Introduction to Chemical Engineering

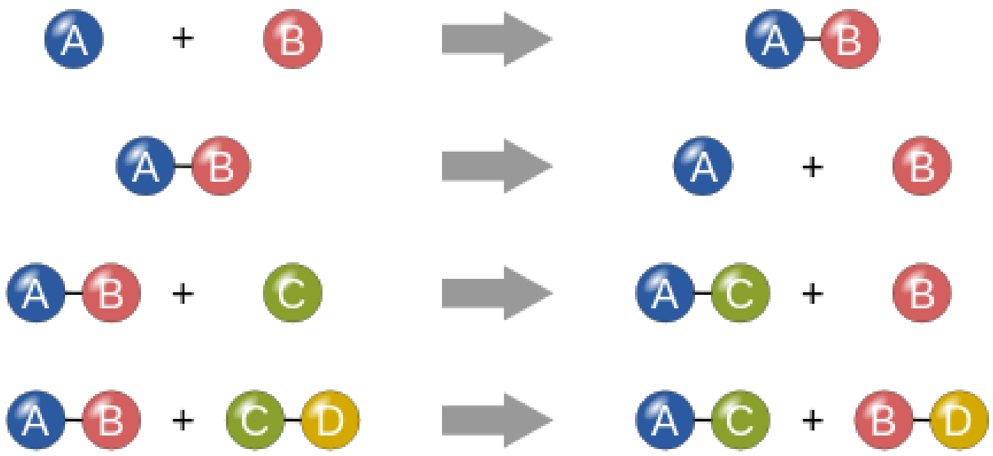
Chapter 09

Reaction Engineering
(*What Size Reactor?*)

9.1 Describing reaction rates

- **A chemical reaction is a process that leads to the transformation of one set of chemical substances to another (reactant → product).**

- **Basic reaction types**



Synthesis

Decomposition

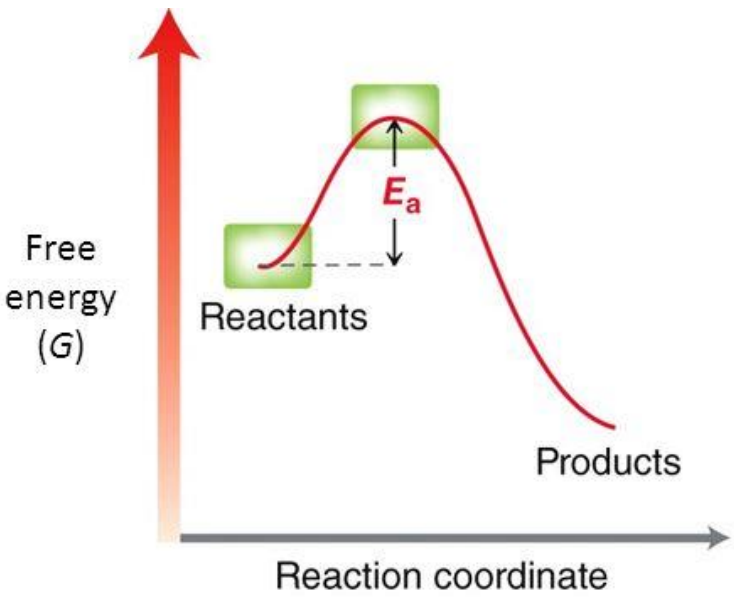
Single replacement

Double replacement

9.1 Describing reaction rates

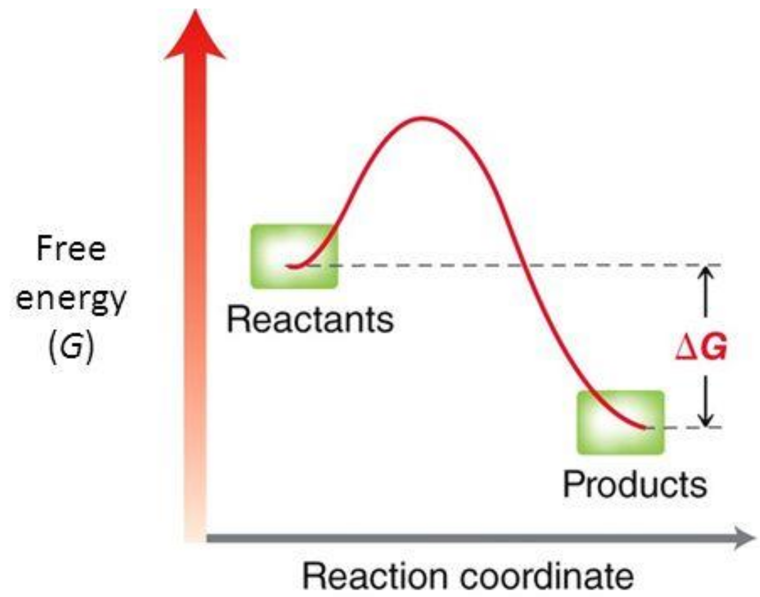
➢ **Kinetics vs. Thermodynamics**

Kinetics
(rate of reaction)



How fast?

