

1. Mole Balances

- The Rate of Reaction, $-r_A$
- The General Mole Balance Equation
- Continuous Flow Reactors
 - CSTR (Continuous-Stirred Tank Reactor)
 - PFR (Tubular Reactor)
 - PBR (Packed-Bed Reactor)
- Industrial Reactors



0. Chemical Identity

○ Reaction

- When a chemical species has lost its chemical identity

○ Identity of a chemical species

- The *kind*, *number*, and *configuration* of that species' atoms



1. Reaction Rate I (p.2)

○ Reaction Rate

- The rate at which a species loses its chemical identity per unit volume



r_A = the rate of formation of species A per unit volume

$-r_A$ = the rate of a disappearance of species A per unit volume

r_B = the rate of formation of species B per unit volume

- ☞ For a catalytic reaction, we refer to $-r_A'$, which is the rate of disappearance of species A on a **per mass of catalyst basis**

1. Reaction Rate II

○ Reaction Rate [Example]



- If B is being created at a rate of 0.2 moles per liter per second, ie, the rate of formation of B is,

$$r_B = 0.2 \text{ mole/l/s}$$

then A is disappearing at the same rate:

$$-r_A = 0.2 \text{ mole/l/s}$$

the rate of formation of A is

$$r_A = -0.2 \text{ mole/l/s}$$

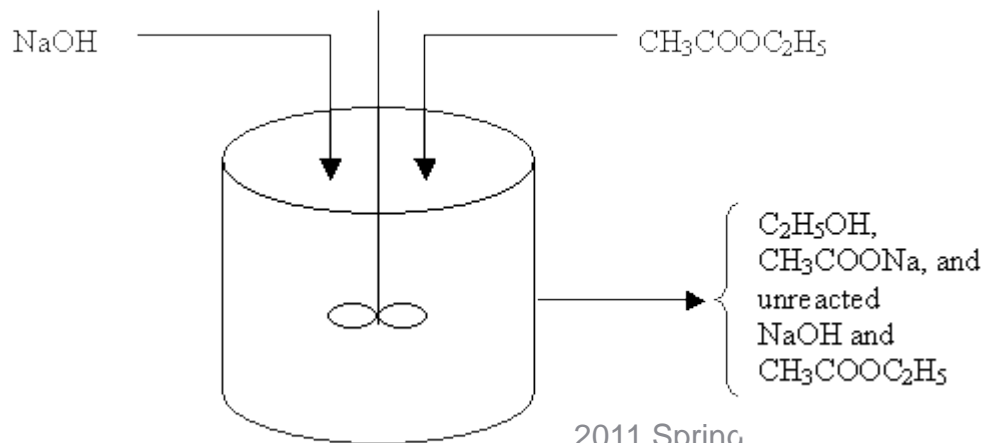
1. Reaction Rate III

○ Is sodium hydroxide reacting?

- Reaction rate definition, $r_A = dC_A/dt$

• **only** holds for constant volume batch system carried out to obtain chemical reaction rate data

- Sodium hydroxide and ethyl acetate are continuously fed to a rapidly stirred tank in which they react to form sodium acetate and ethanol:



$$\frac{dC_A}{dt} = 0$$

1. Reaction Rate IV

- Consider species j
 - r_j is the rate of formation of species j per unit volume [e.g. mol/dm³*s]
 - r_j is a function of concentration, temperature, pressure, and the type of catalyst (if any)
 - r_j is independent of the type of reaction system (batch, plug flow, etc.)
 - r_j is an algebraic equation, not a differential equation
- Examples of other rate laws

$$-r_A = \frac{k_1 C_A}{1 + k_2 C_A} \quad -r_A = k \quad -r_A = k_1 C_A$$

1. Reaction Rate V

○ Self test

- The convention for rates of reaction



in which the rate of disappearance of A is 5 moles of A per dm³ per second at the start of the reaction.

- At the start of the reaction

(a) What is $-r_A$?

(b) What is the rate of formation of B?

(c) What is the rate of formation of C?

