Chapter 9

Reaction Engineering
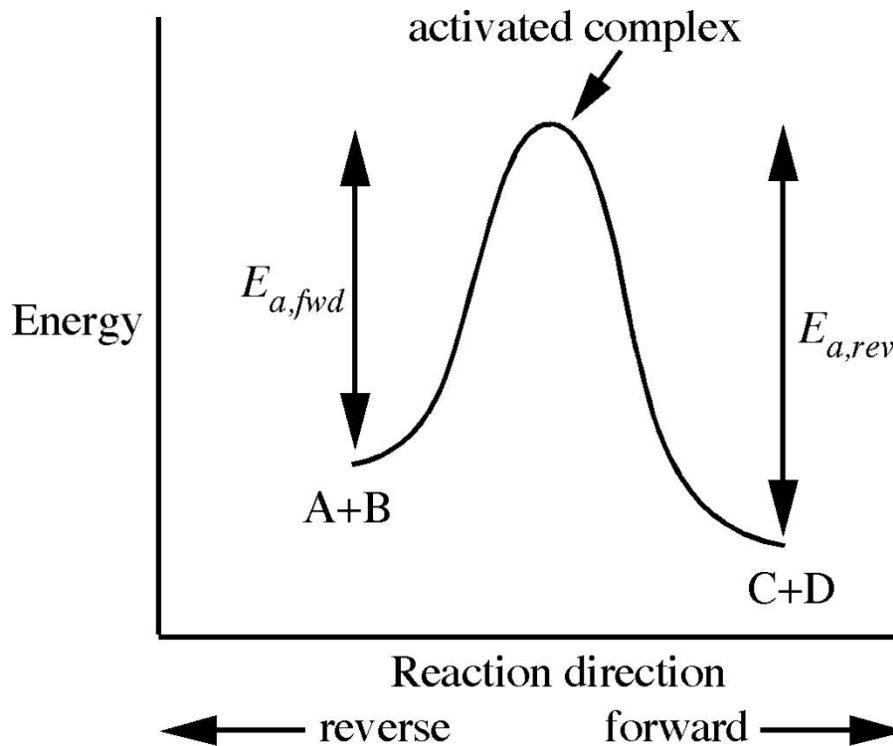
Reaction Rate

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

Reactive sites

A   B

Collision

Activated Complex
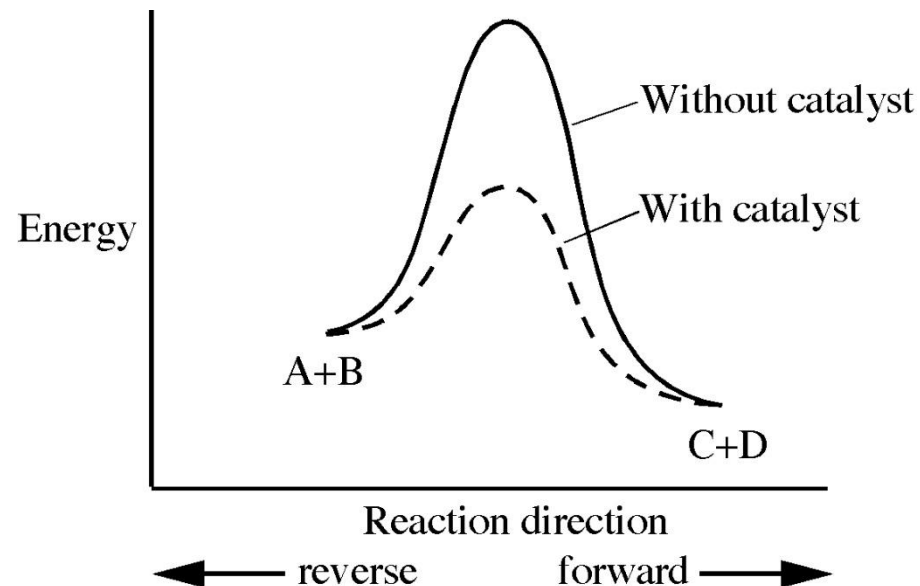
C   D