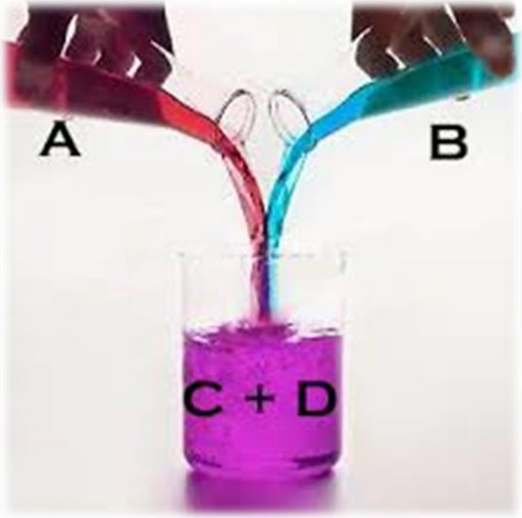
Thermodynamics
(equilibrium)



Feasible?

9.1 Describing reaction rates

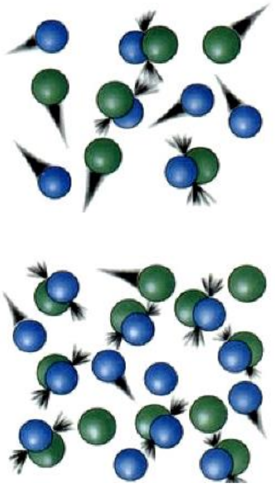
- **Questions about kinetics**
  - **Question 1: What physical variables affect the rate of a reaction between two chemical species?**
  - **Question 2: How do we describe the rate of reaction?**



9.1 Describing reaction rates

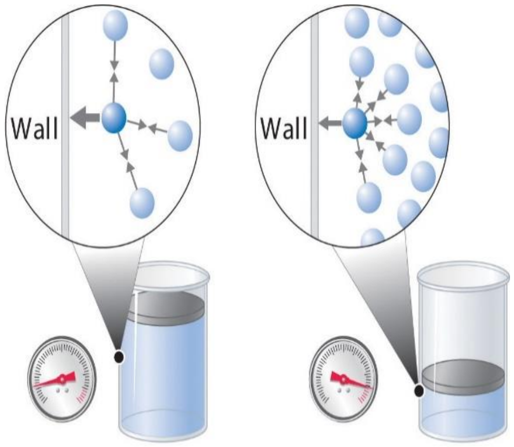
- **What physical variables affect the rate of a reaction between two chemical species?**
  - **Answer 1: Frequency of molecular collision (concentration, phase, temperature, pressure…)**

Concentration



Temperature

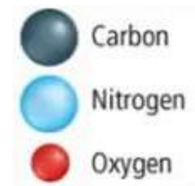
Pressure



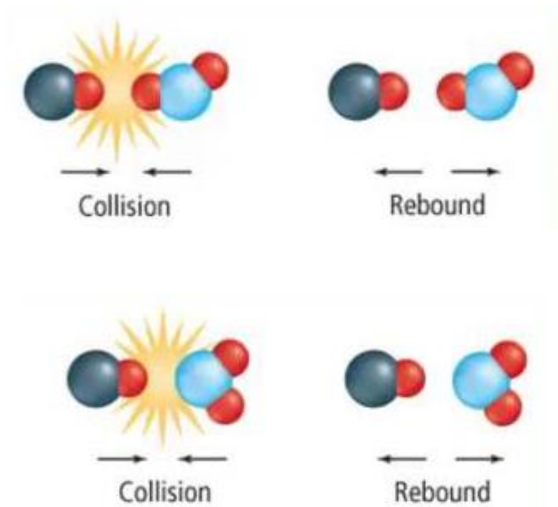
9.1 Describing reaction rates

- **What physical variables affect the rate of a reaction between two chemical species?**
  - **Answer 2: Orientation and force of the collision**

