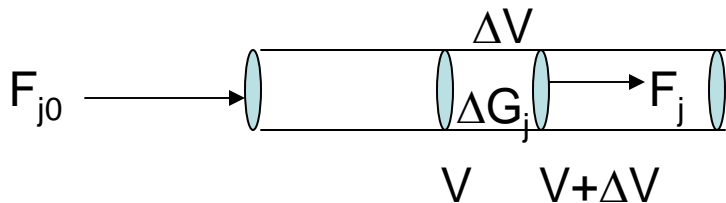
$$V = \frac{F_{j0} - F_j}{-r_j}$$

Remember: $F_j = C_j v$

$$V = \frac{C_{j0}v_0 - C_j v}{-r_j}$$

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1.4.1 Tubular reactor



$$\frac{d(N_j)}{dt} = F_{j0} - F_j + \int_V^{V+\Delta V} r_j dV$$

Input-output + generation = 0

$$F_{j|V} - F_{j|V+\Delta V} + r_j \Delta V = 0$$

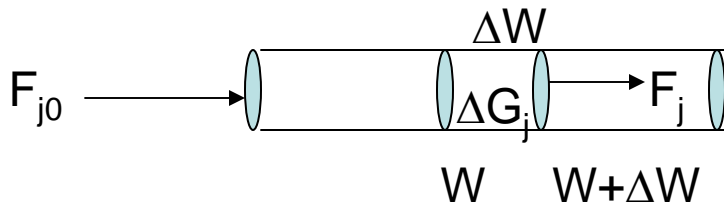
$$\frac{F_{j|V+\Delta V} - F_{j|V}}{\Delta V} = r_j$$

$$\frac{dF_j}{dV} = r_j \quad V_1 = \int_{F_{j1}}^{F_{j0}} \frac{dF_j}{-r_j} = \int_{F_{j0}}^{F_{j1}} \frac{dF_j}{r_j}$$

V_1 is the volume necessary to reduce the entering molar flow rate from F_{j0} to F_{j1}

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1.4.3 Packed-bed reactor



$$\frac{d(N_j)}{dt} = F_{j0} - F_j + \int_0^W r'_j dW$$

Input-output + generation = 0

$$F_{j|W} - F_{j|W+\Delta W} + r'_j \Delta W = 0$$

$$\frac{F_{j|W+\Delta W} - F_{j|W}}{\Delta W} = r'_j$$

$$\frac{dF_j}{dW} = r'_j \quad W_1 = \int_{F_{j1}}^{F_{j0}} \frac{dF_j}{-r'_j} = \int_{F_{j0}}^{F_{j1}} \frac{dF_j}{r'_j}$$

W_1 is the catalyst necessary to reduce the entering molar flow rate F_{j0} to F_{j1}

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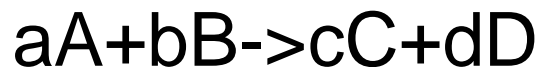
1.5 Industrial reactors

- Liquid-phase reactions (Batch and CSTR)
- Gas-phase reactions (PFR and PBR).
Fluidized-bed reactors are also used.

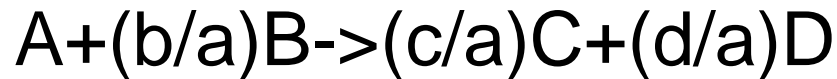
Chapter 2*

Conversion and reactor sizing

2.1 Defining conversion



- A: basis of calculation



“per mole of A” basis

A is the limiting reactant

- $X_A = (\text{moles of A reacted}) / (\text{moles of A fed})$

Chapter 2

2.2 Batch reactor design equation

$$t=0 \rightarrow N_{A0}; t \rightarrow N_{A0}X$$

$$N_A = N_{A0} - N_{A0}X = N_{A0}(1-X)$$

$$N_{A0} \frac{dX}{dt} = -r_A V$$

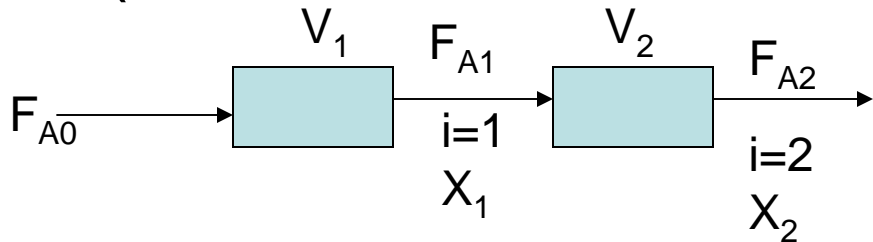
In terms of concentration, we use $N_A = C_A V \rightarrow dC_A/dt = r_A$

$$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$$

Chapter 2

2.5 CSTRs in series

- $X_i = (\text{total moles of A reacted up to point } i) / (\text{moles of A fed to the first reactor})$



Should we use 2 reactors: V_1 and V_2
Or just one reactor V_1+V_2 ?

