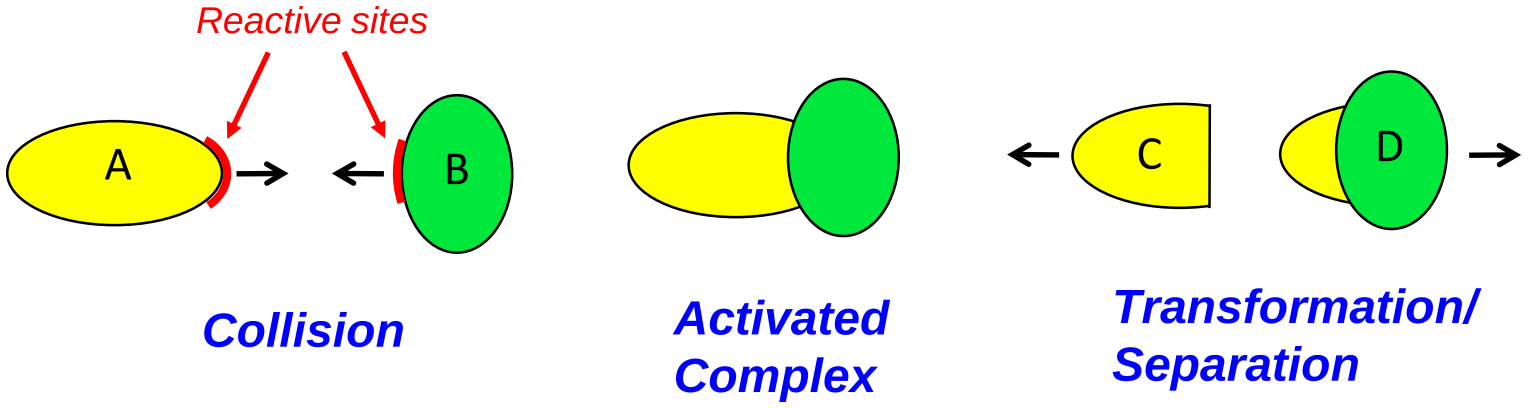
Chapter 9

Reaction Engineering

Reaction Rate

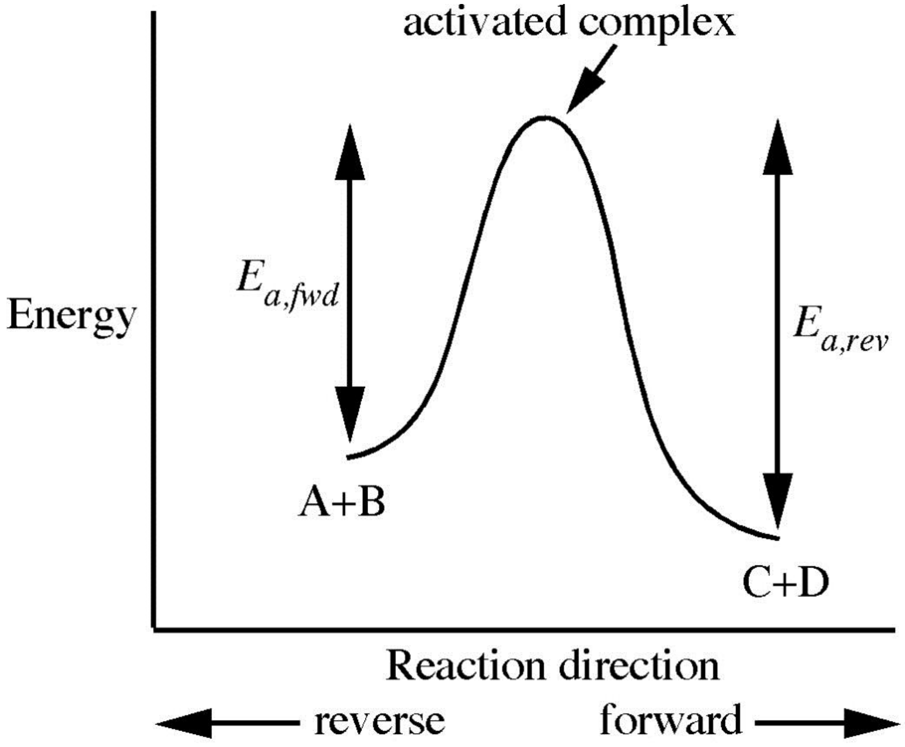
A + B → C + D

- Frequency of Molecular Collision
  - Depends on concentrations
  - Depends on velocity of moving molecules
    - The velocity depends on the temperature.
- Orientation and Force of the Collision
  - Not all collisions lead to reaction