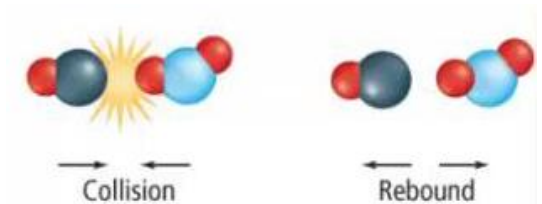
$$CO + NO_2 \rightarrow CO_2 + NO$$



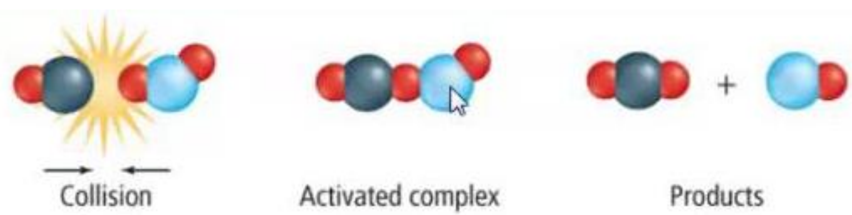
Incorrect orientation



Correct orientation



Insufficient force



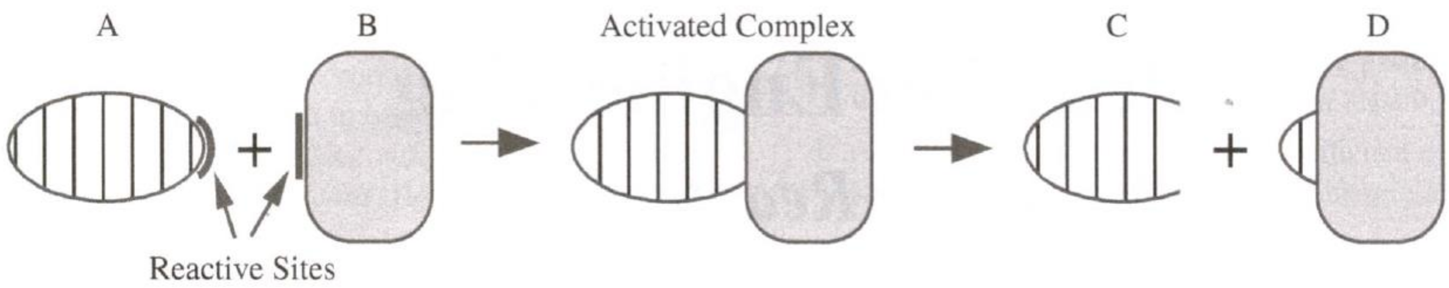
Sufficient force

Chemical reaction occurs.

9.1 Describing reaction rates

- **What physical variables affect the rate of a reaction between two chemical species?**
  - **Answer 2: Orientation and force of the collision**

Activated complex

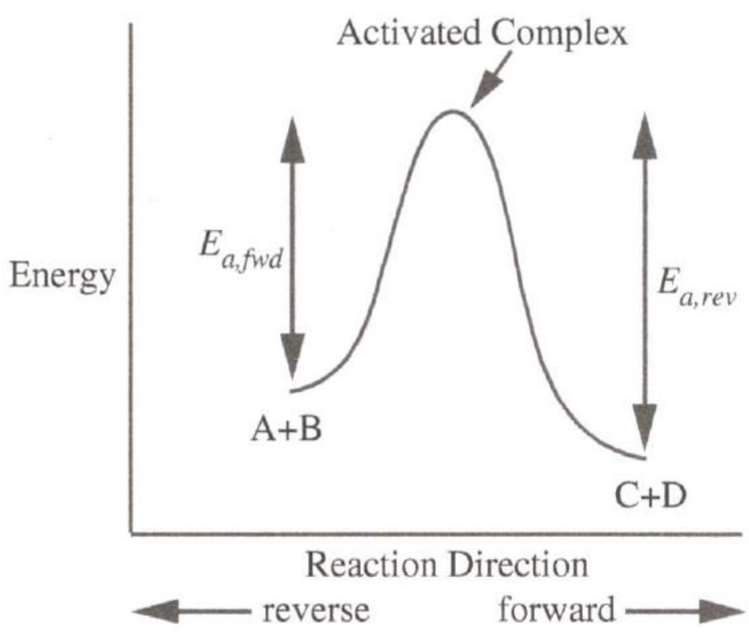


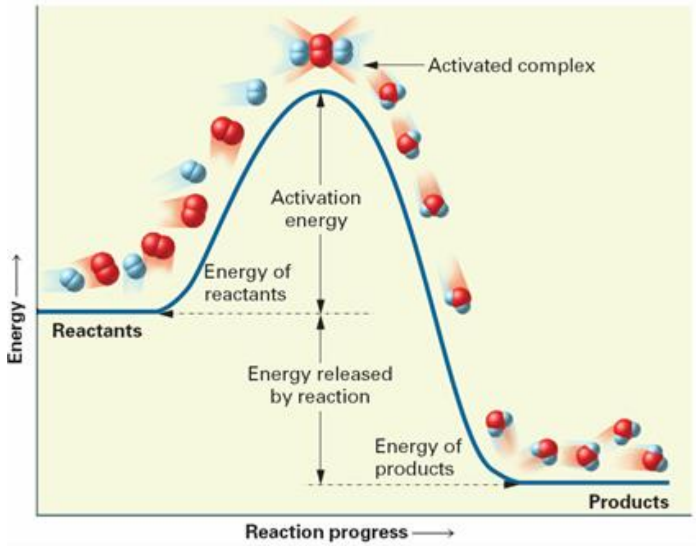
Unstable compound

9.1 Describing reaction rates

- **What physical variables affect the rate of a reaction between two chemical species?**
  - **Answer 3: Energy requirements of the reaction**

