# CHBI 502

## REACTION ENGINEERING

# CHBI 502

- HWs will be distributed after the chapters are covered, deadlines will be posted
  - **NO** late submission
- MT dates will be determined (mid of the semester)
- Final exam date will be determined by the registrar's office
- You can contact me anytime through e-mail (okeskin@..)
- You are wellcome during office hours, you need to ask me if I will be at the office other than these hours.
- No **cheating** (HWs, projects, exams)

POLICY ON COLLABORATION AND ORIGINALITY

Academic dishonesty in the form of cheating, plagiarism, or collusion are serious offenses and are not tolerated at Koç University. University Academic Regulations and the Regulations for Student Disciplinary Matters clearly define the policy and the disciplinary action to be taken in case of academic dishonesty.

Failure in academic integrity may lead to suspension and expulsion from the University.

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- **Textbook** Elements of Chemical Reaction Engineering (4th ed.), H.S. Fogler Prentice Hall, Upper Saddle River, NJ (2005).

- **Course Outline,** Tentative schedule
- 
- Review: Chemical Kinetics and Ch1-6, *Two-three weeks*
- Chapter 1: Mole Balances
- Chapter 2: Conversion and Reactor Sizing
- Chapter 3: Rate Law and Stoichiometry
- Chapter 4: Isothermal Reactor Design
- Chapter 5: Collection and Analysis of Rate Data
- Chapter 6: Multiple Reactions
- Chapter 7: Reaction Mechanisms, Pathways, Bioreactions and Bioreactors , *Two weeks*
- Chapter 8: Steady-State Nonisothermal Reactor Design, *Two weeks*
- Chapter 9: Unsteady-state Nonisothermal Reactor Design, *One week*
- Chapter 10: Catalysis and Catalytic Reactors, *Two weeks*
- Chapter 11: External Diffusion Effects on Heterogeneous Reactions, *One Week*
- Chapter 12: Diffusion and Reaction in Porous Catalysts, *Two Weeks*
- Student presentations on projects, One week

# Elements of Chemical Rxn Enginnering

- Chemical kinetics is the study of chemical rxn rates and reaction mechanisms.
- Chemical reaction engineering (CRE) combines the study of chemical kinetics with the reactors in which the reactions occur.

**Objective of the course:** Learn how to design equipment for carrying out desirable chemical reactions *(what size and what type of equipment)*

**Chemical Kinetics & Reactor Design**

The reaction system thet operates in the safest and most efficient manner can be the key to the success of the plant.

Modelling of;

Chemical plant
Pharmacokinetics
Microelectronics
Digestive system of an animal

# Chapter1 MOLE BALANCES

**1. Chemical Identity**

A chemical species is said to have reacted when it has lost its chemical identity. The identity of a chemical species is determinde by the kind, number, and configuration of that species' atoms.

Three ways a chemical species can lose its chemical identity:

1. Decomposition $CH_3CH_3 \rightarrow H_2 + H_2C = CH_2$
2. Combination $N_2 + O_2 \rightarrow 2NO$
3. Isomerization $C_2H_5CH = CH_2 \rightarrow CH_2 = C(CH_3)_2$

**2. Reaction Rate:**

The reaction rate is the rate at which a species looses its chemical identity per unit volume. The rate of a reaction can be expressed as the rate of disappearance of a reactant or as the rate of appearance of a product. Consider species A:

$$\mathbf{A \rightarrow B}$$

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

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

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

**Example:** $A \rightarrow B$

If B is being created 0.2 moles per decimeter cubed per second, ie,

$r_B$ = 0.2 mole/$dm^3$ s

Then A is disappearing at the same rate:

$-r_A$ = 0.2 mole/$dm^3$ s

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

**NOTE:** $dC_A/dt$ is not the rate of reaction *(This is only true for a batch system, we will see)*

If continuous → $dC_A/dt = 0$

The rate law does not depend on reactor type!

