

# Chap 1 Overview of CRE

## — What are we going to learn in CRE

In “Principles of Chemical Engineering” (in the US it is called Unit Operation), we have learned how to design kinds of equipments for driving fluid, heating or cooling fluid, and separating a mix of substances etc. All of them undergo a physical process without chemical change.

Chemical Reaction Engineering is talking about the equipment where chemical reactions take place — “**Reactor**” . Not only are we going to analyze a reactor, but also design it for given process.

## 二 What affects a reactor's performance

The following factors should be taken into consideration:

- **Kinetics** how fast a reaction goes. You should learned some of it in Physical Chemistry
- **Contacting Pattern** how materials flow through and contact each other in the reactor.

The composition of inlet fluid (input) and outlet fluid (output) have relationship below:

Performance Equation : output = $f[\text{input, kinetics, contacting}]$
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## 三 Type of reaction kinetics

- **Homogeneous** : reactants that take part in the reactions are all in only one phase
- **Heterogeneous** : reactions that take part in the reactions are in different phase

Even if there are only liquid phases, its still heterogeneous because they are not completely soluble in each other. Heterogeneous reactions take place in various position, like interface of both phase, one of the phase ..... Mass transport are always taken into consideration thus the kinetics are much more complex than homogeneous reaction.

## 四 Definition of Reaction Rate

The rate is defined by the rate of change in numbers of moles of one reaction component i  $\frac{dN_i}{dt}$

It is extensive properties so we divide it by something related to “amount” :

Homogeneous Reaction	1 $r_i = \frac{1}{V} \frac{dN_i}{dt}$	V : volume of fluid
Solid – Fluid System	2 $r'_i = \frac{1}{W} \frac{dN_i}{dt}$	W : mass of solid
	3 $r''_i = \frac{1}{S} \frac{dN_i}{dt}$	S : interfacial surface of solid
	4 $r'''_i = \frac{1}{V_s} \frac{dN_i}{dt}$	V <sub>s</sub> : volume of solid
Multiple-Phase System	5 $r_i''' = \frac{1}{V_r} \frac{dN_i}{dt}$	V <sub>r</sub> : volume of reactor

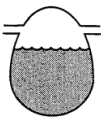
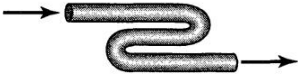
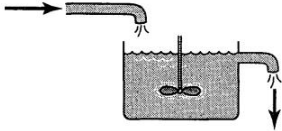
In part I II and V definition 1 are mostly used, In part III and IV definition 3 and 5 are mostly used.

## PART 1 Homogeneous Reactions in Ideal Reactors

### Chap 2 Kinetics of Homogeneous Reactions

#### — Ideal Reactor Types

When said “Ideal Reactors” , it is the flow patterns in reactors that are ideal.

Flow patterns	Batch	Stady-state flow	
		Plug Flow	Mixed Flow
			
mix	Well mixed	No mixing of earlier and later entering fluid	Well mixed
Composition	Uniform everywhere	Differs along path	Uniform everywhere including exit
	Change with time	Unchanged	Unchanged

Steady-state flow means “continuous production” , which materials move in and out at the same time, unlike batch reactor which materials move in and out by a fixed sequence.

#### 二 Basic Concepts in Kinetics ※

The following part in Chap 2 and some part in Chap 3 have temporarily no notes because you have learned them in Physical Chemistry. If you are unfamiliar of these materials, just have a review of physical chemistry or read Chap 2 and Chap 3.

## Chap 3 Interpretation of Batch Reactor Data

This Chapter tells us how to get kinetics by data gained in batch reactor.