Two CSTRs in series:

Reactor 1: input – output + generation = 0

$$F_{A0} - F_{A1} + r_{A1}V_1 = 0$$

$$\text{But } F_{A1} = F_{A0} - F_{A0}X_1$$

As a result

$$V_1 = F_{A0} (1/r_A)X_1$$

Reactor 2: input – output + generation = 0

$$F_{A1} - F_{A2} + r_{A2}V_2 = 0$$

As a result

$$V_2 = F_{A0} (1/r_A)(X_2 - X_1)$$

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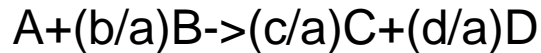
Rate laws and Stoichiometry

- **Basic definitions**

- Homogeneous reaction: one phase
- Heterogeneous reaction: more than one phase
- Irreversible reaction: \longrightarrow
- Reversible reaction: \rightleftharpoons
- Unimolecular: involving one atom (or molecule)
- Bimolecular: two atoms (or molecules)
- Termolecular: Three atoms

Chapter 3

3.1.1 Relative rates of reaction



- For every mole of A consumed, c/a moles of C appear.
- Rate of formation of C = (c/a) rate of disappearance of A:
 $r_C = (c/a) (-r_A) = -(c/a) r_A$

Also: $r_C = (c/d) (r_D)$

In general: $(-r_A/a) = (-r_B/b) = (r_C/c) = (r_D/d)$

3.2 Reaction order and rate law

$$-r_A = k_A (T) f (C_A, C_B, \dots)$$

This is called a kinetic expression or a rate law

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3.2.1 Power law model and elementary rate laws

$$-r_A = k_A C_A^\alpha C_B^\beta$$

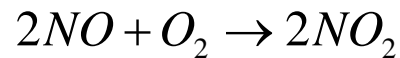
- The order of a reaction: the power to which the concentrations are raised in the rate law.
- The reaction is α order with respect to reactant A
- The reaction is β order with respect to reactant B
- $N = \alpha + \beta$ is the overall order of the reaction
- Units: $-r_A$ (concentration/time)
- k_A (vary with the reaction order)

Ex: $-r_A = k_A C_A^3$

k_A (dm³/mol)².s⁻¹

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- Elementary reaction involves a single step. The stoichiometric coefficients are identical to the power in the rate law.



$$-r_{NO} = kC_{NO}^2 C_{O_2}$$

3.2.2 Non elementary rate laws

A large number of both homogeneous and heterogeneous reactions do not follow single reaction laws

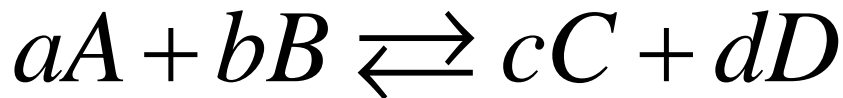
- Homogeneous: $CO + Cl_2 \rightarrow COCl_2$ $-r_{CO} = kC_{CO}C_{Cl_2}^{3/2}$ gas phase
- Heterogeneous: $C_6H_5CH_3 + H_2 \xrightarrow{\text{Solid cat}} C_6H_6 + CH_4$ Methane: M
Toluene: T Benzene: B

$$-r_T = \frac{kP_{H_2}P_T}{1 + K_B P_B + K_T P_T}$$

K_B and K_T are absorption rate constants

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3.2.3 Reversible reactions



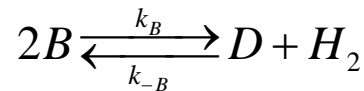
$$K_c = \frac{C_C^c C_D^d}{C_A^a C_B^b} \quad \text{Thermodynamic equilibrium (e) relationship}$$

Unit of K_c : $(\text{mol/dm}^3)^{d+c-b-a}$

$$2C_6H_6 \xrightleftharpoons[k_{-B}]{k_B} C_{12}H_{10} + H_2$$

benzene diphenyl

How do we derive rate laws?



Forward:

$$-r_{B,f} = k_B C_B^2; \quad r_{B,f} = -k_B C_B^2$$

Reverse:

$$r_{B,r} = k_{-B} C_B C_{H_2}$$

$$r_B = r_{B,\text{net}} = r_{B,f} + r_{B,r}$$

Concentration equilibrium constant

$$-r_B = k_B \left(C_B^2 - \frac{k_{-B}}{k_B} C_D C_{H_2} \right); \quad -r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right); \quad K_c = \frac{k_B}{k_{-B}}$$

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- K_c ↓ as T ↑ for exothermic reaction
- K_c ↑ as T ↑ for endothermic reaction
- Keep in mind that $(-r_A/a) = (-r_B/b) = (r_C/c) = (r_D/d)$

$$\frac{r_D}{1} = \frac{r_B}{-2} = \frac{k_B}{2} \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right); \quad k_D = \frac{k_B}{2}$$

This is why we need to define a rate constant in term of particular species

At equilibrium:
$$K_c = \frac{C_{De} C_{H_2e}}{C_{Be}^2}$$

$$K_c(T) = K_c(T_1) \exp \left[\frac{\Delta H_{RX}}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad \Delta H_{RX}: \text{heat of reaction}$$

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3.3 The reaction rate constant

$$k_A(T) = Ae^{-E/(RT)}$$

Arrhenius equation

$$\ln k_A = \ln A - \frac{E}{R} \left(\frac{1}{T} \right)$$

A: pre-exponential factor or frequency factor

E: activation energy in J/mol, cal/mol

R: gas constant = 8.314 J/mol.K = 1.987 cal/mol.K

T: absolute temperature in K

$$k(T) = k(T_0) e^{\frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}$$

E: energy to break bonds and overcome repulsion forces between reactants

“reaction coordinate” helps to visualize the process.

Energy distribution of reactant molecules: compare fraction of collisions at two different temperatures. As the temperature increases, more molecules have sufficient energy to react.