Activation energy (E_a)

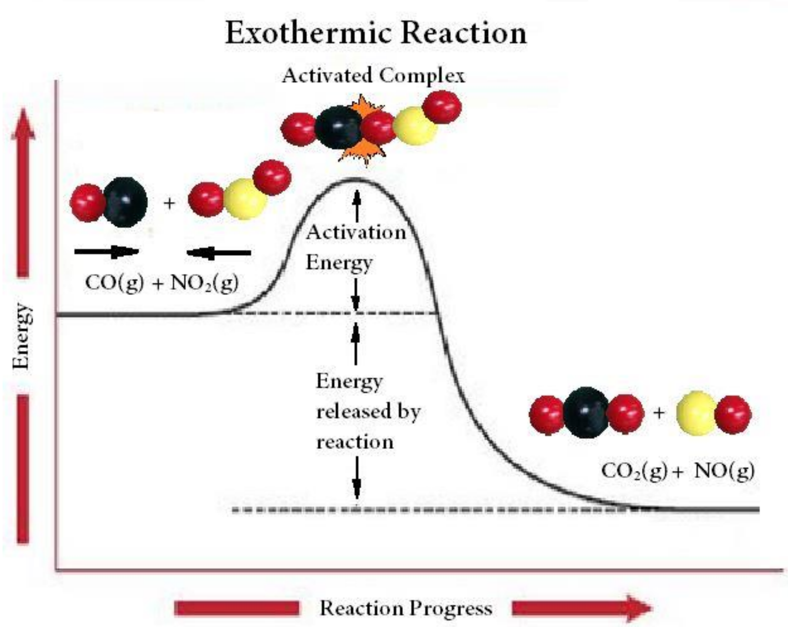




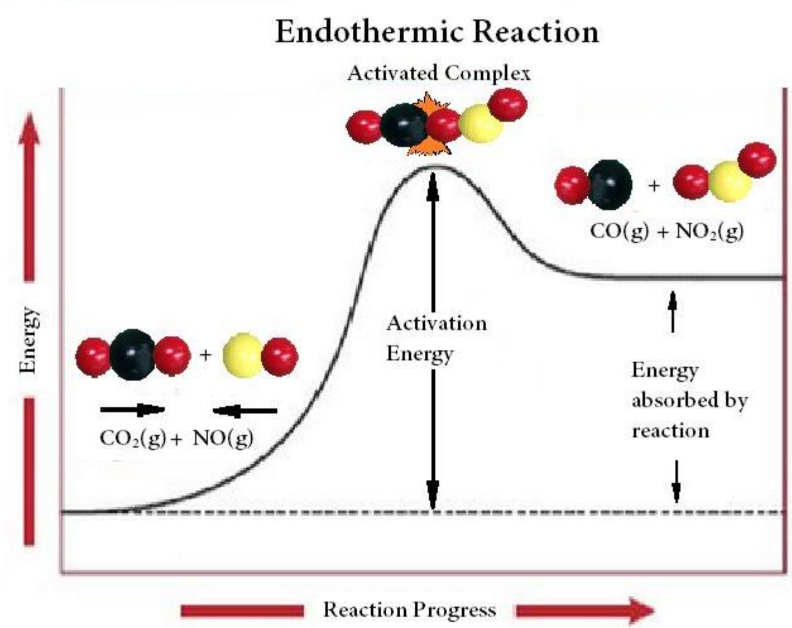
9.1 Describing reaction rates

- **What physical variables affect the rate of a reaction between two chemical species?**
  - **Answer 3: Energy requirements of the reaction**