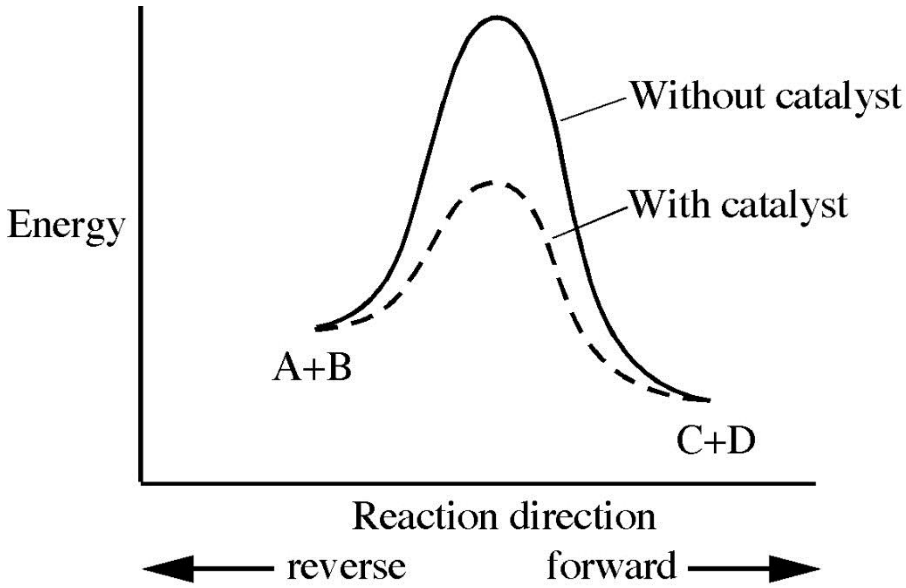
Reaction Rate

- Energy Requirements of the Reaction



Reaction Rate

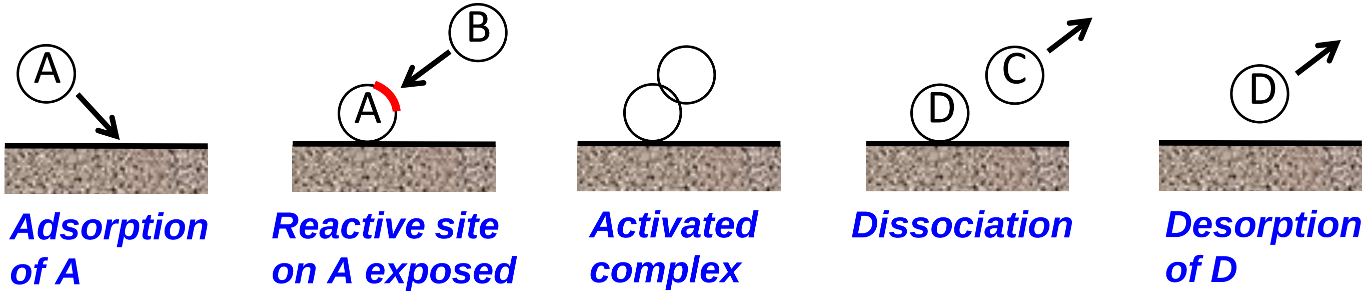
- How could you alter reactor conditions to increase the reaction rate?
  - Increase temperature (collision rate, energy)
  - Increase pressure or concentration (collision rate)
  - Use catalysts (activation energy)



Catalyst

- Catalysts are porous.