Transformation/ Separation
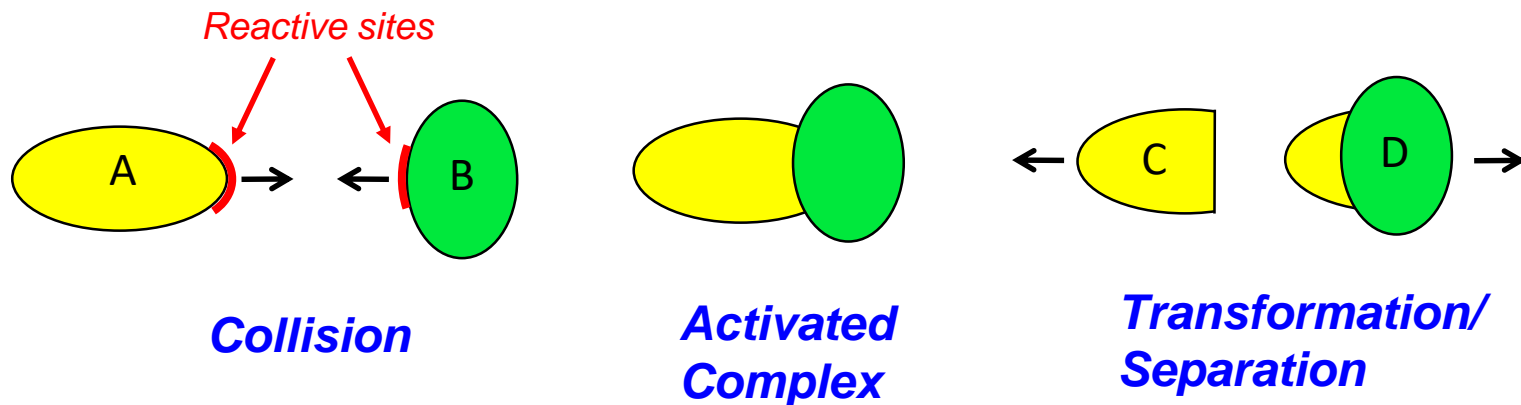
Reaction Rate

- 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)
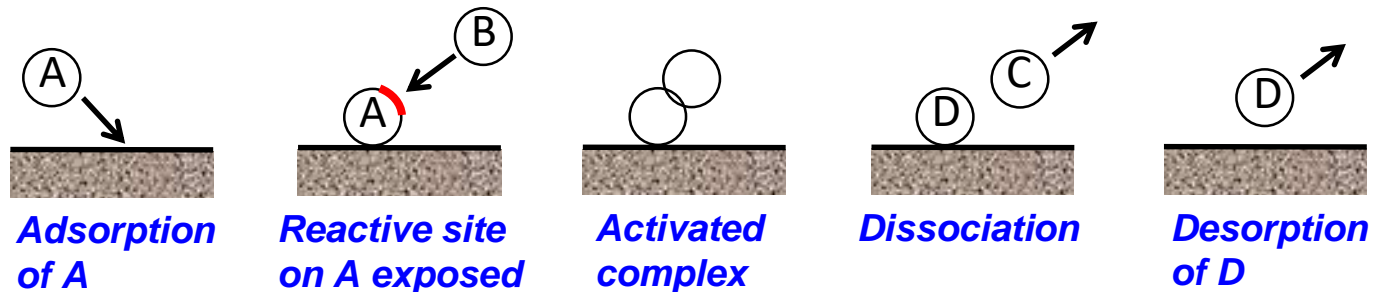 - Use catalysts (activation energy)

Catalyst

- Catalysts are porous.

