BITS, PILANI – K. K. BIRLA GOA CAMPUS

KINETICS & REACTOR DESIGN
2015 - 2016

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BITS PILANI, K. K. BIRLA GOA CAMPUS

Lecture information

- M W F : 9:00 am

- Instructor for Tutorial: Prof. Srinivas Krishnaswamy / Narendra Chundi

- Tutorial timings: Thursday 8:00 am

What is KRD or CRE?

- Study of reaction rates and reaction mechanisms
- Deals with chemically reactive systems of engineering significance
- It quantifies the interactions of transport phenomena and reaction kinetics in relating reactor performance to operating conditions and feed variables
- Helps you design safe, energy and cost efficient reactors to yield required quality products

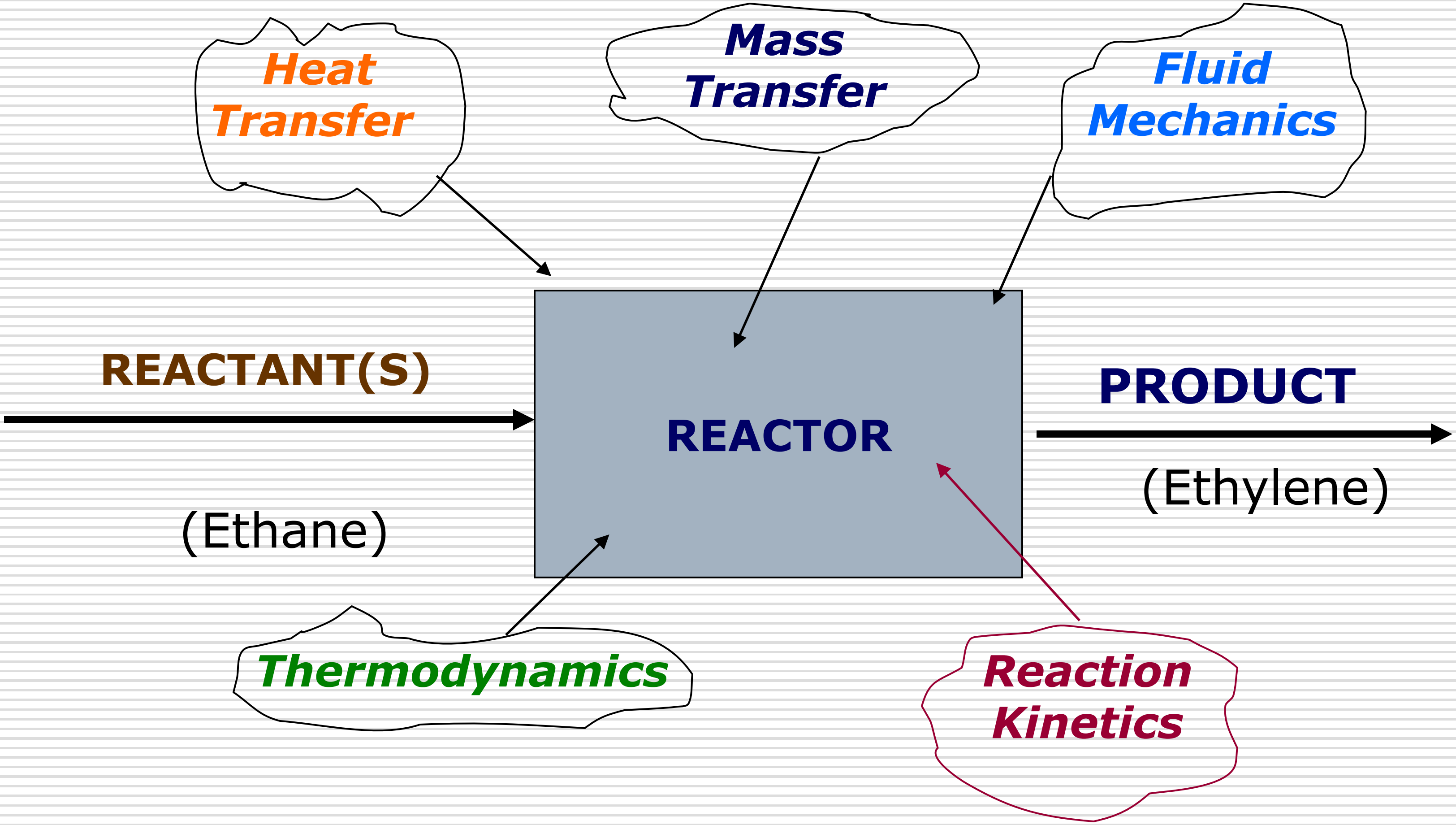
What is this course important?

- Continuous need to improve existing processes
- Continuous development of new processes to replace existing ones
- Use of improved feed stocks
- Increased quality products

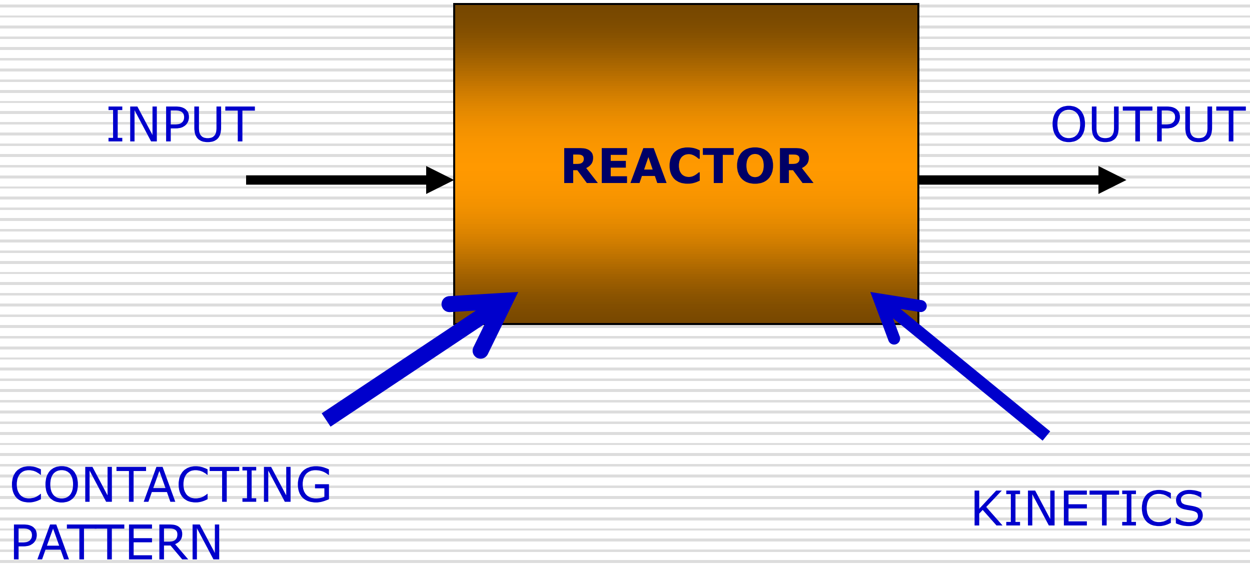
Knowledge basis

- Strong foundation in Chemistry: www.chemguide.co.uk
- Strong foundation in Transport Phenomena
- A Strong foundation in Mathematics
- A Good basis of course in Year 2

What is involved in reactor design?