(d) What is the rate of disappearance of C?

(e) What is the rate of formation of A, r_A ?

(f) What is $-r_B$?

2. General Mole Balance Equation (p.8) I

○ In a given boundary system

- F_{A0} = Entering molar flow rate of A (mol/time)

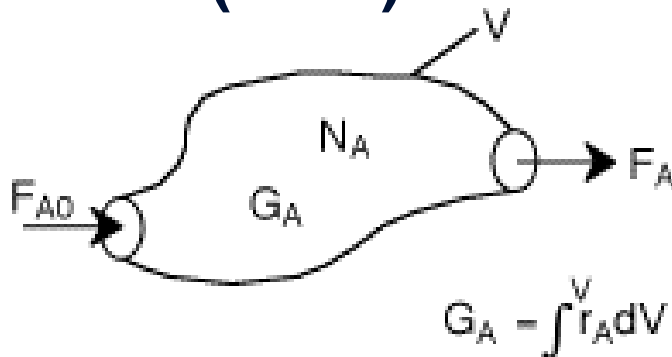
F_A = Exiting molar flow rate of A (mol/time)

G_A = Rate of generation(formation) of A (mol/time)

V = Volume (vol e.g. m³)

r_A = rate of generation(formation) of A (mole/time•vol)

N_A = number of moles of A inside the system Volume
 V (mols)



IN-OUT+GENERATION=ACCUMULATION

$$F_{A0} - F_A + \int_0^V r_A dV = \frac{dN_A}{dt}$$

2. General Mole Balance Equation II

○ Self Test

1. The rate law

(a) is a differential equation T F

(b) relates reaction rate and concentration of reacting species T F

(c) is a function of temperature; T F

2. The rate of formation of species A is per unit volume

(a) r_A T F

(b) $-r_A$ T F

(c) the rate of generation of species A per unit volume T F

(d) r'_A T F

(e) none of the above T F

2. General Mole Balance Equation III

3. At a particular time t , the rate of formation of B in the reaction, r_B , is $10 \text{ mole/dm}^3\cdot\text{min}$. Which of the following are true? $A \rightarrow B$

- a. The rate of disappearance of B is $-10 \text{ moles/dm}^3\cdot\text{min}$.
- b. The rate of formation of A is $-10 \text{ mole/dm}^3\cdot\text{min}$.
- c. The rate of disappearance of A is $10 \text{ moles/dm}^3\cdot\text{min}$.
- d. $r_A = -10 \text{ moles/dm}^3\cdot\text{min}$
- e. $-r_A = 10 \text{ moles/dm}^3\cdot\text{min}$
- f. $-r_B = -10 \text{ moles/dm}^3\cdot\text{min}$
- g. Some of the above
- h. All of the above
- i. None of the above
- j. A will disappear faster if a magician is present

3. Batch Reactors I

- **Batch Reactors**
 - **Used for a small-scale operation,**
 - **testing a new process not fully developed**
 - **manufacturing expensive products**
 - **processes difficult to convert to continuous operation**
 - **Advantages**
 - **high conversion**
 - **Disadvantages**
 - **high labor cost per batch**
 - **variability of product quality**
 - **difficulty of large-scale production**



3. Batch Reactors II

- Reaction rate

- Neither inflow not outflow

$$\int^V r_A dV = \frac{dN_A}{dt}$$

- Rxn rate is uniform throughout the reactor volume

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

- For isomerization of species A



$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt}$$

3. Batch Reactors III

- Reaction time

- Time t_1 to change $N_{A0} \rightarrow N_{A1}$, (Generally $N_{A0} > N_{A1}$)