### — Constant-volume Batch Reactor

Constant-volume means the volume of fluid doesn't change after reaction

Thus the rate can be presented as  $r_i = \frac{d(N_i / V)}{dt} = \frac{dC_i}{dt}$

For ideal gas:  $r_i = \frac{1}{RT} \frac{dp_i}{dt}$  In gas reactions:  $p_A = p_{A0} - \frac{\nu_A}{\Delta n} (\pi - \pi_0)$

$p_{A0}$ : initial partial pressure of A     $\nu_A$ : stoichiometric number     $\Delta n$ : molecule number change  
 $\pi$ : total pressure     $\pi_0$ : initial total pressure

### 二 Fractional Conversion ※

Definition:

$$X_A = \frac{N_{A0} - N_A}{N_{A0}}$$

For constant - volume

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} = 1 - \frac{C_A}{C_{A0}}$$

For varying - volume

define  $\epsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}$  (fractional change of volume between  $X_A = 0 \sim 1$ )

now  $X_A = \frac{1 - C_A / C_{A0}}{1 + \epsilon_A C_A / C_{A0}}$

## Chap 4 Introduction to Reactor Design

### — Material and Energy Balance

The performance equation are based on material balance. Some of them will also be based on energy balance if the process is nonisothermal. Both of them count material or heat in a element of volume, and are presented as differential equations.

**Material Balance:** accumulation = in – out – reaction (all the terms means rate)

**Energy Balance:** accumulation = in – out – reaction (all the terms means rate)

### 二 Relationship between $C_A$ and $X_A$

.....

# Chap 5 Ideal Reactors for a Single Reaction

## — Space-Time and Space-Velocity

**Space-Time**  $\tau$  the time the reactor take to process one reactor volume of feed

$$\tau = \frac{1}{s} = \frac{C_{A0} V}{F_{A0}} = \frac{V}{v_0}$$

$F_{A0}$  : moles of A entering the reactor per unit time

$v_0$  : volume of fluid entering the reactor per unit time

$C_{A0}$  : concentration of A in entering fluid

$V$  : volume of reactor

**Space-Velocity**  $s$  number of reactor volumes of feed treated per unit time

## 二 Performance Equation of Ideal Reactor ✖

	Batch Reactor	PFR	MFR
Performance Equation	$t = \frac{N_{A0}}{V} \int_{X_{A0}}^{X_A} \frac{dX_A}{-r_A}$	$\frac{V}{F_{A0}} = \int_{X_{A0}}^{X_A} \frac{dX_A}{-r_A}$	$\frac{V}{F_{A0}} = \frac{X_A - X_{A0}}{-r_A}$
Constant Volume & $X_{A0} = 0$	$t = \int_{C_{A0}}^{C_A} \frac{dC_A}{-r_A}$	$\tau = - \int_{C_{A0}}^{C_A} \frac{dC_A}{-r_A}$	$\tau = \frac{C_{A0} - C_A}{-r_A}$

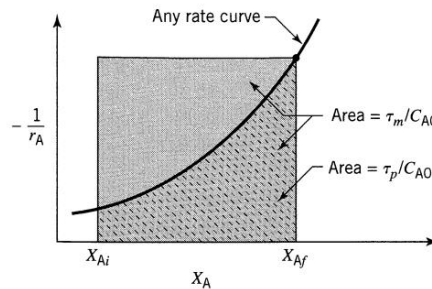
## Chap 6 Design for Single Reaction

In this chapter, we are going to choose right kind of reactors for single reaction.

### — Choose one from BR, PFR and MFR

Firstly, batch reactor is seldom a option for large scale production.

So it is essential to compare MFR and PFR



When  $n > 0$ , choose PFR;  $n < 0$ , choose MFR

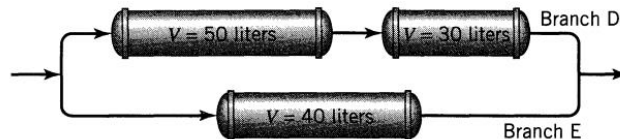
We can consider in this way: In PFR there is no mixing forward and backward to decrease the concentration of reactant, but MFR does. Thus PFR favors reaction need high concentration while MFR favors reaction need low concentration.