Information needed to predict what a reactor can do



OUTPUT = F (INPUT, KINETICS, CONTACTING)

PERFORMANCE EQUATION

Information needed to predict what a reactor can do

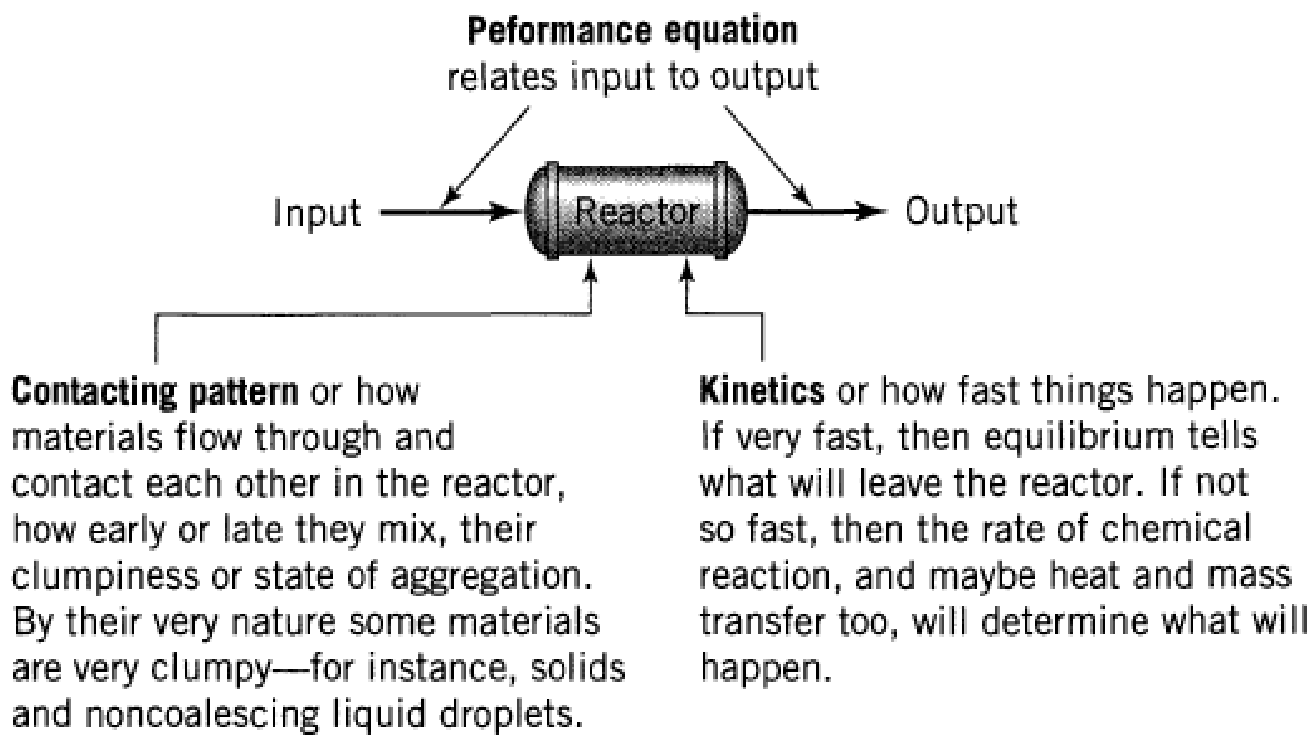
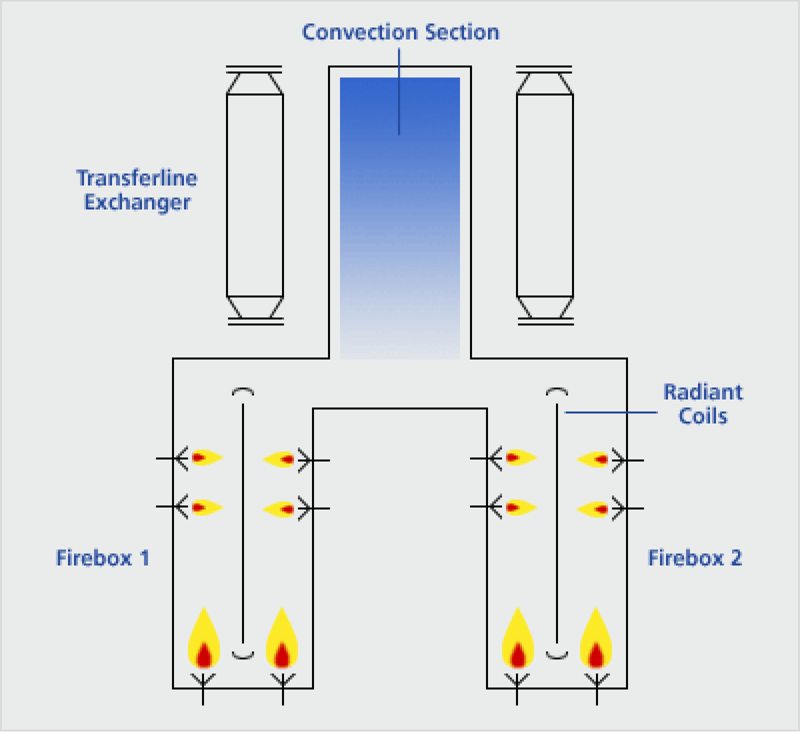


Figure 1.2 Information needed to predict what a reactor can do.

Is KRD difficult?

All truths are easy to understand once they are discovered; the point is to discover them. Galileo Galilei

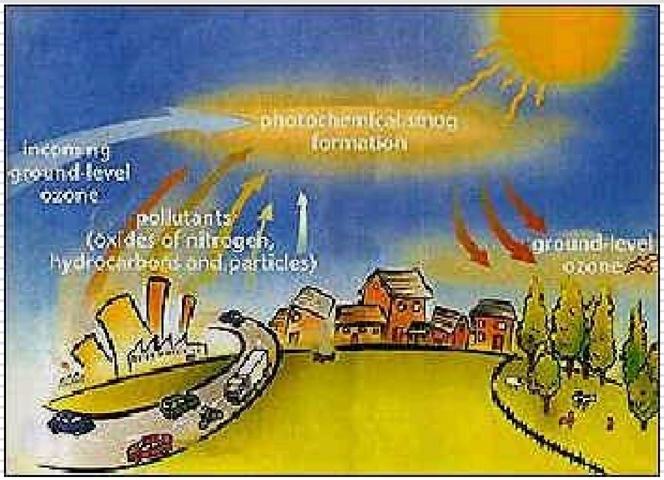
KRD Applications (Ethylene production)