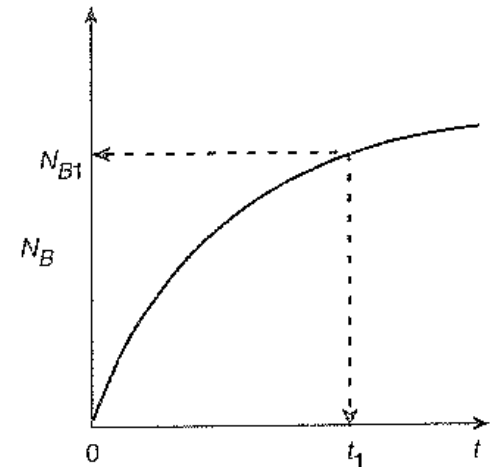
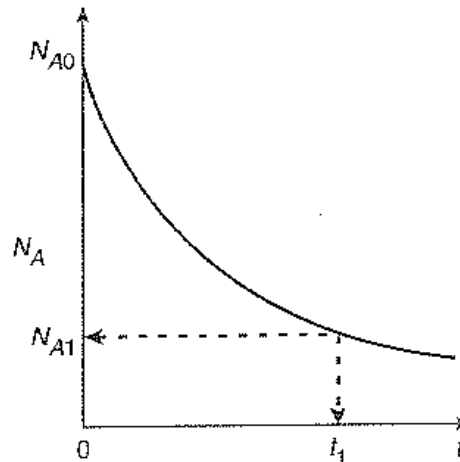
$$\frac{dN_A}{dt} = r_A V$$

- Rearranging

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

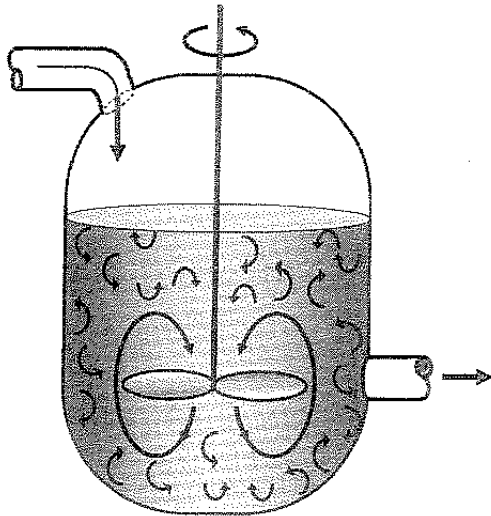
- Integrating

$$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$$



4. Continuous Flow Reactors I

- **Continuous-Stirred tank Reactor 1**
 - **CSTR, vat, or Backmix reactor**
 - **Primarily for liquid phase reactions**
 - **Operated at steady state (perfectly mixed)**
 - **T, C_j, r_j inside CSTR is uniform**
- ☞ **residence-time distribution study for highly non-ideal mixing system**