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

Adsorption of A   **Reactive site on A exposed**   **Activated complex**   **Dissociation**   **Desorption of D**

3. Products diffuse out of the pores.

Biocatalyst (Enzyme)

- Enzyme
  - Protein which accelerates chemical reactions
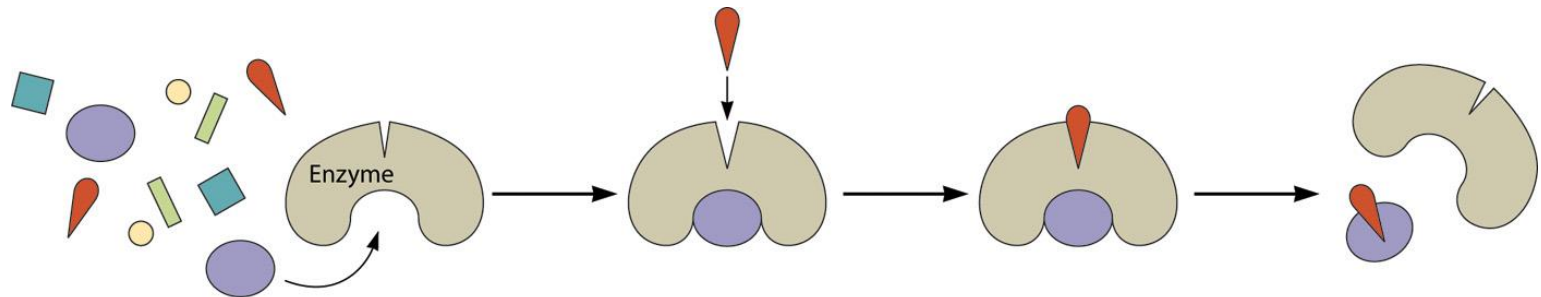
Reversible Reaction

- ## 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

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

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

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

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

Reaction Rate

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

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

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

(p = partial pressure)

- Reaction Rate Constant

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

  - k_0 : frequency factor
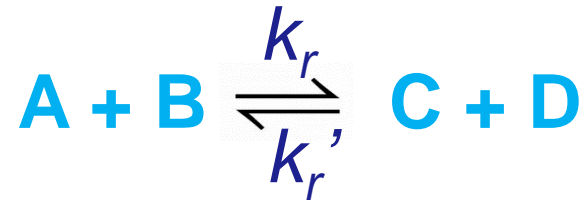 - E_a : activation energy

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

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

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

Reactor

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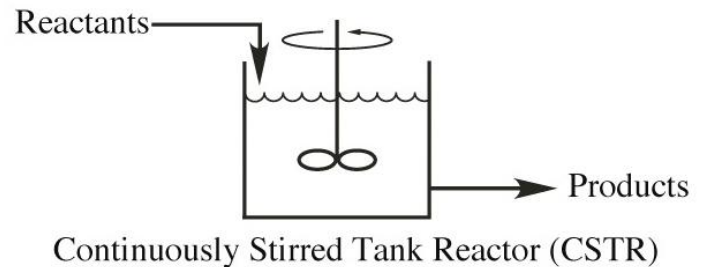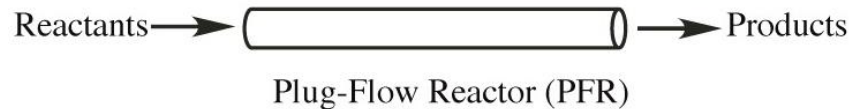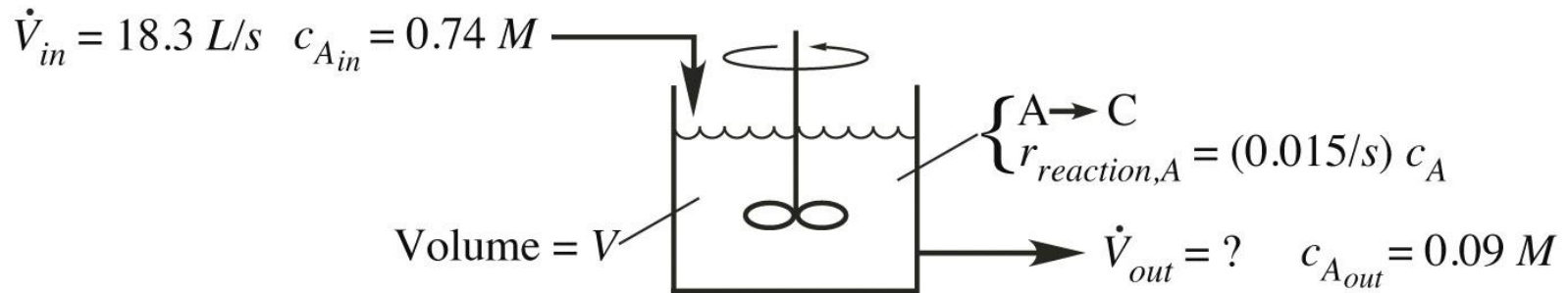   - Continuously Stirred Tank Reactor (CSTR), Chemostat