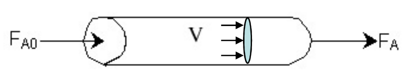
$-r_A$ is the # of moles of A reacting (disappearing) per unit time per unit volume (mol/$dm^3$ s)

In a reactor, two extreme conditions are considered:

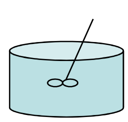
1. No mixing of streams
2. Complete mixing (desirable)

**Classification of reactions**

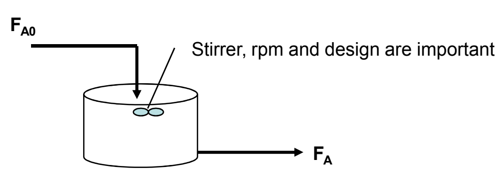
- **Ideal mixing (no axial mixing, complete radial mixing)**
- Steady-state : conditions donot change with time at any point (PFR)




- **Complete mixing**
- non-steady-state**:** Uniform composition and temperture at any given instant, change with time (t)



**Batch**




**CSTR)**

# Thus,

- Batch or continuous
- Tank or tubular
- Homogeneous or heterogeneous

Consider species j:

- $r_j$ is the rate of formation of species j per unit volume [e.g. mol/dm$^3$ 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.

We use an algebraic equation to relate the rate of reaction, $-r_A$, to the concentration of reacting species and to the temperature at which the reaction occurs [e.g. $-r_A = k(T)\, C_A^2$]

For example, the algebraic form of the rate law for $-r_A$ for A (products) may be;

a linear function of concentrations: $\Longrightarrow$ $-r_A = k \cdot C_A$

or, it may be some other algebraic function of conc'n as: $\Longrightarrow$ $-r_A = k \cdot C_A^2$

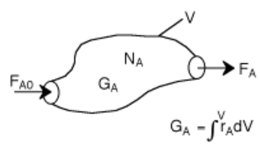
or can be determined by experiments: $\Longrightarrow$ $-r_A = \dfrac{k_1 \cdot C_A}{1 + k_2 \cdot C_A}$

3. **General Mole Balance Equation:**

IN – OUT + GENERATION = ACCUMULATION

$$F_{A0} - F_A + \int_0^V r_A \cdot dV = \frac{dN_A}{dt} \qquad [moles/time]$$

$N_A$: # of moles of species A in the system at time t.

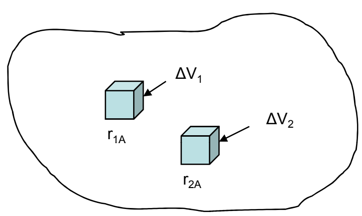



$G_A = r_A V$ (if all system variables (T, $C_A$, etc.) are spatially uniform throughout system volume)

$$G_A = r_A \cdot V$$

$$\left[\frac{moles}{time}\right] = \left[\frac{moles}{time \cdot volume}\right] \cdot [volume]$$

If the rate of formation of A varies with position:




$$\Delta G_{A1} = r_{1A} \cdot \Delta V_1 \quad etc.\ \ for\ \ all\ subvolumes$$

$$G_A = \sum_{i=1}^{m} \Delta G_{iA} = \sum_{i=1}^{m} r_{iA} \cdot \Delta V_i \quad for\ \ M\ \ subvolumes$$

$$G_A = \int r_A \cdot dV$$

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

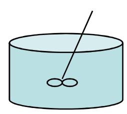
⟹ Basic equation for any species A entering, leaving, reacting ...

# Mole Balance on Different Reactor Types

**Batch Reactor** is used for small-scale operations, for testing new processes, for the manufacture of expensive products, and for the processes that are not easy to convert to continuous.

high conversion rates (time spend is longer)

high labor cost and & variability of products from batch-to-batch



$$F_{A0} = 0 \qquad F_A = 0$$

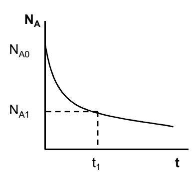
$$\frac{dN_A}{dt} = r_A \cdot V$$

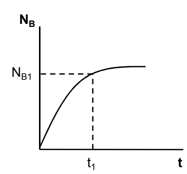
$$\frac{dN_j}{dt} = \int r_j \cdot dV$$

If perfect mixing

(no volume change throughout volume)

The # of moles changing (in A → B) is as follows:




What time is the necessary to produce $N_{A1}$ starting from $N_{A0}$?