4. Continuous Flow Reactors II

○ Continuous-Stirred tank Reactor 2

- General mole balance

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt}$$

- Operated at st-st

$$\frac{dN_A}{dt} = 0 \quad \int^V r_A dV = Vr_A$$

- Design equation for CSTR

$$F_{A0} - F_A + \int^V r_A dV = \frac{dN_A}{dt} \quad \text{or}$$

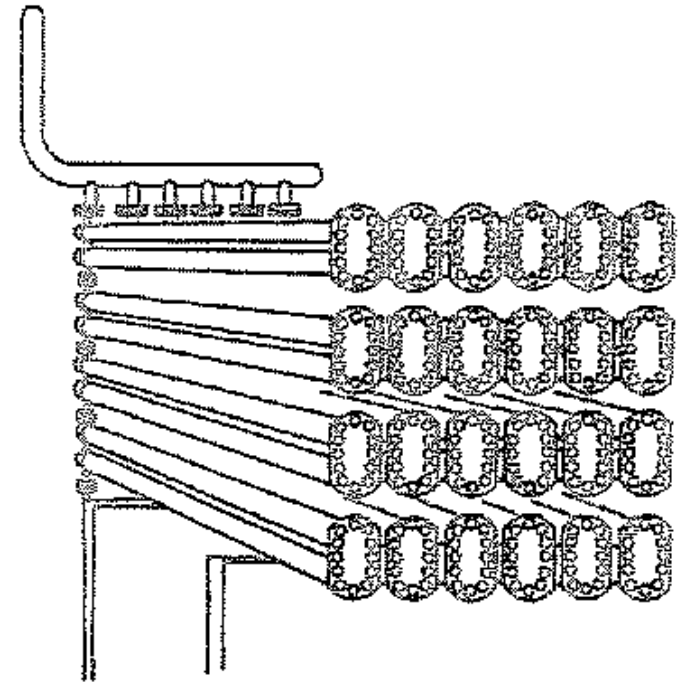
$$V = \frac{F_{A0} - F_A}{-r_A}$$

- With volumetric flow rate v , $F_A = C_A \cdot v$

4. Continuous Flow Reactors III

○ Tubular Reactor 1

- A cylindrical pipe normally operated at st-st
- Used most often for gas-phase rxn
- Reactants are continually consumed as they flow down the length of the reactor
- Plug flow along pipe



4. Continuous Flow Reactors IV

○ Tubular Reactor 2

- General mole balance

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt}$$

- Operated at st-st

$$\frac{dN_A}{dt} = 0$$

- Design equation for PFR

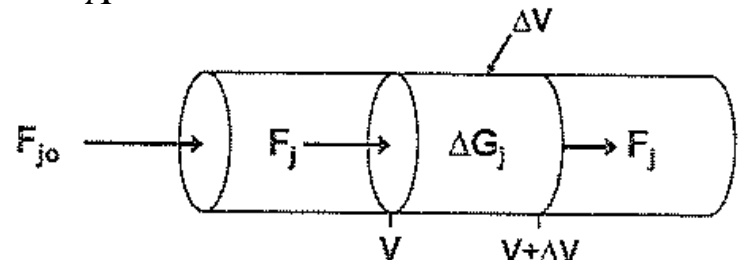
$$F_{A0} - F_A + \int^V r_A dV = 0$$

- Differential w.r.t V

$$0 - \frac{dF_A}{dV} = -r_A$$

- Or

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



4. Continuous Flow Reactors V

- Tubular Reactor 3

- Rearranging and integrating between

$$V = 0, F_A = F_{A0}$$

$$V = V_1, F_A = F_{A1}$$

$$V_1 = \int_{F_{A0}}^{F_{A1}} \frac{dF_A}{r_A} = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$$



4. Continuous Flow Reactors VI

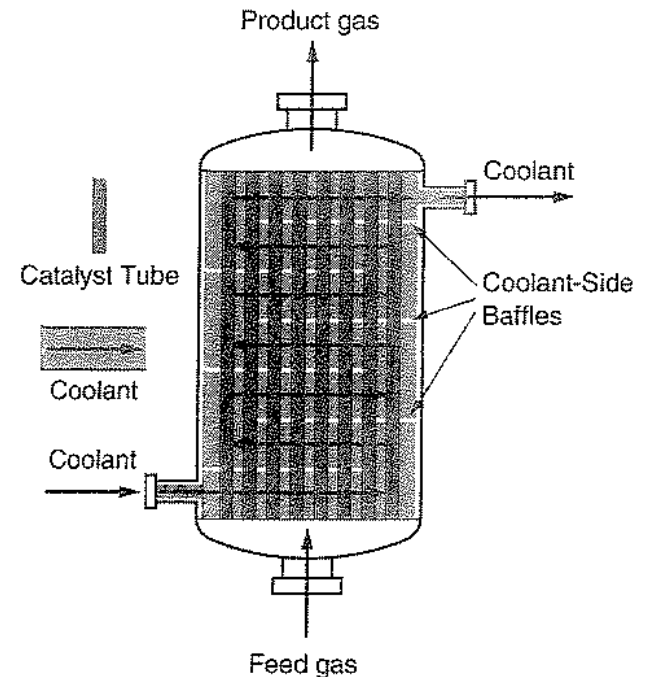
○ Pack-Bed Reactor 1

- Involving fluid-solid heterogeneous rxns

• the rxn takes place on the surface of the catalysts

• rxn rat is based on mass of solid catalyst W (rather than on volume V)