Reactants → | Plug-Flow Reactor (PFR) | → Products

Plug-Flow Reactor (PFR)

Reactants → Continuously Stirred Tank Reactor (CSTR) → Products

Continuously Stirred Tank Reactor (CSTR)

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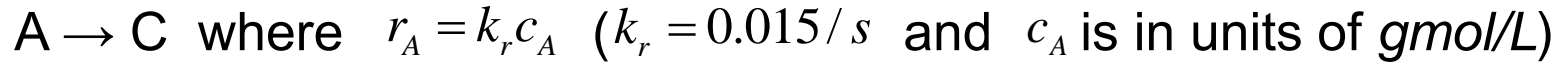
What reactor volume is needed so that the concentration of A leaving the reactor equals 0.09M? The density can be assumed to be constant.

$\dot{V}_{in} = 18.3\ L/s$ $c_{A_{in}} = 0.74\ M$

$\begin{cases} A \rightarrow C \\ r_{reaction,A} = (0.015/s)\ c_A \end{cases}$

Volume = V

$\dot{V}_{out} = ?$ $c_{A_{out}} = 0.09\ M$

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 → C where $r_A = k_r c_A c_B$

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

$speciesA : \overset{\square}{n}_A = 110 \, lbmol / hr \quad (MW = 59 lb_m / lbmol)$

$speciesB : \overset{\square}{n}_B = 68 \, lbmol / hr \quad (MW = 133 lb_m / lbmol)$

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?

A: 110 *lbmol/hr*, 59 *lb$_m$/lbmol*
B: 68 *lbmol/hr*, 133 *lb$_m$/lbmol*

$\begin{cases} 2A+B \rightarrow C \\ rate = (24.7 \, ft^3/lbmol \cdot hr) \, c_A \, c_B \\ 90\% \text{ conversion of } A \end{cases}$

$50.5 \, lb_m/ft^3, \, \dot{V}_{out}$

Reactor Volume = V
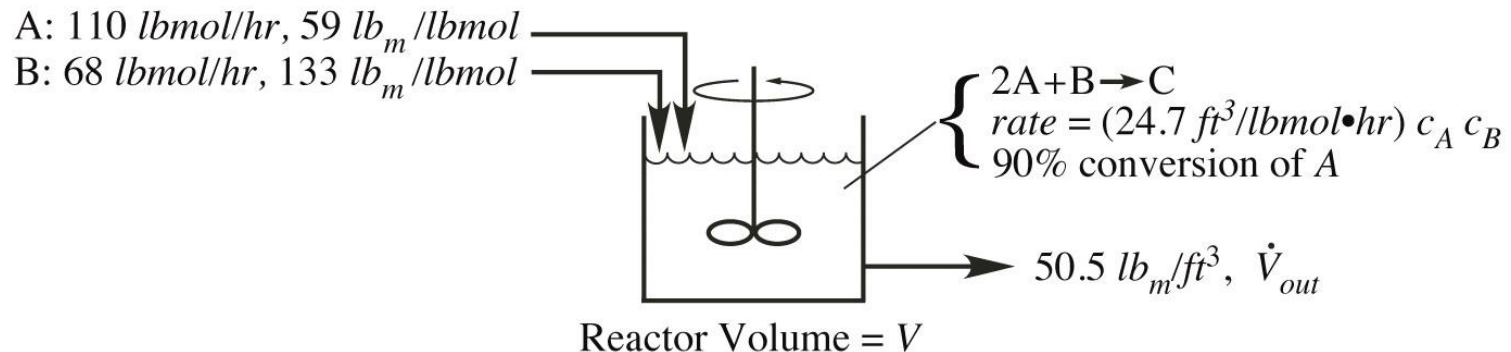
HCl: 0.014 gmol/L, 11600 L/hr
NaOH: 0.025 gmol/L, ~6500 L/hr