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

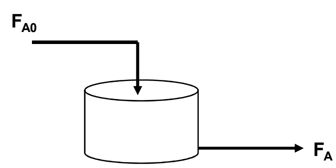
$$dt = \frac{dN_A}{r_A \cdot V}$$

$$\int_0^{t_1} dt = \int_{N_{A0}}^{N_{A1}} \frac{dN_A}{r_A \cdot V} \quad \Rightarrow \quad t_1 = \int_{N_{A0}}^{N_{A1}} \frac{dN_A}{r_A \cdot V}$$

**Continuous Flow Reactors (CFR)** operate at steady state.

- Continuous Stirred Tank Reactor (CSTR)
- Plug Flow Reactor (PFR)
- Packed Bed Reactor (PBR)

**CSTR**




usually used for liquid-phase rxns

usually operated at steady state

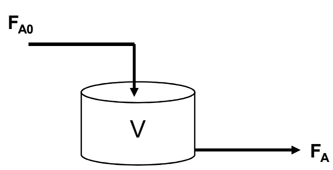
usually assumed to be perfectly mixed

T ≠ f(t,V)

General Mole Balance on System Volume V

IN – OUT + GENERATION = ACCUMULATION

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




**Assumptions**

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

Well mixed $\int r_A \cdot dV = r_A \cdot V$

$$F_{A0} - F_A + r_A \cdot V = 0$$

Design eq'n for CSTR $$V = \frac{F_{A0} - F_A}{-r_A}$$

$F_{A0} = C_{A0} \cdot v$ ⟶ $V = \frac{C_{A0} \cdot v_0 - C_A \cdot v}{-r_A}$

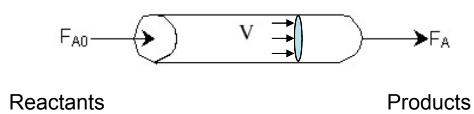
Molar flow rate ($F_{A0}$); concentration ($C_{A0}$)

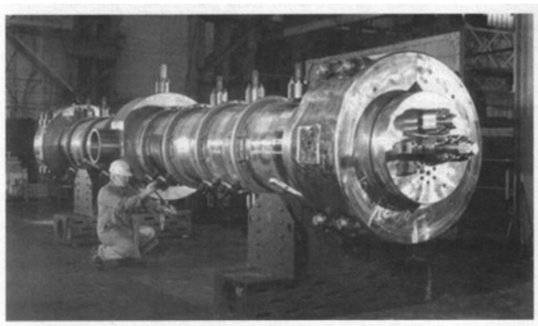
**Tubular Reactors** consists of a cylindirical pipe and is operated at steady state. Mostly used for gas phase rxns.

PFR Derivation: uniform velocity in turbulent flow (no radial variation in velocity, concentration, temperature, reaction rate)

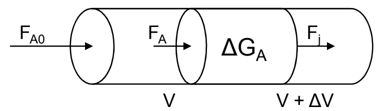
IN – OUT + GENERATION = ACCUMULATION

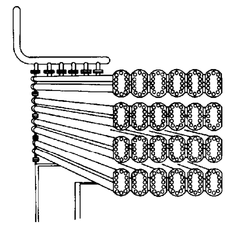
$$F_{A0} - F_A + \int_0^V r_A \cdot dV = \frac{dN_A}{dt}$$



Polyethylene reactor; this 16-in inner-diameter reactor is designed to operate at 35,000 psi and 600°F; in operation, this reactor is in a vertical configuration. Courtesy of Autoclave Engineers, Division of Snap-tite, Inc.



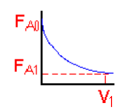
$$\Delta G_A = \int^{\Delta V} r_A \cdot dV = r_A \cdot \Delta V$$

$$F_A\big|_V - F_A\big|_{V+\Delta V} + r_A \cdot \Delta V = 0$$

Divide by ΔV and rearrange: $$\left[\frac{F_A\big|_{V+\Delta V} - F_A\big|_V}{\Delta V}\right] = r_A$$

Taking the limit as ΔV→0: $$\frac{dF_A}{dV} = r_A$$

$$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$$



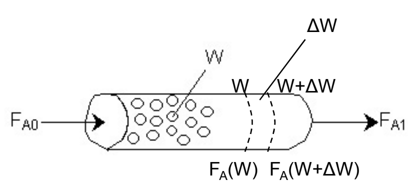

**Packed Bed Reactors (PBR)** are not homogenous, the fluid-solid heterogenous rxn take place on the surface of the catalyst. Rate (r') is dependent on the mass of catalyst (W).