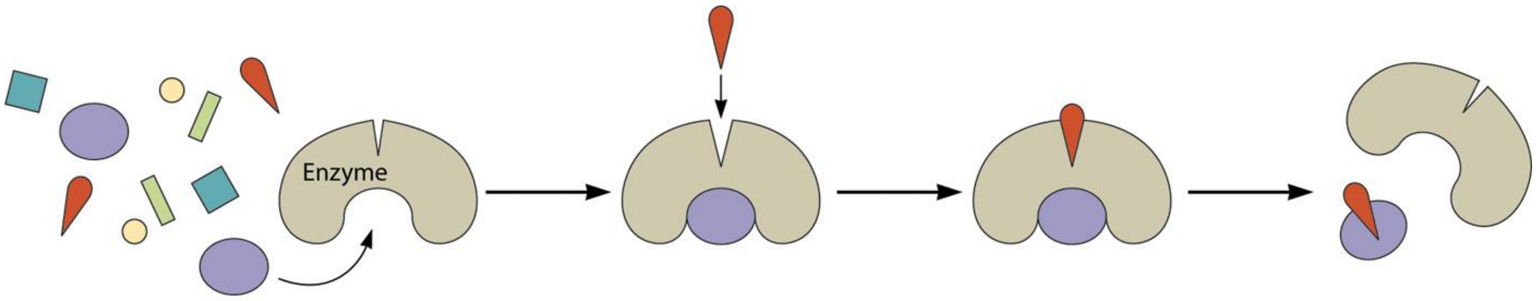
1. Reactants diffuse into the pores.
2. Reaction proceeds.



3. Products diffuse out of the pores.

Biocatalyst (Enzyme)

- Enzyme
  - Protein which accelerates chemical reactions



Reversible Reaction

- Irreversible Reaction
  - when the reverse reaction rate is insignificant compared with the forward reaction rate

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

- Reversible Reaction
  - if the reverse reaction rate is significant

$$A + B \rightleftharpoons C + D$$

Reaction Rate

A + B → C + D

$$\text{Reaction rate} \left(\frac{\text{moles of A}}{\text{time volume}}\right)$$

$$r_{reaction,A} = k_r\, c_A^{\,n}\, c_B^{\,m}$$

$$r_{consumption,A} = r_{reaction,A}\, V_{reactor}$$

- "Order" of this reaction
  - Overall order: n+m
  - with respect to reactant A: n

Reaction Rate

A + B → C + D

Liquid: $r_{reaction,A} = k_r c_A^n c_B^m$

Gas: $r_{reaction,A} = k_r p_A^n p_B^m$

(p = partial pressure)

- Reaction Rate Constant

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

  - k_0 : frequency factor
  - E_a : activation energy

Arrhenius Equation

- Reaction Rate Constant

$$k_r = k_0\, e^{-E_a/RT}$$

  - k_0 : frequency factor (with the same unit as k_r)
  - E_a : activation energy (in units of energy per mole)
  - R : universal gas constant
  - T : absolute temperature

Reaction Rate

- Reversible Reaction

$$\mathbf{A + B} \underset{k_r'}{\overset{k_r}{\rightleftharpoons}} \mathbf{C + D}$$

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

Reactor

- Batch Reactor
- Continuous Reactor
  - Plug-Flow Reactor (PFR)
  - Continuously Stirred Tank Reactor (CSTR), Chemostat