$CO + NO_2 \rightarrow CO_2 + NO$



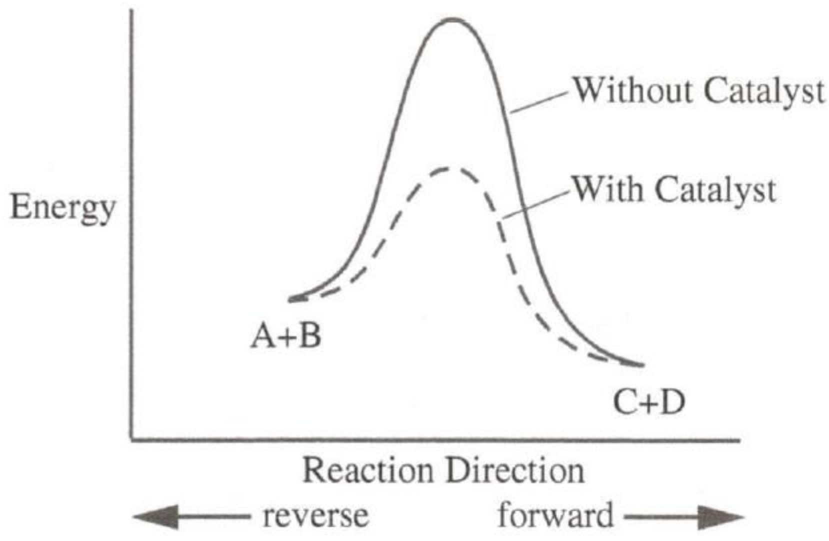
$CO_2 + NO \rightarrow CO + NO_2$

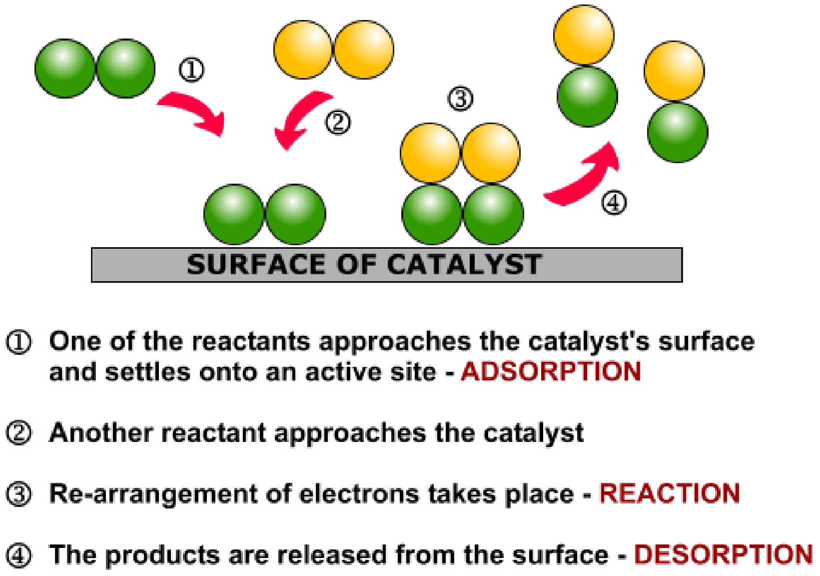


9.1 Describing reaction rates

- **What physical variables affect the rate of a reaction between two chemical species?**
  - **Answer 3: Energy requirements of the reaction**

Catalyst



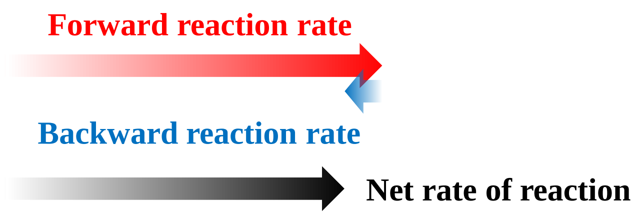


9.1 Describing reaction rates

- **What physical variables affect the rate of a reaction between two chemical species?**
  - **Answer 3: Energy requirements of the reaction**

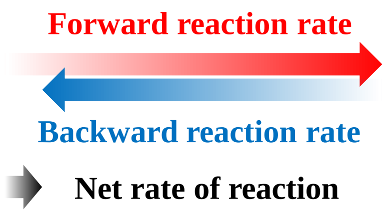
Irreversible reaction

$$A + B \longrightarrow C + D$$



Reversible reaction

$$A + B \longleftrightarrow C + D$$



9.1 Describing reaction rates

- **How do we describe the rate of reaction?**

1. For irreversible reaction $A + B \rightarrow C + D$

For liquid phase

$$\text{reaction rate}\left(\text{in units of } \frac{\text{moles of } A}{\text{time volume}}\right) = r_{reaction,A} = k_r c_A^n c_B^m$$

For gas phase

$$\text{reaction rate}\left(\text{in units of } \frac{\text{moles of } A}{\text{time volume}}\right) = r_{reaction,A} = k_r p_A^n p_B^m$$

Reaction order

n^{th} for species A

m^{th} for species B

$(n+m)^{th}$ for overall

Reaction rate constant

$$k_r = k_0 e^{-Ea/RT}$$

k_0 = frequency factor (with the same units as k_r)

E_a = activation energy (energy / mole)

R = universal gas constant

T = reaction temperature (absolute)

9.1 Describing reaction rates

➢ **How do we describe the rate of reaction?**

Elementary reactions

: the order of reaction with respect to each of the reactants matches the stoichiometry of the reaction equation.

$$2NO + O_2 \rightarrow 2NO_2 \qquad r_{reaction,NO} = k_r c_{NO}^2 c_{O_2}$$

Other reactions (in many cases)