$-r'_A = \text{mol A reacted/s} \cdot \text{g cat.}$



4. Continuous Flow Reactors VII

○ Pack-Bed Reactor 2

- General mole balance

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt}$$

- Operated at st-st

$$\frac{dN_A}{dt} = 0$$

- Design equation for PBR

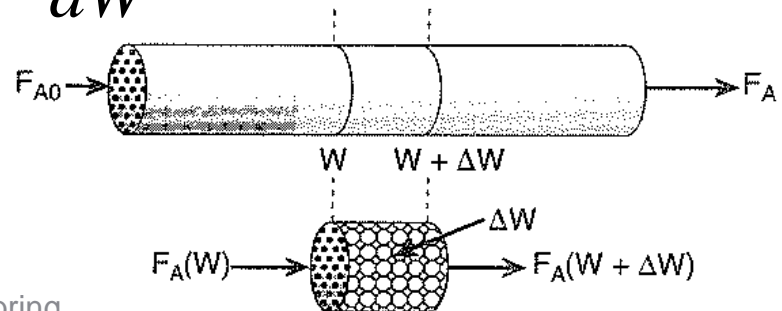
$$F_{A0} - F_A + \int^V r'_A dW = 0$$

- Differential w.r.t W

$$0 - \frac{dF_A}{dW} = -r'_A$$

- Or

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



4. Continuous Flow Reactors VIII

○ Pack-Bed Reactor 3

- Rearranging and integrating between

$$W = 0, F_A = F_{A0}$$

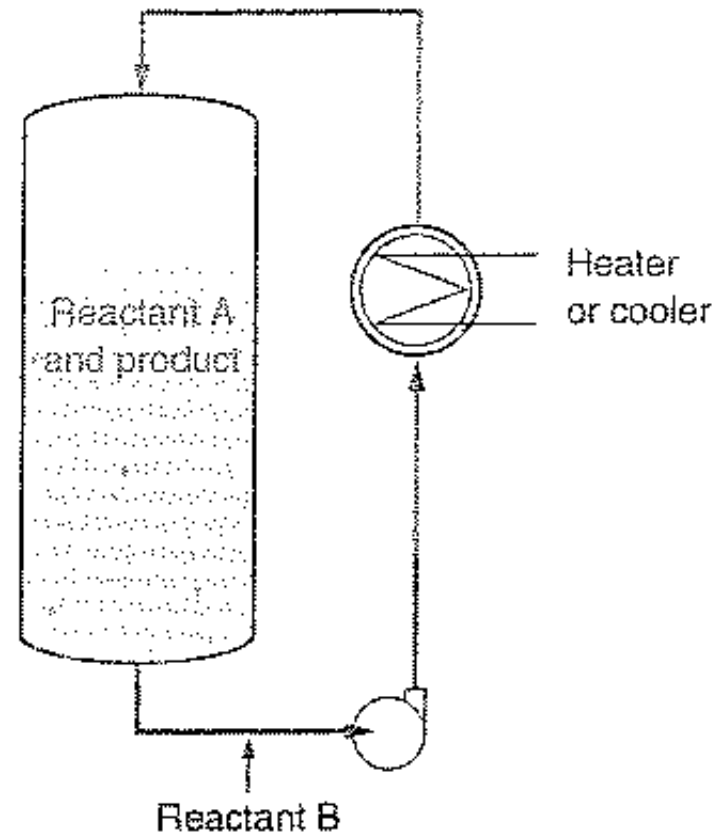
$$W = W_1, F_A = F_{A1}$$

$$W_1 = \int_{F_{A0}}^{F_{A1}} \frac{dF_A}{r'_A} = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r'_A}$$



5. Industrial Reactors I

- **Liquid-Phase Reactions 1**
 - **Semibatch reactors**
 - **T control by regulation of feed rate**
 - **minimizing side rxns to maintain conc of one of the reactants**
 - **2-phase rxns where gas bubbled out**