### — Combine PFR and MFR

#### 1. PFR in series and in parallel

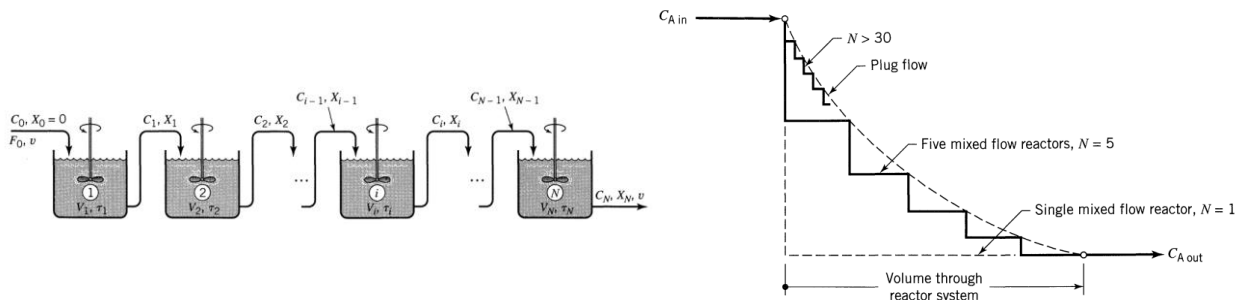
PFR in series with a total volume of  $V$  = a single PFR of volume  $V$

PFR in parallel must have the same  $\tau$  for each line to get the same composition



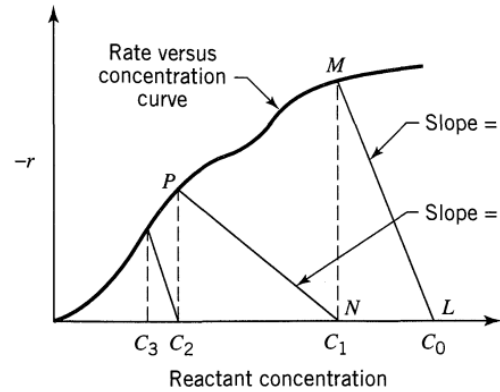
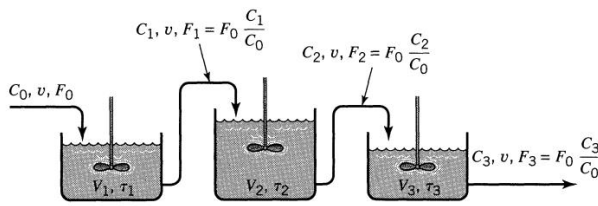
#### 2. Equal-size MFR in series

N equal-size MFR combine to give a PFR when N is large enough



#### 3. MFR in series

We can use graphics to get conversion at each stage

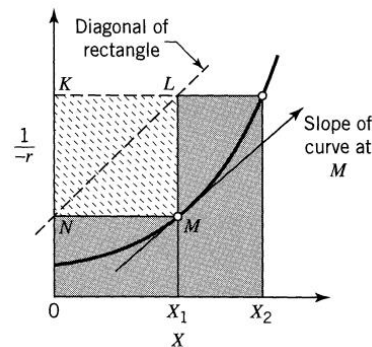


When use 2 MFR in different sizes in series, to make total volume smaller:

$n = 1$  : 2 equal size are best

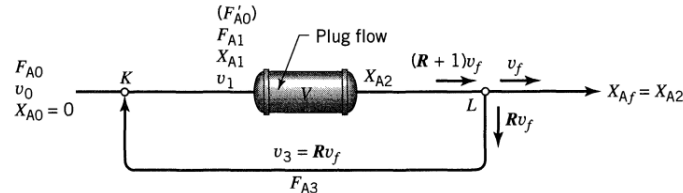
$n > 1$  : the smaller reactor should come first

$n < 1$  : the larger reactor should come first



### ≡ Recycle Reactor

Recycle : The product stream is divided into 2 streams, one of which is returned to entrance.