: the order of reaction in the reaction rate equation do **not** match the stoichiometry of the reaction.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad r_{reaction,CO} = k_r c_{CO} c_{H_2O}^{0.5} c_{O_2}^{0.25}$$

9.1 Describing reaction rates

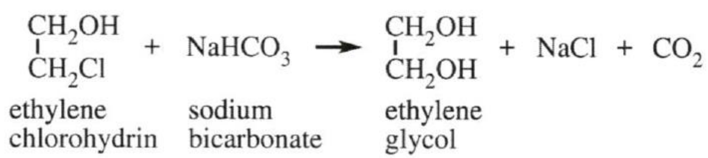
➢ **How do we describe the rate of reaction?**

For the acid-neutralization reaction,

$$HCl + NaOH \rightarrow H_2O + NaCl \qquad r_{reaction,HCl} = k_r c_{HCl} c_{NaOH}$$

Example 9.1

Ethylene glycol, a common antifreeze, is made from the reaction of ethylene chlorohydrin and sodium bicarbonate as shown below:



The reaction is essentially irreversible and is first-order in each reactant, and the reaction rate constant at 82˚*C* is 5.2 *L*/*gmol hr* (from reference 1, p. 123).

A reaction mixture at 82˚*C* with a volume of 17.5 *liters* contains ethylene chlorohydrin and sodium bicarbonate, both at concentrations of 0.5 *M*. What is the reaction rate of ethylene glycol (in *gmol*/*hr*)?

9.1 Describing reaction rates

- **How do we describe the rate of reaction?**

2. For reversible reaction $A + B \leftrightarrow C + D$

For liquid phase

$$r_{reaction,A} = k_r c_A^n c_B^m - k_r' c_C^r c_D^s$$

For gas phase

$$r_{reaction,A} = k_r p_A^n p_B^m - k_r' p_C^r p_D^s$$

9.1 Describing reaction rates

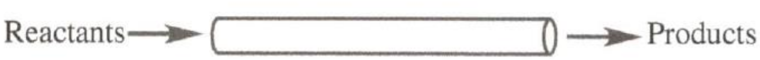
➢ **How do we describe the rate of reaction?**

Desirability

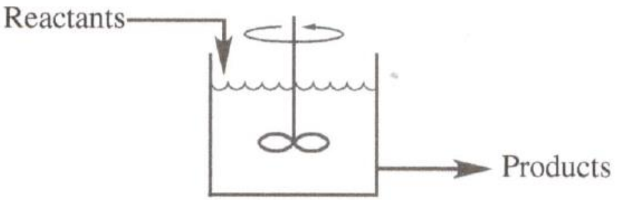
$A + B \rightarrow C + D$ **Desired reaction**

$A + B \rightarrow E + F$ **Undesired reaction (side reaction)**

Idealized types of reactors



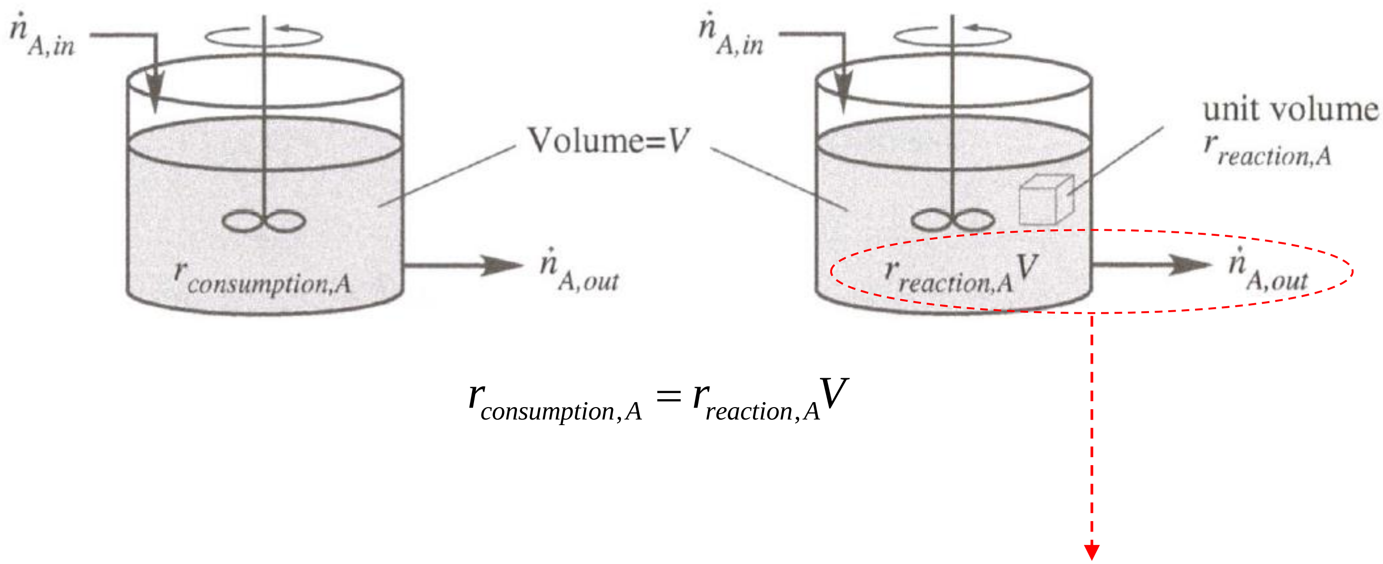
Plug-Flow Reactor (PFR)