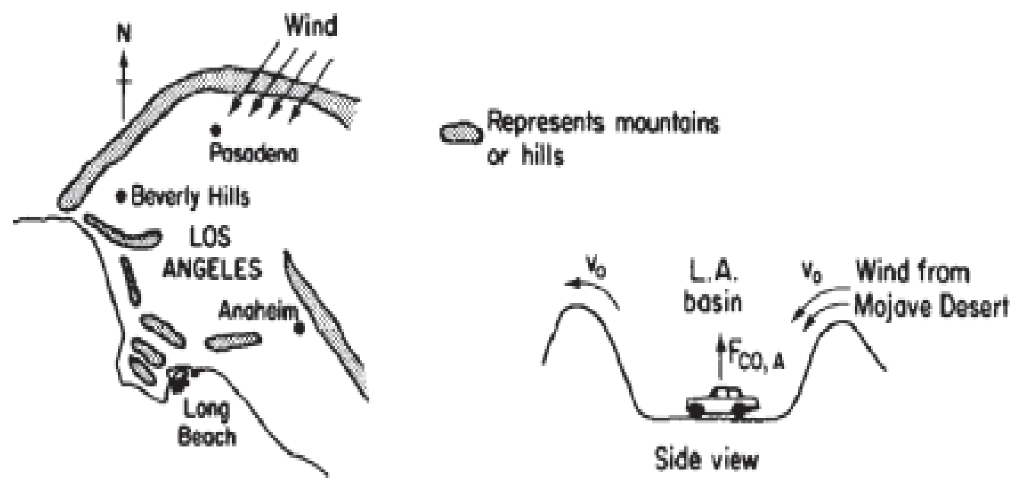


$C_2H_6 \rightarrow C_2H_4 + H_2$

(High-temperature tubular reactors) – 1200 ^oC

KRD Applications (Smog formation)

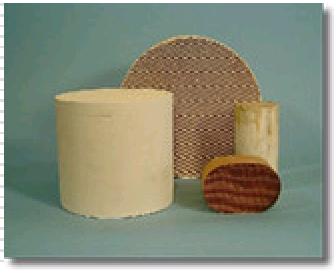


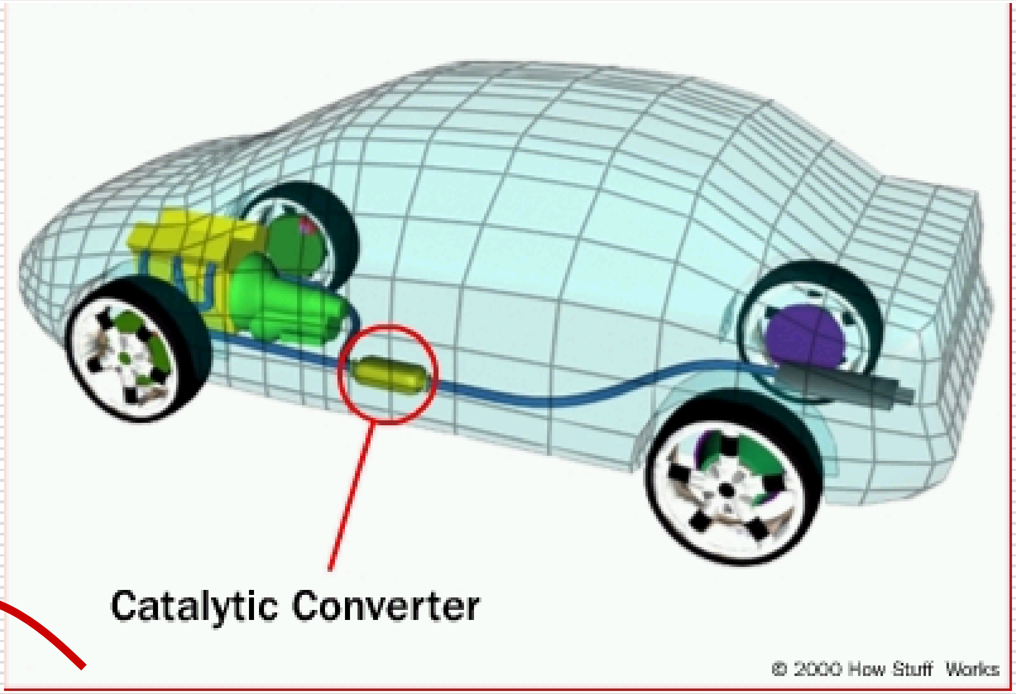


Smog (Ch. 1, Ch. 7)

Allows us to estimate the extent of smog formation ...

KRD Applications (Catalyst Converter)

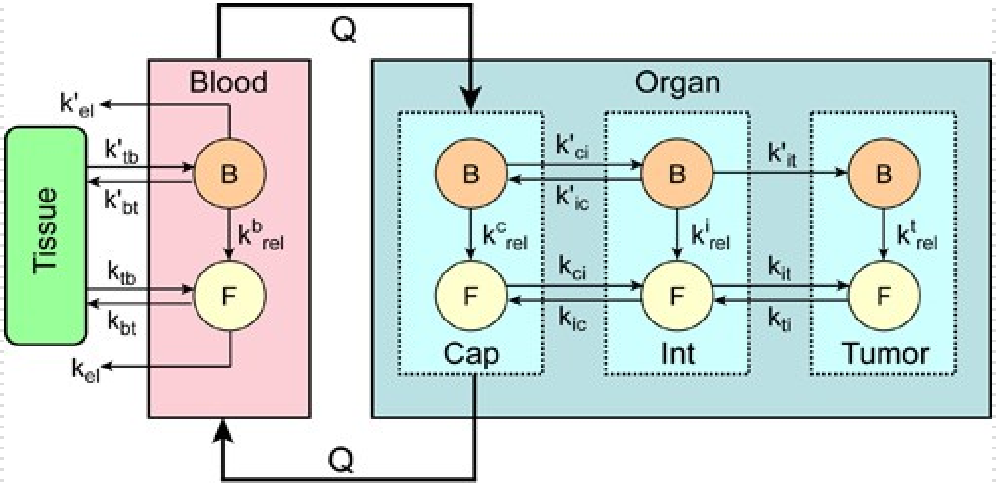


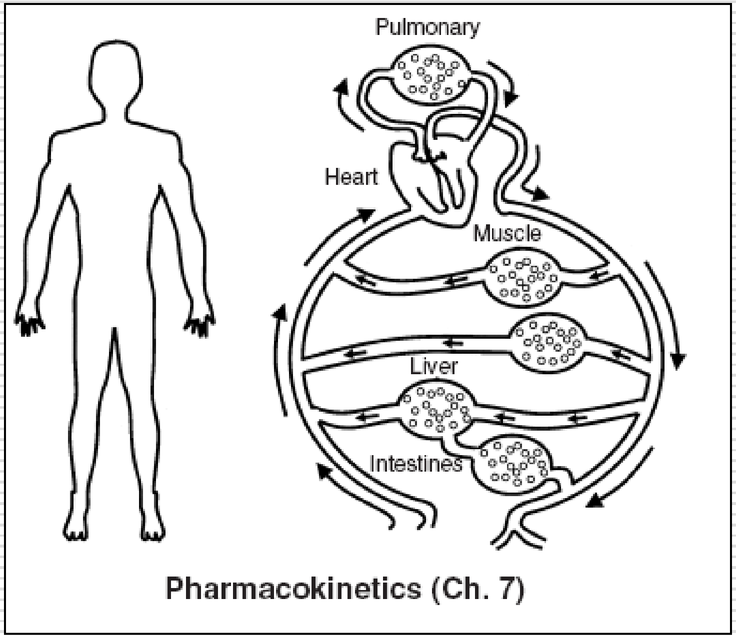


KRD Applications (Bio-kinetics)

- The challenge is to grow large quantities of viable cell….