Recycle ratio

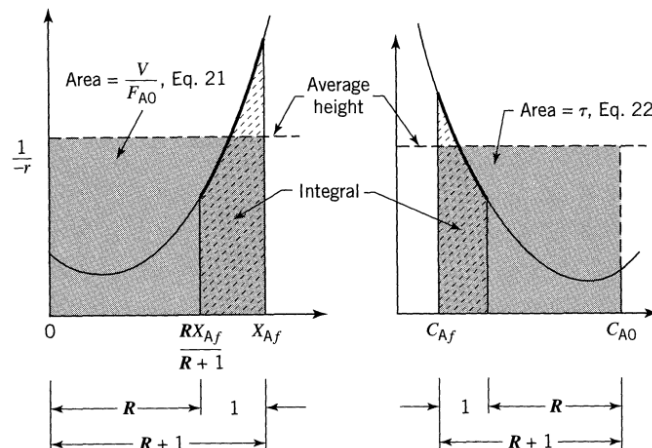
$$R = \frac{\text{volume of fluid returned}}{\text{volume leaving the system}}$$

we can deduce that

$$\frac{V}{F_{A0}} = (R+1) \int_{\frac{R}{R+1} X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A}$$

and

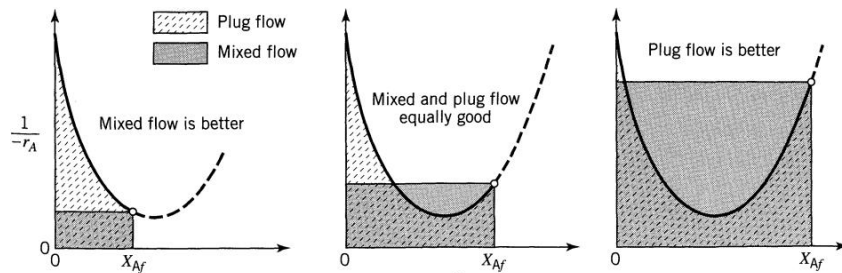
$$\tau = \frac{C_{A0} V}{F_{A0}} = -(R+1) \int_{\frac{C_{A0}}{R+1}}^{C_{Af}} \frac{dC_A}{-r_A}$$



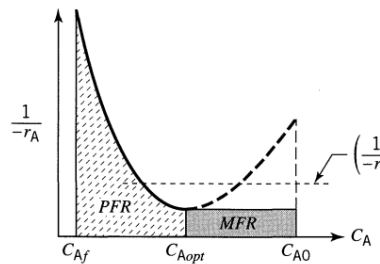
Through the graphs, the larger R, the more it behave like MFR

#### 四 Autocatalytic Reactions

The product of the reaction can be a catalyst, so the  $r_A - C_A$  curve remains a maximum  
Either PFR or MFR is better depends on goal conversion



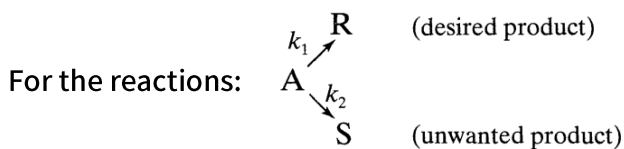
Of course the best reactor is combination of PFR + MFR



## Chap 7 & 8 Design for Multiple Reactions

In multiple reactions we care for the **distribution** of potential products, not the conversion

### — Parallel Reaction



The rate equations tell us  $\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_2}{k_1} C_A^{a_1 - a_2}$ :

- **High** reactant concentration favors the reaction of **Higher Order**
- **Low** reactant concentration favors the reaction of **Lower Order**
- concentration level has no effect for reactions of the same order

### 二 Reactions in Series

For irreversible reactions in series the mixing of fluid of different composition is the key to the formation of intermediate. The maximum possible amount of any and all intermediates is obtained if fluids of different compositions and at different stages of conversion are not allowed to mix.