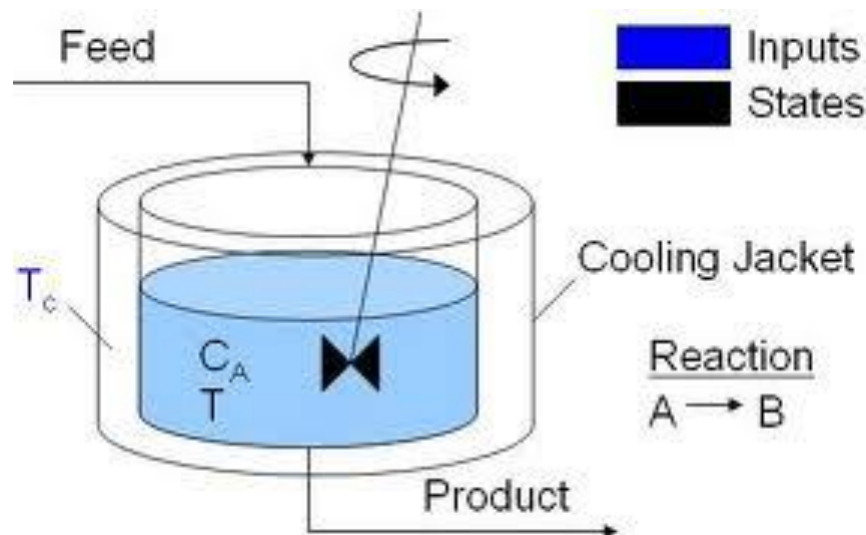


5. Industrial Reactors II

○ Liquid-Phase Reactions 2

- CSTRs

- intense agitation required
- stand alone or in series
- relatively good T control
- the smallest conversion \Rightarrow large size necessary



5. Industrial Reactors III

○ Gas-Phase Reactions 1

- PFRs

- easy to maintain (no moving parts)
- the highest conversion
- difficult T control \Rightarrow
hot spot if exothermic rxn

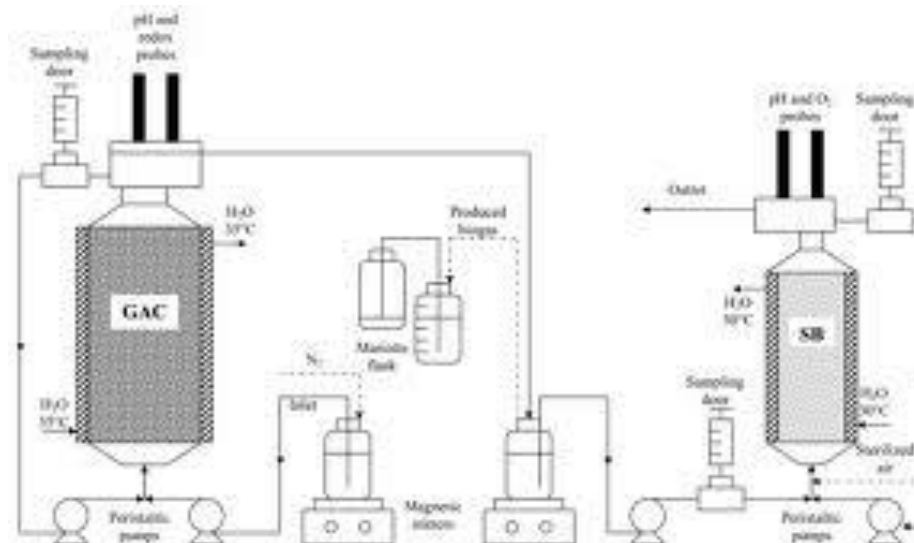


5. Industrial Reactors IV

○ Gas-Phase Reactions 2

- PBRs

- basically the same to PFRs with solid catalyst particles
- the catalyst is troublesome to replace
- channeling of the gas flow \Rightarrow dead zone



5. Industrial Reactors V

○ Gas-Phase Reactions 3

- Fluidized-Bed Reactors

- analogous to CSTR – well mixed, even T distribution
- approximately modeled as a CSTR [for exact design, it need customizing]
- often high cost of reactor and catalyst regeneration