KRD Applications (Pharmacokinetics)

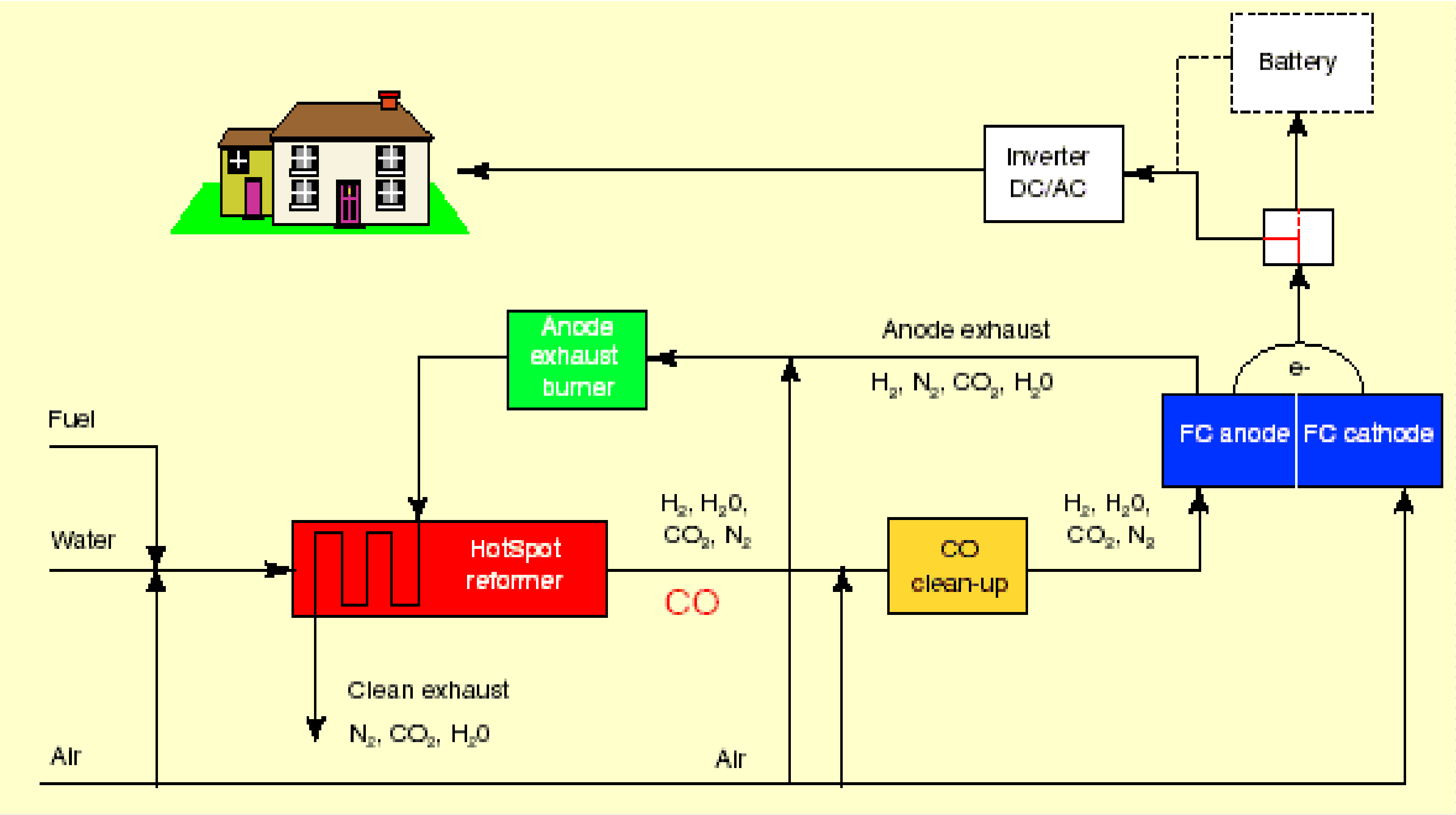




KRD can be applied to describe
Human body-drug interaction

http://habanero.ibme.wustl.edu/PK-model.jpg

KRD Applications (Fuel Cells)

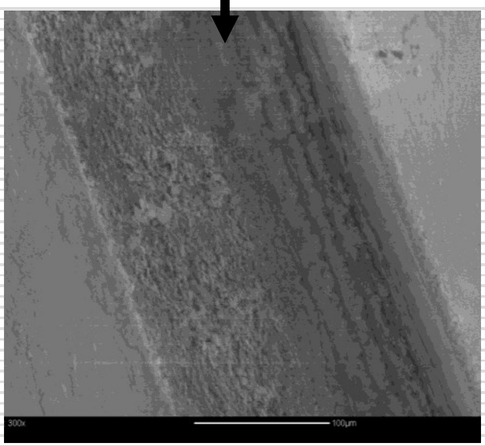


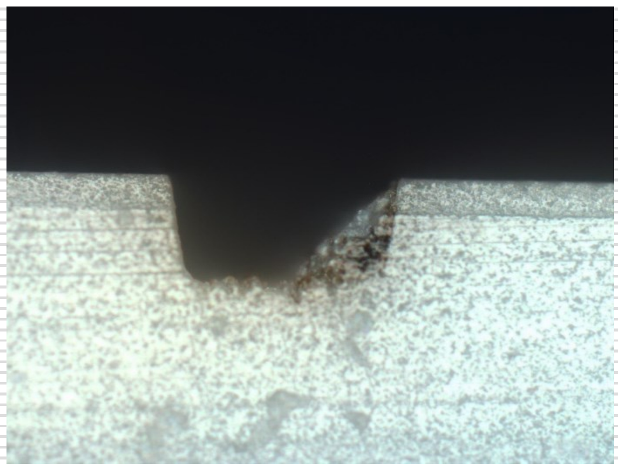
KRD Applications (Micro-fluidics)