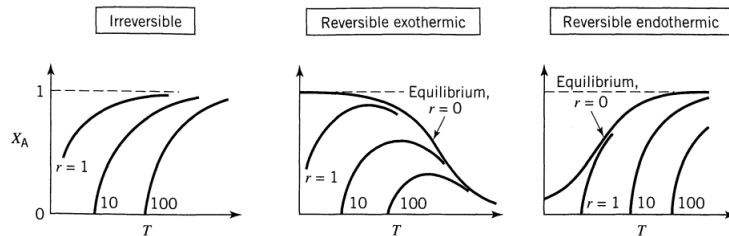
## Chap 9 Temperature and Pressure Effects

In this chapter we need to learn how to take temperature into consideration

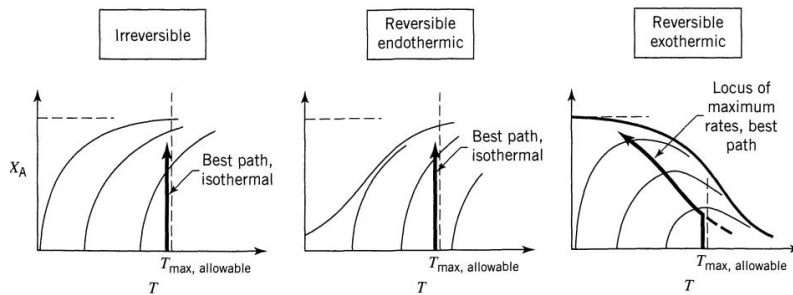
### — General Grapical Design Procedure

When take T into consideration, rate equation becomes  $r = f(c, T)$

To represent the equation on the graph,  $r$  is fixed and a series of  $c = f(T)$  curves are drawn.



To get maximum rate, the temperature should be as higher as possible, except for reversible endothermic reactions, which the temperature should follow a “maximum rates path”



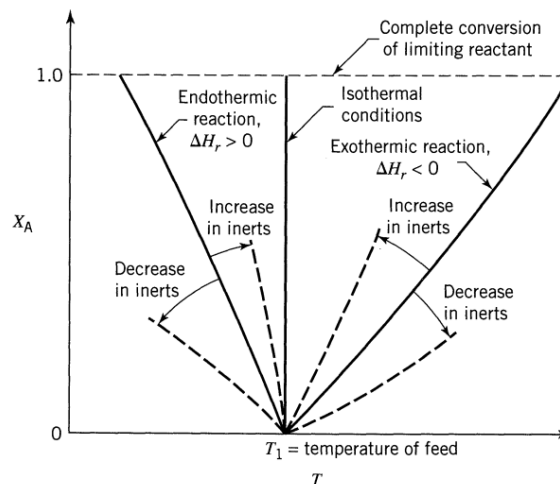
To design a reactor, get the  $\frac{1}{-r_A} - X_A$  relationship along the path, then follow Chap 5.

### 二 Heat Effects

#### 1. Adiabatic Operations

In adiabatic systems, all the heat generated by reactions will turn to thermodynamic energy of fluid to increase the temperature. By calculation of energy balance:

$$X_A = \frac{C_p \Delta T}{-\Delta H_r} \quad \text{--- Adiabatic Operating Line}$$