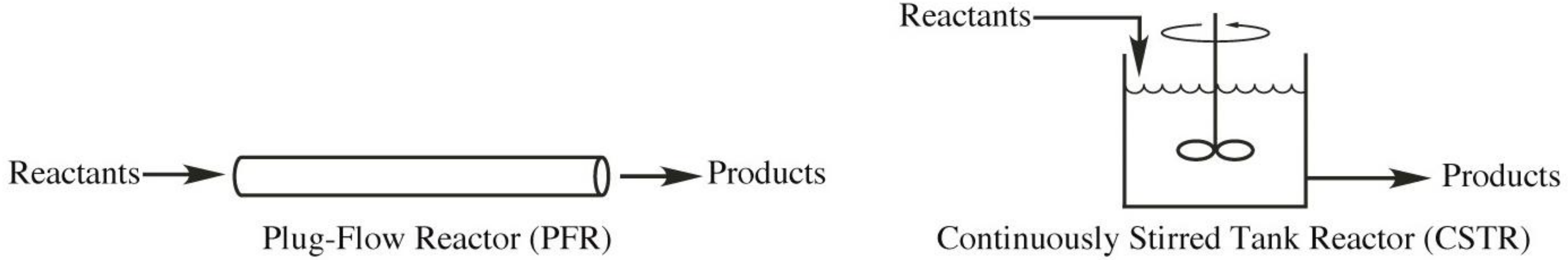
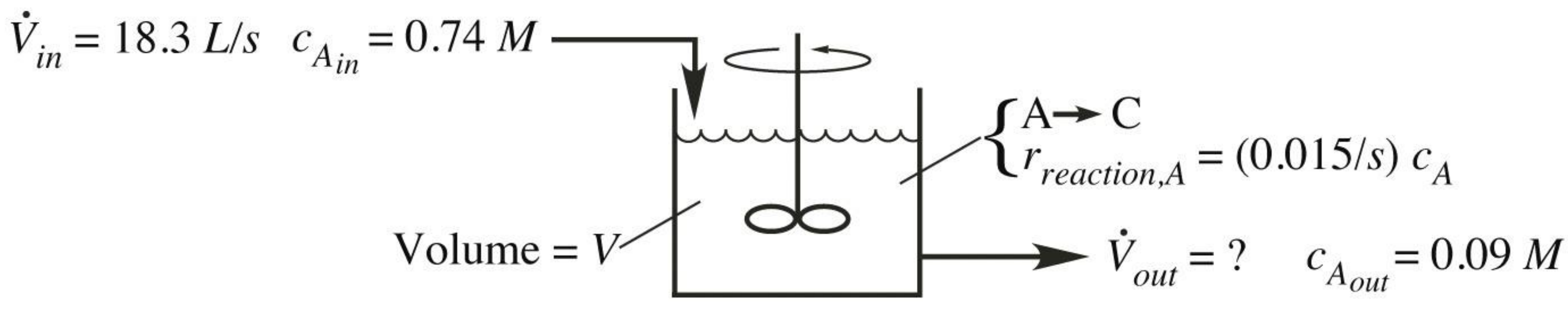


Figure 9.4

Ex. 9.2. Species A in liquid solution (concentration=0.74M) enters a CSTR at 18.3 L/s, where it is consumed by the irreversible reaction

A $\rightarrow$ C where $r_A = k_r c_A$ ($k_r = 0.015/s$ and c_A is in units of *gmol/L*)

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



Example 9.2

Ex. 9.3. In the design of a process, separate liquid streams of pure species A and B will enter a CSTR, where they will be consumed by the irreversible reaction:

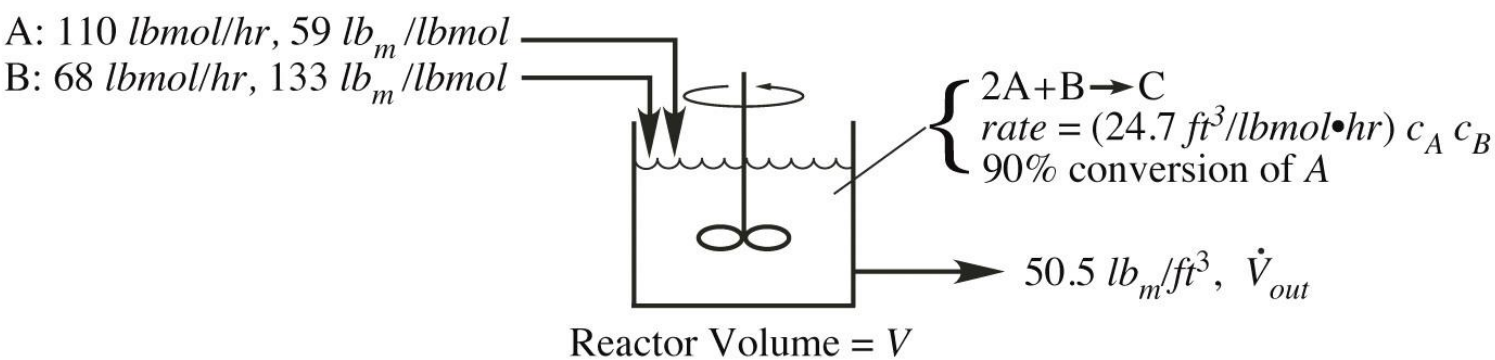
2A+B $\rightarrow$ C where $r_A = k_r c_A c_B$

$$k_r = 24.7\, ft^3 / lbmol\, hr, \quad c_A, c_B \; in\; lbmol / ft^3$$

$$species A : \dot{n}_A = 110\, lbmol / hr \quad (MW = 59 lb_m / lbmol)$$

$$species B : \dot{n}_B = 68\, lbmol / hr \quad (MW = 133 lb_m / lbmol)$$

In the reactor, 90% of species A is to be reacted, and the output stream will have a density of $50.5\, lb_m / ft^3$. What volume must the reactor have?