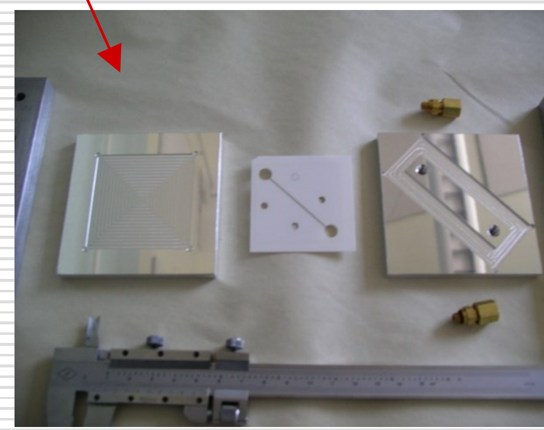
Channel

Channel

Micro-channels on a wafer







Compact reactors for compact fuel cells
Production of hazardous chemicals in controlled quantities
Potential application in bio-chemical systems

Reaction Nomenclature

- Homogeneous reaction : One phase
- Heterogeneous reaction: At least 2 phases
- There is not always a clear cut (biological reactions, burning gas flame): Non-homogeneity in composition and temperature exist
- Catalytic reactions
- Single / Multiple reactions

Classification of reactions

Table 1.1 Classification of Chemical Reactions Useful in Reactor Design

	Noncatalytic	Catalytic
Homogeneous	Most gas-phase reactions	Most liquid-phase reactions
	Fast reactions such as burning of a flame	Reactions in colloidal systems Enzyme and microbial reactions
Heterogeneous	Burning of coal Roasting of ores Attack of solids by acids Gas-liquid absorption with reaction Reduction of iron ore to iron and steel	Ammonia synthesis Oxidation of ammonia to produce nitric acid Cracking of crude oil Oxidation of SO_2 to SO_3

Rate of reaction ($-r_A$)

- Tells us how fast a number of moles of one chemical species are being consumed to form another chemical species
- Species – Component or element with given identity (kind, number or configuration of atoms)
- Effect chemical and physical properties
- Chemical reaction – Identity loss due to change in structure or configuration of atoms
- Decomposition, Combination and Isomerization

Rate of reaction ($-r_A$)

To Summarize a given number of molecules of a chemical species has reacted or disappeared if the molecules lose their chemical identity

$$\text{Chloral} + \text{Chlorobenzene} \rightarrow \text{DDT} + \text{water}$$

$$A + 2B \rightarrow C + D$$

Rate of reaction of A i.e. $-r_A$ is the number of moles of A reacting or disappearing per unit time per unit volume (mol / m^3.s)

Rate of reaction (r_A)

$$r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid})(\text{time})}$$

$$r_i' = \frac{1}{W}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{mass of solid})(\text{time})}$$

Rate of reaction (r_A)

$$r_i'' = \frac{1}{S}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{surface})(\text{time})}$$

$$r_i''' = \frac{1}{V_s}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of solid})(\text{time})}$$

Rate of reaction (r_A)

$$\boxed{r_i'''' = \frac{1}{V_r}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor})(\text{time})}}$$

$$\begin{pmatrix}\text{volume}\\ \text{of fluid}\end{pmatrix} r_i = \begin{pmatrix}\text{mass of}\\ \text{solid}\end{pmatrix} r_i' = \begin{pmatrix}\text{surface}\\ \text{of solid}\end{pmatrix} r_i'' = \begin{pmatrix}\text{volume}\\ \text{of solid}\end{pmatrix} r_i''' = \begin{pmatrix}\text{volume}\\ \text{of reactor}\end{pmatrix} r_i''''$$

$$\boxed{Vr_i = Wr_i' = Sr_i'' = V_s r_i''' = V_r r_i''''}$$

Species losing Identity

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 $C_2H_5CH = CH_2 \rightarrow CH_2 = C(CH_3)_2$

Rate of reaction ($-r_A$)

To Summarize a given number of molecules of a chemical species has reacted or disappeared if the molecules lose their chemical identity

Chloral + Chlorobenzene $\rightarrow$ DDT + water

$A + 2B \rightarrow C + D$

Rate of reaction of A i.e. $-r_A$ is the number of moles of A reacting or disappearing per unit time per unit volume ($mol / m^3.s$)

Rate of reaction ($-r_A$)

Example: $A \rightarrow B$
If B is being created at 0.2 moles /dm^3/s

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

Rate of reaction ($-r_A$)

Wish things were so easy and simple!!!

Rate of reaction ($-r_A$) : Issues

- Mathematical definition of rate
- The Sodium Hydroxide example
- General definition
- Rate equation is an algebraic equation
- $-r_A = f$ (species conc., temp, pressure, catalyst type) at any point in the system
- Rate equation is independent of reactor type

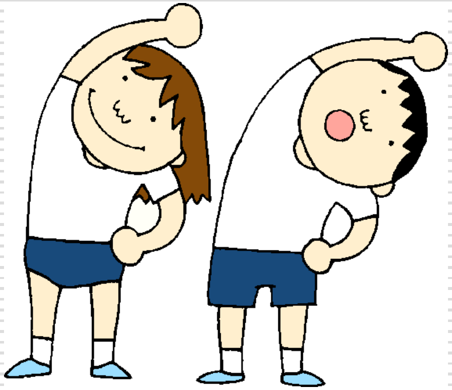
$$-r_A = kC_A \qquad -r_A = \frac{k_1 C_A}{1 + k_2 C_A} \qquad -r_A = k$$

Take a break.. Solve a problem

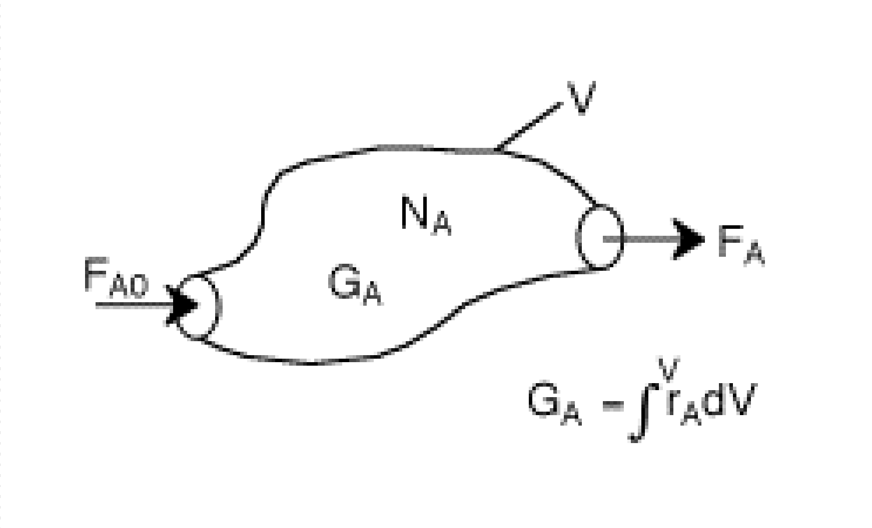
Consider the reaction in which the rate of disappearance of A is 5 moles of A per dm^3 per second at the start of the reaction. ($A + 2B \rightarrow 3C$)

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 $-r_B$?