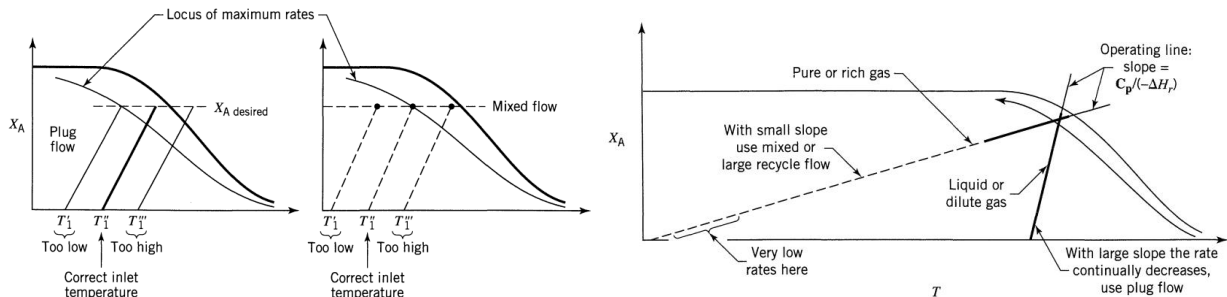


∴ For plug flow, the reaction would undergo along the adiabatic line

For mixed flow, the reaction would jump to the final value

! Small slope : For PFR it takes a long time for reaction to undergo the path, so MFR better.

Large slope : Use PFR

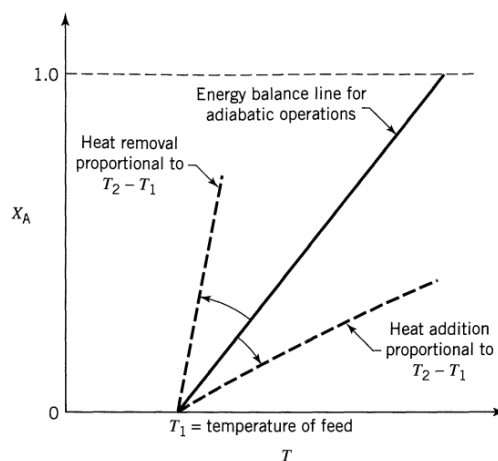


## 2. Nonadiabatic operations

define  $Q$  to be the total heat added to reactor per mole of entering reactant A

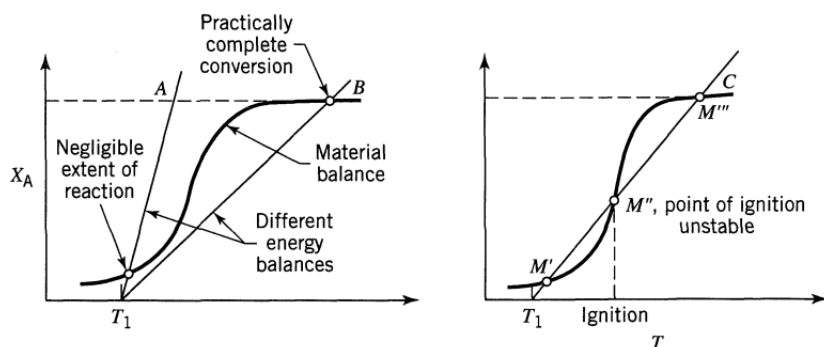
$$X_A = \frac{C_p \Delta T - Q}{-\Delta H_r}$$

Compared to adiabatic operation lines, the slope changes.



## 3. Stability Problem

For MFR, the energy balance line (straight line) and material balance line (S curve) determine the condition MFR works at. There may be 3 possible points, but the middle one is unstable. Once the state is even slightly interrupted, it will move to other points rather than move back.



! This situation can be deduced by stability theory in ODE.

## Chap 10 Choosing the Right Kind of Reactor

This chapter is a conclusion of general rules of reactor design

### Rule 1 For Single Reactions

$n > 0$  high concentration PFR       $n < 0$  low concentration MFR

### Rule 2 For Reactions in Series

Maximize intermediate  $\rightarrow$  no mixing of different concentrations  $\rightarrow$  PFR

### Rule 3 For Parallel Reactions

Low  $C_A$  favors lowest order      high  $C_A$  favors highest order

Intermediate order  $\rightarrow$  best intermediate  $C_A$

### Rule 4 Complex Reactions

Break them down into Parallel and Series

### Rule 6 Effects of T in Product Distribution

A high temperature favors the reaction with larger  $E$

A low temperature favors the reaction with smaller  $E$

! Example 10.2 are important