-rA' = mol A reacted / (s) (g catalyst)

General Balance on W

IN – OUT + GENERATION = ACCUMULATION

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



Steady State

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

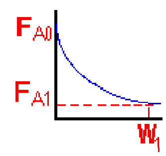
$$F_{A0} - F_A + \int_0^V r_A' \cdot dV = \frac{dN_A}{dt}$$

Differentiate with respect to W and rearrange

$$\boxed{\frac{dF_A}{dW} = r_A'}$$

When pressure drop through the reactor and catalyst decay are neglected, the integral eg'n can be used to find W:

$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A'} = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r_A'}$$




**Batch Reactor Times**

A → B

Calculate the time to reduce the number of moles by a factor of 10 ($N_A = N_{A0}/10$) in a batch reactor for the above reaction with

$-r_{A'} = k\ C_A$ when k = 0.046 min$^{-1}$


$$Mol\ \ balance:$$

$$In - Out + Generation = Accumulation$$

$$0 - 0 + r_A \cdot V = \frac{dN_A}{dt}$$

$$Rate\ \ law:$$

$$-r_A = k \cdot C_A \quad \Rightarrow \quad r_A = -k \cdot C_A = -k \cdot \left(\frac{N_A}{V}\right)$$

$$r_A \cdot V = -k \cdot N_A \quad \Rightarrow \quad \frac{dN_A}{dt} = -k \cdot N_A$$

*Solve*:

$$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A \cdot V} = -\int_{N_{A0}}^{N_A} \frac{dN_A}{-r_A \cdot V}$$

$$-r_A \cdot V = k \cdot C_A \cdot V = k \cdot \frac{N_A}{V} \cdot V = k \cdot N_A$$

$$t = \int_{N_A}^{N_{A0}} \frac{dN_A}{k \cdot N_A} = \frac{1}{k} \cdot \ln \frac{N_{A0}}{N_A}$$

$$N_A = \frac{N_{A0}}{10} \quad \Rightarrow t = \frac{1}{0.046\,\text{min}} \cdot \ln(10)$$

Therefore, t = 50 minutes

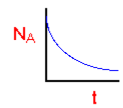
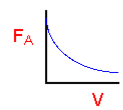
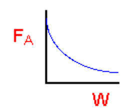
# Summary of Chapter 1

- Define the rate of chemical reaction.
- Apply the mole balance equations to a batch reactor, CSTR, PFR, and PBR.

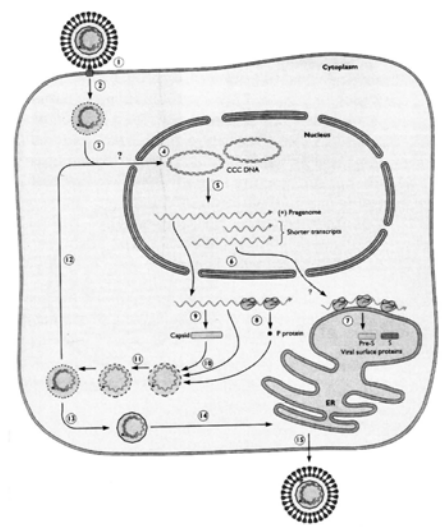
- **Batch reactor:** no in-out streams, no spatial variations in conc'n
- **CSTR:** no spatial variations in the tank, steady state
- **PFR:** spatial variations along the reactor, steady state
- **PBR:** spatial variations along the reactor, steady state

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

⟹ Basic equation for any species A entering, leaving, reacting ...

| Reactor | Differential | Algebraic | Integral | |
|---|---|---|---|---|
| **Batch** | $\frac{dN_A}{dt} = r_A V$ | | $t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$ |   |
| **CSTR** | | $V = \frac{F_{A0} - F_A}{-r_A}$ | | |
| **PFR** | $\frac{dF_A}{dV} = r_A$ | | $V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$ |   |
| **PBR** | $\frac{dF_A}{dW} = r_A'$ | | $W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A'}$ |   |

general reaction, A->B



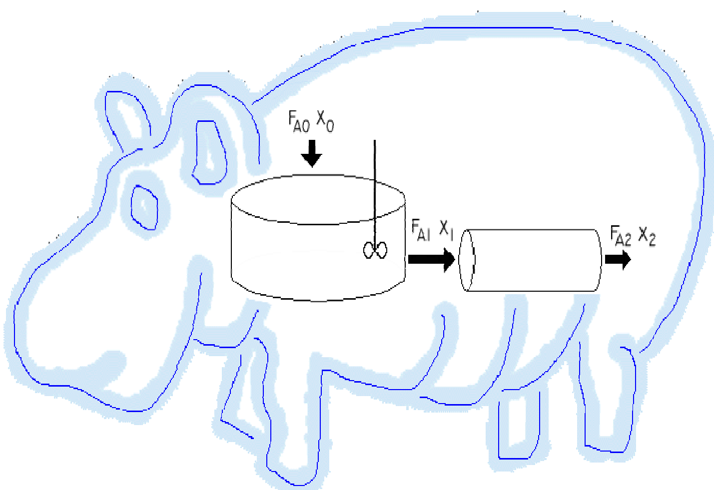

The chemical events comprising the reproduction cycle of the hepatitis B virus. Courtesy of ASM Press [4].