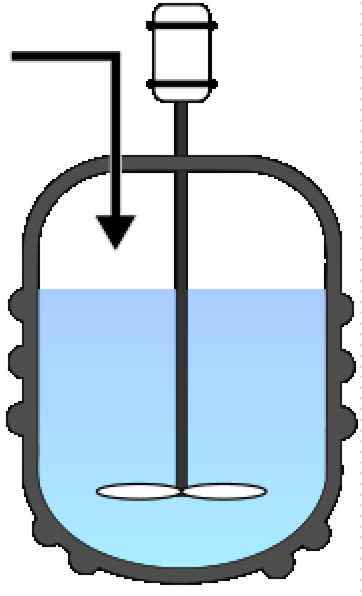
The General mole balance equation



- System variables spatially uniform
- This is modeling
- Spatial variation makes things more complex

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

Batch Reactor



Uniform concentration varying with time

Batch Reactor design equation

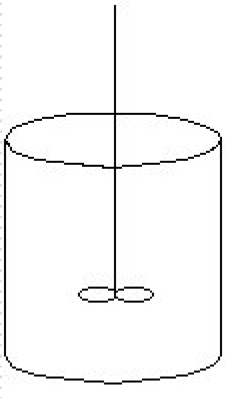
No inflow or outflow-

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

Assumptions

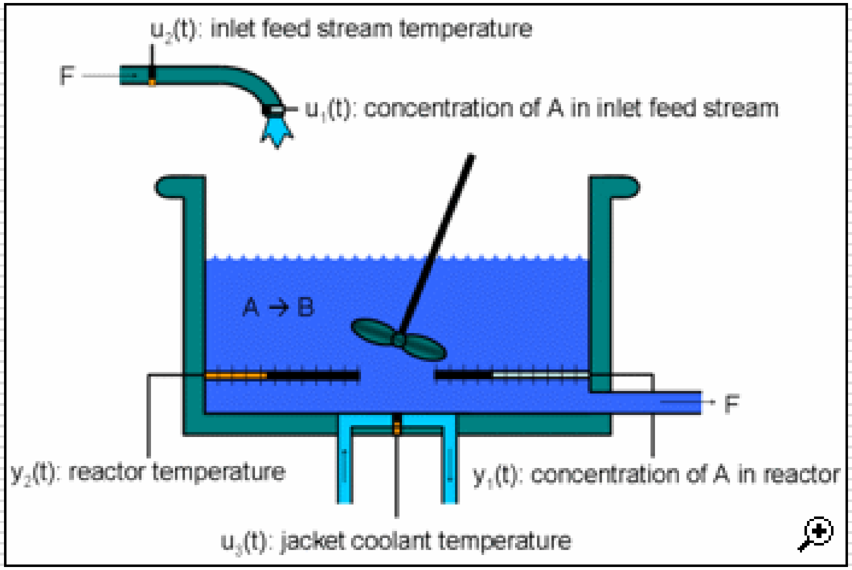
Well mixed

$$\int r_A dV = r_A V$$

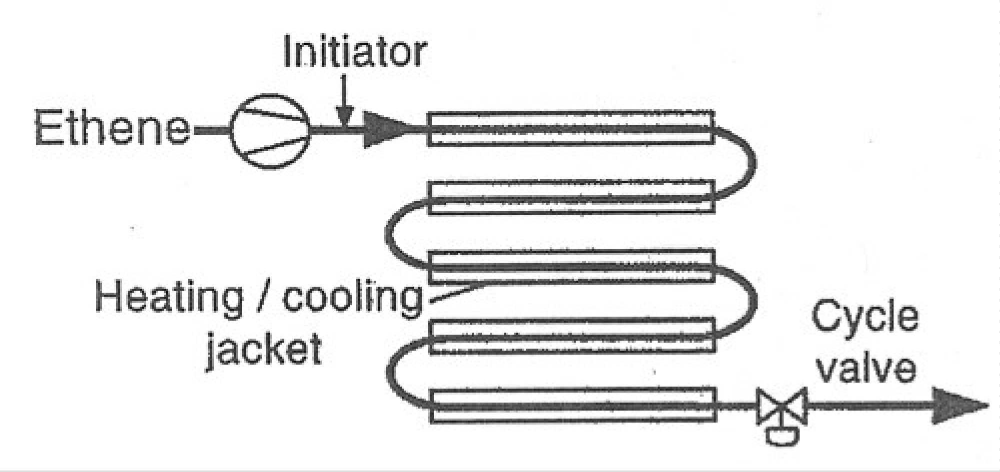


$$\frac{dN_A}{dt} = r_A V$$

Continuous flow reactors (CSTR)



Continuous flow reactors (PFR)



Continuous flow reactors (PBR)

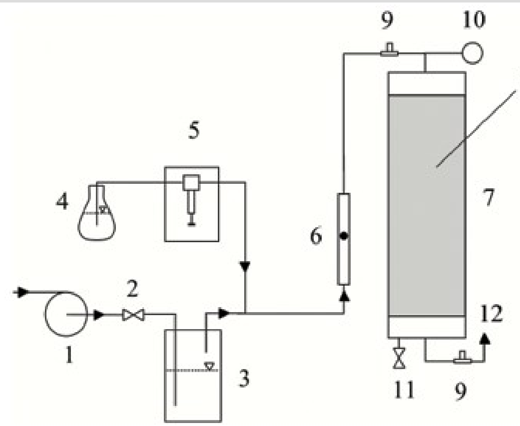


Figure 1 - Experimental set-up of biofilter system. 1 - blower, 2 - needle valve for flow rate control, 3 - humidification vessel, 4 - vessel with toluene and xylene, 5 - syringe pump, 6 - rotameter, 7 - biofilter, 8 - packing, 9 - sampling ports, 10 - manometer, 11 - valve for leachate, 12 - outlet

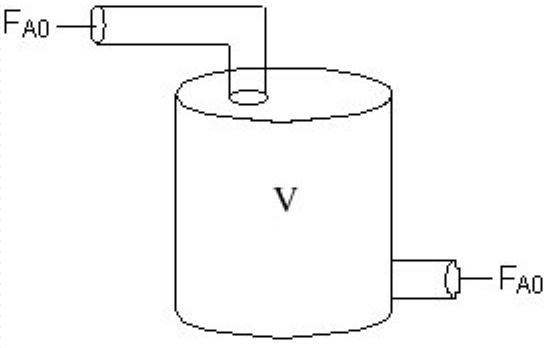
CSTR design equation

Assumptions

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

- Well mixed
- Temp and concentration same at exist and outlet
- Steady State (Time derivative zero)