$$HCl + NaOH \rightarrow H_2O + NaCl$$
$$rate = (1.4\times10^{11}\ L/gmol\ s)\ c_{HCl}\ c_{NaOH}$$

$$c_{HCl_{out}} = 3.16\times10^{-7}\ gmol/L$$
$$c_{NaOH_{out}}\quad \dot{V}_{out}$$
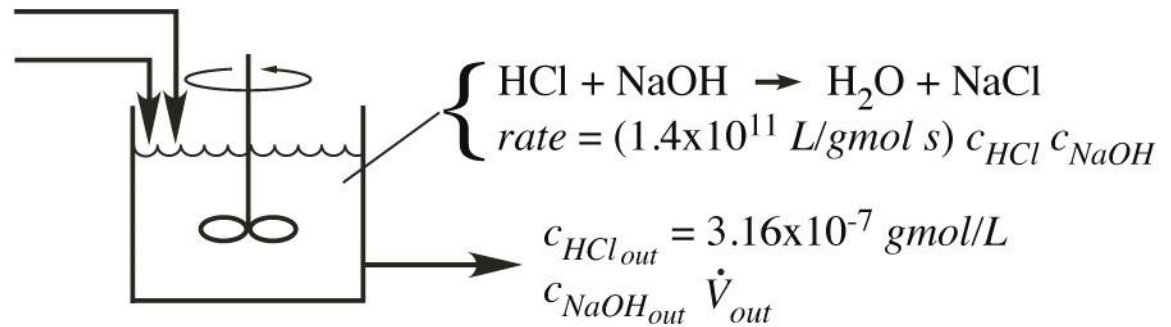
Figure 9.6

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

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

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

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

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

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

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.

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

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

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

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

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

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.

Chapter 10

Heat Transfer

Energy Balance for a Closed System

- *First Law of Thermodynamics for a closed system* (a fixed volume or space with no streams entering or leaving the system)

$$\Delta E = Q + W \qquad \text{(10.1)}$$

E = total energy of a system

Q = heat transferred into the system (e.g. through the boundaries)

W = work done on the system

Energy Balance for an Open System

- Open system
  - a system with streams entering and leaving
- For a steady-state open system

$$\sum_{\substack{output \\ streams}} \left\{\dot{m}\,\hat{E}\right\}_{out} - \sum_{\substack{input \\ streams}} \left\{\dot{m}\,\hat{E}\right\}_{in} = \dot{Q} + \dot{W} \qquad (10.2)$$

$\dot{m}$ = mass flow rate of a stream (units of mass per time)

$\hat{E}$ = energy per mass of a stream of flowing material

$\dot{Q}$ = rate of transfer of energy across the boundaries of a stream
    into the system (units of energy per time)

$\dot{W}$ = rate that work is done on a system (units of energy per time)

$$\hat{E}_{total} = \hat{E}_{\mathrm{int}\,ernal} + \hat{E}_{kinetic} + \hat{E}_{potential} = \hat{U} + \frac{1}{2}\alpha v^2 + gz \quad \text{(10.3)}$$

$$\sum_{\substack{output \\ streams}} \left\{ \dot{m}\,\hat{E} \right\}_{out} - \sum_{\substack{input \\ streams}} \left\{ \dot{m}\,\hat{E} \right\}_{in} = \dot{Q} + \dot{W} \quad \text{(10.2)}$$

$$\sum_{\substack{output \\ streams}} \dot{m}\left[\hat{U} + \frac{1}{2}\alpha v^2 + gz \right]_{out} - \sum_{\substack{input \\ streams}} \dot{m}\left[\hat{U} + \frac{1}{2}\alpha v^2 + gz \right]_{in} = \dot{Q} + \dot{W}$$