Continuously Stirred Tank Reactor (CSTR)

9.2 Designing the reactor

- **Irreversible reaction**
- **Continuously stirred tank reactor (CSTR)**



$$r_{consumption,A} = r_{reaction,A}V$$

$$r_{reaction,A} = k_r c_A^n c_B^m = k_r c_{A,out}^n c_{B,out}^m$$

9.2 Designing the reactor

- **Steps for finding reactor volume**
  1. Perform the material balance analysis for multiple species.
  2. Compute the reactor volume.

Example 9.2

Species A in liquid solution (concentration = 0.74 M) enters a CSTR at 18.3 L/s, where it is consumed by the irreversible reaction

$$A \rightarrow C \quad where \quad r_{reaction,A} = k_r c_A \quad \left(k_r = 0.015/s \ and \ c_A \ is \ in \ units \ of \ gmol/L\right)$$

What reactor volume is needed so that the concentration of species A leaving the reactor equals 0.09 M? The density can be assumed to be constant.

9.2 Designing the reactor

Example 9.3

In the design of a process, liquid streams of pure species A and B will enter a CSTR, where they will be consumed by the irreversible reaction:

$$2A + B \rightarrow C \quad where \quad r_{reaction,A} = k_r c_A c_B \quad \left(k_r = 24.7\ ft^3/lbmol\ hr\ and\ c_A\ and\ c_B\ are\ in\ units\ of\ lbmol/ft^3\right)$$

The molar flow rates of the inlet streams will be

$$Species\ A: \dot{n}_A = 110\ lbmol/hr \quad MW = 59\ lb_m/lbmol$$
$$Species\ B: \dot{n}_B = 68\ lbmol/hr \quad MW = 133\ lb_m/lbmol$$

In the reactor, 90% of species A is to be reacted (i.e., 90% conversion of species A is desired), and the output stream will have a density of 50.5 lb_m/ft^3. What volume must the reactor have?

9.2 Designing the reactor

- **Neutralization of HCl**

Given information

$$c_{HCl_{in}} = 0.014\ gmol/L \qquad \dot{V}_{HCl_{in}} = 11,600\ L/hr$$

$$c_{NaOH_{in}} = 0.0254\ gmol/L \qquad \dot{V}_{NaOH_{in}} = 6,500\ L/hr$$

Reaction

$$HCl + NaOH \rightarrow H_2O + NaCl$$

Reaction rate constant

$$r_{reaction,HCl} = k_r c_{HCl} c_{NaOH} \qquad in\ units\ of\ moles\ of\ HCl\ or\ NaOH/(volume\ time)$$

Reaction rate constant at 25 °C

$$k_{r,HCl} = 1.4\times10^{11}\ L/gmol\ s$$

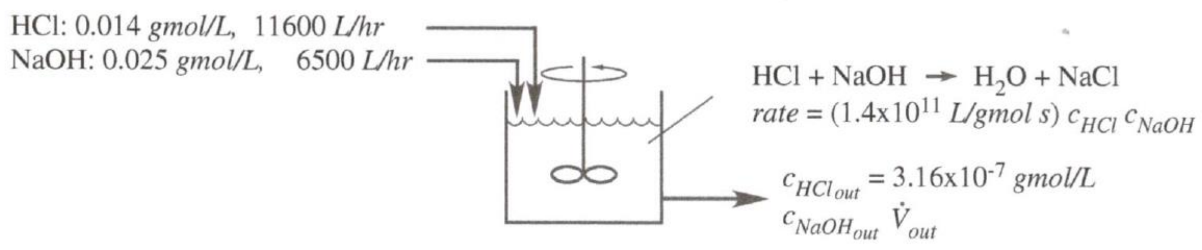
Allowed HCl concentration at final state by law (pH = 6.5)

$$c_{HCl} = 10^{-6.5} = 3.16\times10^{-7}\ M$$

9.2 Designing the reactor

➢ **Neutralization of HCl**

Working diagram



- **Mole balance on HCl:** $c_{HCl_{in}}\dot{V}_{HCl_{in}} = c_{HCl_{out}}\dot{V}_{HCl_{out}} + r_{consumption,HCl}$
- **Mole balance on NaOH:** $c_{NaOH_{in}}\dot{V}_{NaOH_{in}} = c_{NaOH_{out}}\dot{V}_{NaOH_{out}} + r_{consumption,NaOH}$
- **Total mass balance (with constant ρ):** $\dot{V}_{HCl_{in}} + \dot{V}_{NaOH_{in}} = \dot{V}_{out}$
- **Additional relationships**