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

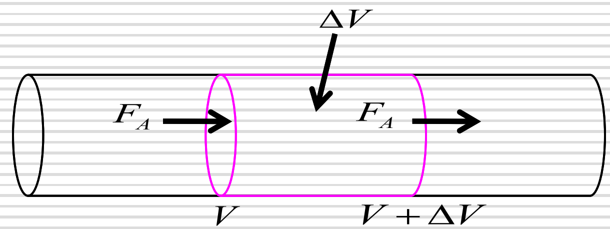


$$\int r_A dV = r_A V$$

IMPLICATION

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

PFR design equation

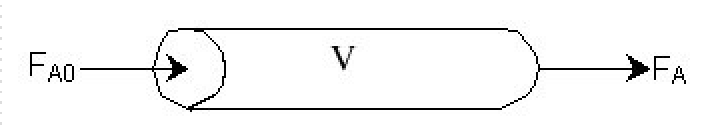


Assumptions

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

- Axial Concentration variation
- No radial variation
- Steady State (Time derivative zero)

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



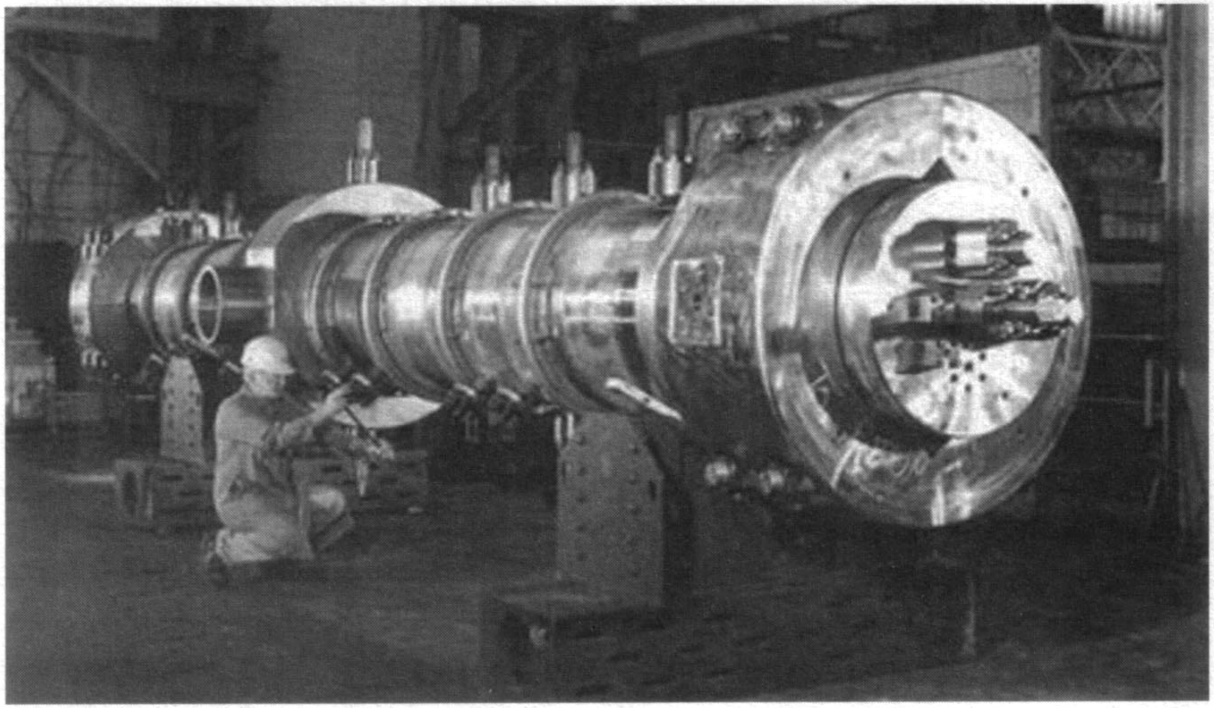
$$\int r_A \, dV = r_A V$$

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

IMPLICATION

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

PFR design equation



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.

PBR design equation

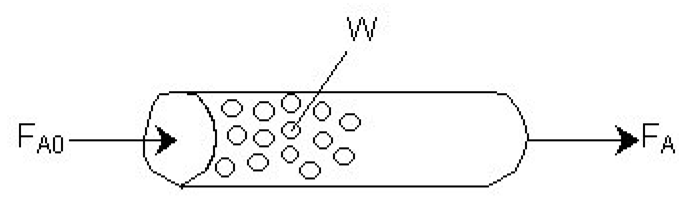
Assumptions

- Axial Concentration variation
- No radial variation
- Steady State (Time derivative zero)
- Heterogeneous reactions