Example 9.3

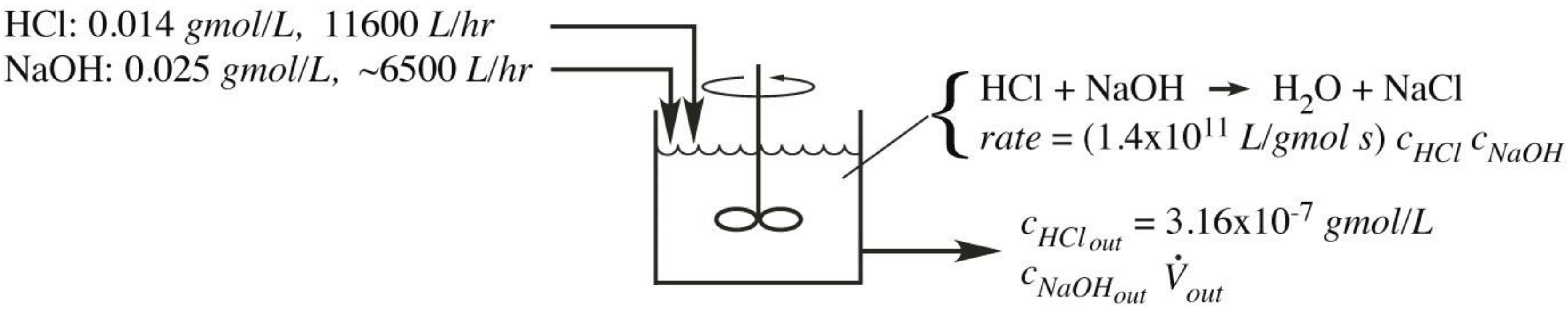


Figure 9.6

State law: the lowest pH allowable for water added to a lake or river is 6.5

$$\rightarrow c_{HCl} = 10^{-6.5} = 3.16 \times 10^{-7}\, M$$

Mole balance on HCl $\quad c_{HCl,in}\dot{V}_{HCl,in} = c_{HCl,out}\dot{V}_{out} + r_{consumption,HCl}$

Mole balance on NaOH $\quad c_{NaOH,in}\dot{V}_{NaOH,in} = c_{NaOH,out}\dot{V}_{out} + r_{consumption,NaOH}$

Total mass balance $\quad \dot{V}_{HCl,in} + \dot{V}_{NaOH,in} = \dot{V}_{out}$

Stoichiometry $\quad r_{consumption,HCl} = r_{consumption,NaOH}$

Molar flow rate balance:

The flow rate given in Figure 9.6 is given as an approximate value, because the pH of the final solution is very sensitive to the balance between HCl and NaOH. Thus we will vary the NaOH flow rate carefully as we monitor the pH. For the sake of our present calculation, we need to preset the inlet molar flow rate of NaOH to balance against the molar flow rate of HCl.

$$r_{consumption,HCl} = r_{consumption,NaOH} \qquad c_{NaOH,in}\dot{V}_{NaOH,in} = c_{HCl,in}\dot{V}_{HCl,in}$$

$$\dot{V}_{HCl,in} + \dot{V}_{NaOH,in} = \dot{V}_{out} \qquad \dot{V}_{out} = 11,600 L/hr + 6500 L/hr = 18,100 L/hr$$

$$c_{HCl,in}\dot{V}_{HCl,in} = c_{HCl,out}\dot{V}_{out} + r_{consumption,HCl} \qquad r_{consumption,HCl} = 162 gmol/hr$$

$$c_{NaOH,out} = c_{HCl,out}$$

$$r_{consumption,HCl} = k_r c_{HCl,out} c_{NaOH,out} V \qquad V = 3.22 L$$

very small reactor -> the reaction proceeds so rapidly that only a very small residence time in the reactor is needed to achieve the desired results.