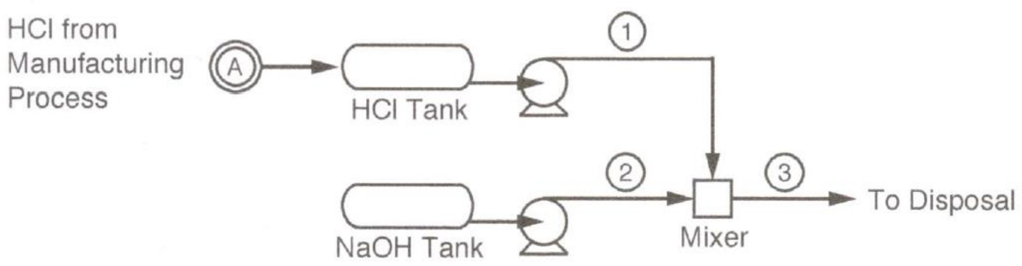
Stoichiometry: $\frac{r_{consumption,HCl}}{r_{consumption,NaOH}} = \frac{1}{1} = 1$

Molar flow rate balance: $c_{NaOH_{in}}\dot{V}_{NaOH_{in}} = c_{HCl_{in}}\dot{V}_{HCl_{in}}$

9.2 Designing the reactor

- **Neutralization of HCl**

Process flow diagram (PFD)



Flows kg/h

Line no.	1	2	3		
Stream / Component	Acid feed	Base feed	Mixer outlet	ABC Chemical Co.	
HCl	6	—	—	Acid neutralization	
NaOH	—	6	—	$1x10^8$ L/yr	
H_2O	11594	6490	18096	Sheet no. 1	
Total	11600	6496	18096	Dwg by	Date
				Checked	1 Sep.2010

Homework problems

Homework problem 4.

A prevalent form of toxic pollutant NO_x formed in power plant combustors is NO. Under favorable conditions, NO can be decomposed ("*reduced*") via the following reaction:

$$2NO \rightarrow N_2 + O_2$$

At 1620 *K*, for a reaction rate expressed in *gmol*/*L s* and the amount of NO expressed in atmospheres, the reaction rate constant for this irreversible reaction is 0.0108 *gmol*/*L s* $(atm)^2$ (from reference 2, p. 813).

a. Assuming that NO is the only reactant, use the units of the rate constant to determine the order of this reaction in terms of NO.
b. If a reactor is designed to reduce NO at a rate of 0.056 *gmol*/*min L* at 1620 *K*, what partial pressure of NO is needed in the reactor?

Homework problems

Homework problem 5.

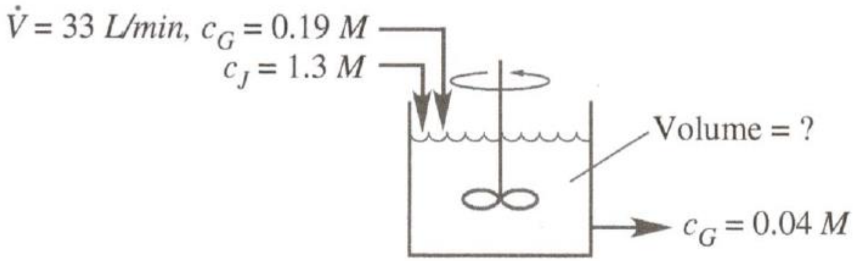
For the acid-neutralization process, we calculated the reactor size required for a reaction temperature of $25^{\circ}C$. Estimate the reactor volume for a reaction temperature of $5^{\circ}C$ (a cold winder day) using the following values:

$$k_0 = 5.2 \times 10^{13}\ L / gmol\ s$$
$$E_a = 3500\ cal / gmol$$

Homework problems

Homework problem 6.

As an engineer in a production facility, your assignment is to specify the size of a reactor needed to react a liquid stream (33 *L/min*) containing species G (concentration = 0.19 *M*). The goal is to produce a reactor outlet stream with a concentration of G equal to 0.04 *M*. To accomplish that, a second stream containing species J (concentration = 1.3 *M*) is also to enter the reactor but at 75% of the volumetric flow rate of the first stream, as shown.



The irreversible reaction is

$$G + J \rightarrow P$$

Where the reaction rate only depends on species G according to the following kinetic relation:

$$r_{reaction,G} = \left(1.8 \frac{L}{gmol\ min}\right) c_G^2$$

Given these requirements, what size reactor (*L*) is needed to produce these results? (Assume equal densities for all streams.)