$$\text{In} - \text{Out} + \text{Generation} = \text{Accumulation}$$

$$F_{A0} - F_A + \int r_A' dW = \frac{dN_A}{dt}$$

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

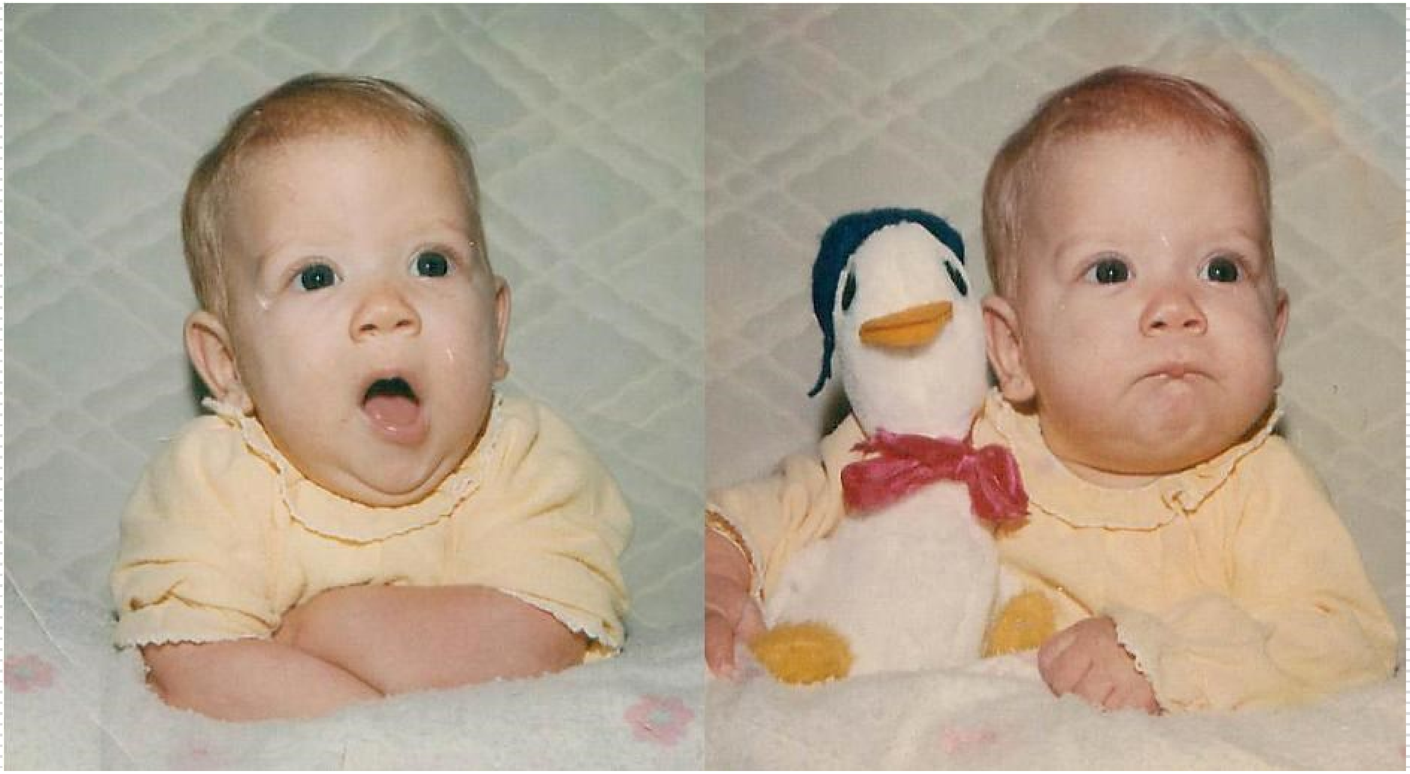


$$F_{A0} - F_A + \int r_A' dW = 0$$

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

Implication of differential and integral form

Bored and Angry!!! Problem Time



Multiple Choice

Which equation is used in arriving at the design equation for a batch reactor?

A. $G_j = V * r_j$

B. $dN_j/dt = 0$

C. $F_{jo} = F_j = 0$

D. $E=mc^2$

Batch Reactor time

Calculate the time to reduce the number of moles by a factor of 10 in a batch reactor for the above reaction with $-r_A = kC_A$, when $k = 0.046\ min^{-1}$

$$N_A = \frac{N_{A0}}{10}$$

Did I forget something?

$C_A = N_A / V$

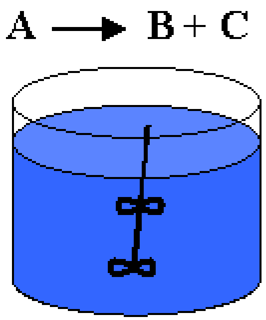
$F_A = C_A v$

$PV = NRT$

You know me. I do this deliberately.

Signs of Things to come

A 200-dm^3 constant-volume batch reactor is pressurized to 20 atm. with a mixture of 75% A and 25% inert. The gas-phase reaction is carried out isothermally at 227 ^oC.



a. Assuming that the ideal gas law is valid, how many moles of A are in the reactor initially? What is the initial concentration of A?

b. If the reaction is first order: $-r_A = kC_A \quad \text{with } k = 0.1 \dfrac{1}{\text{min}}$

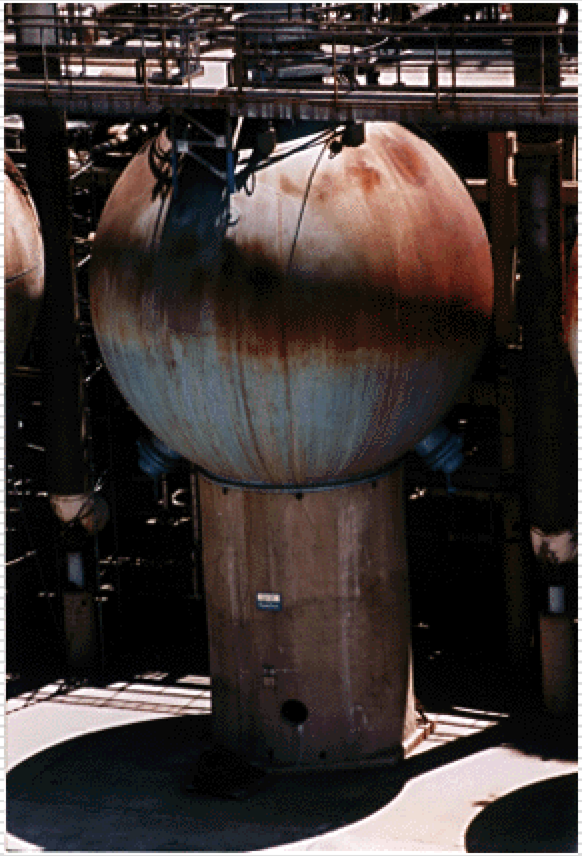
Calculate the time necessary to consume 99% of A.

V = 200-dm^3
P = 20 atm
T = 227 ^oC

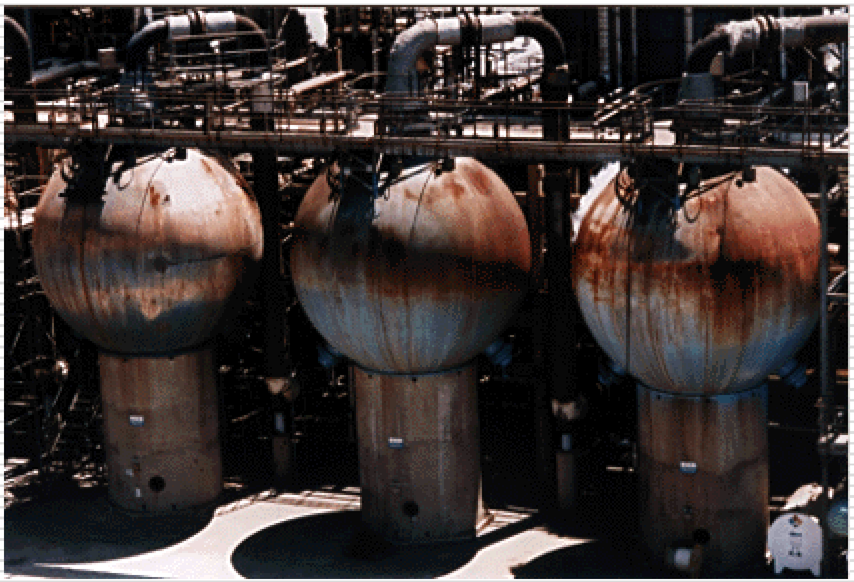
c. If the reaction is second order: $-r_A = kC_A^2 \quad \text{with } k = 0.7 \dfrac{\text{dm}^3}{\text{mol} \bullet \text{min}}$

calculate the time to consume 80% of A. Also calculate the pressure in the reactor at this time if the temperature is 127 ^oC

Industrial Reactors



Industrial Reactors



Industrial Reactors

Objective Assessment of Chapter

- Understand the importance of KRD in the context of the Chemical Engg. curriculum
- Understand rate of a reaction
- Getting familiar with modeling through general mole balance
- Understand type of reactors and design equations for the same
- Start solving KRD problems

Now this is not the end. It is not even the beginning of the end. But it is, perhaps, the end of the beginning.