# Modeling the Digestive System of a Hippopotamus*

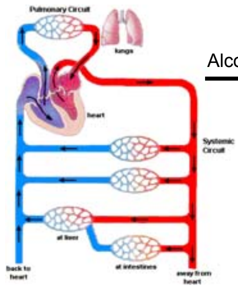
Matthew Robertson, Fredrik Persson, Brian Vicente, Professor H. Scott Fogler

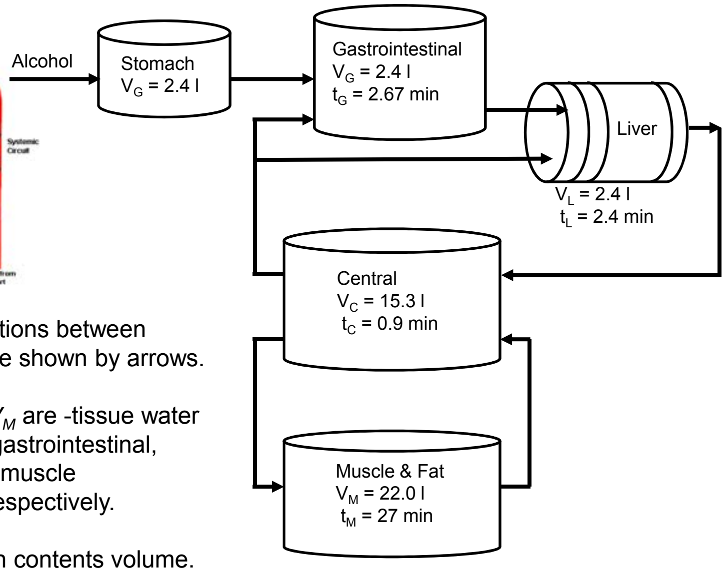
"Even hippo's like Chemical Reaction Engineering."

*From a problem suggested by **Professor Alice P. Gast**
["Animal Guts as Ideal Reactors", Chemical Engineering Education, Winter 1998, pp 24-29]



# Compartments for perfusion

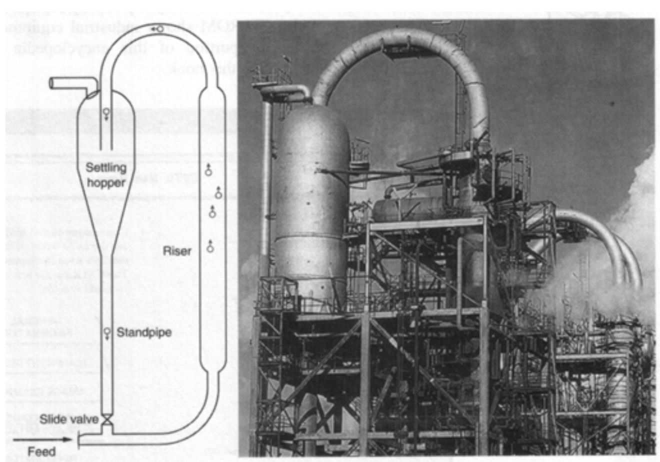





Perfusion interactions between compartments are shown by arrows.

$V_G$, $V_L$, $V_C$, and $V_M$ are -tissue water volumes for the gastrointestinal, liver, central and muscle compartments, respectively.

$V_S$ is the stomach contents volume.




The reactor is 3.5 m in diameter and 38 m tall.
[Schematic and photo courtesy of Sasol/Sastech PT Limited.]

### Chemical Reaction Engineering

*Chemical reaction engineering* is at the heart of virtually every chemical process. It separates the chemical engineer from other engineers.

**Industries that Draw Heavily on Chemical Reaction Engineering (CRE) are:**

CPI (Chemical Process Industries)

Dow, DuPont, Amoco, Chevron

Pharmaceutical – Antivenom, Drug Delivery

Medicine –Pharmacokinetics, Drinking and Driving

Microelectronics – CVD