$$\text{(10.4)}$$

Heat Transfer

- Conduction
  - through a stationary medium
  - by temperature difference
- Convection
  - through a moving medium
- Radiation
  - As electromagnetic waves
  - without a medium (even through a vacuum)
  - e.g. sun radiating its heat to the earth
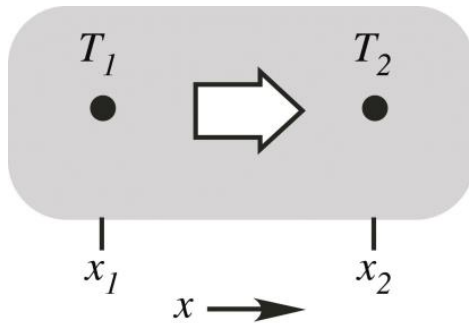
Conduction

- Fourier's Law of Heat Conduction

$$\dot{Q}_{cond,x} = -kA\,\frac{T_2 - T_1}{x_2 - x_1}$$

k = thermal conductivity

A = cross-sectional area through which the heat conducts

- cf. Fick's Law of Diffusion

$$\dot{N}_A = -D_{AB}\,A\,\frac{c_{A,2} - c_{A,1}}{x_2 - x_1}$$

Conductivity (k)

k (W/m℃) @25℃	
air	.026
water	.61
glass	1.4
aluminum	237

Which has the lowest k, gas or solid?

What are the best insulations?

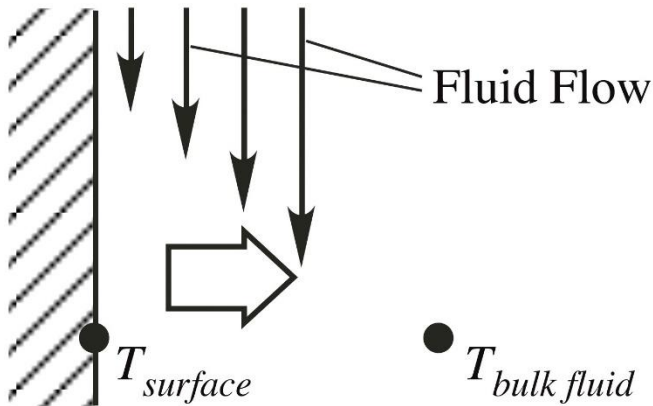Why is a double-pane window an effective thermal barrier?

Convection

Fluid Flow

$T_{surface}$

$T_{bulk\,fluid}$

$$\dot{Q}_{conv} = h\,A\,(T_{surface} - T_{bulk\,fluid})$$

h = heat-transfer coefficient (depends on geometry and flow)

A = cross-sectional area

cf. Mass Transfer Rate: $\dot{N}_A = h_m\,A\,(c_{A,1} - c_{A,2})$
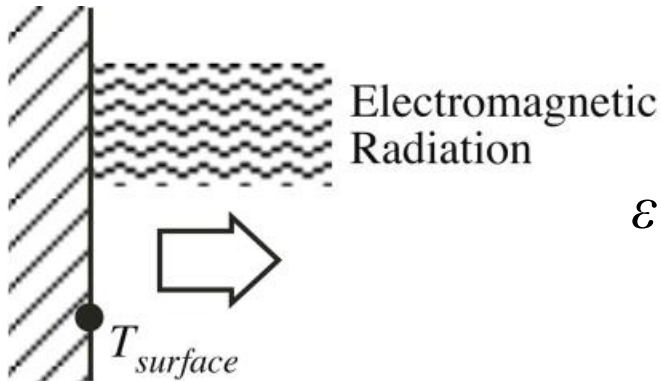
Radiation

Figure 16.3
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$$\dot{Q}_{rad} = \varepsilon\, \sigma\, A\, (T_{surface})^4$$

ε = emissivity, which indicates how well the surface emits radiation compared with a "perfect" radiator (unit-less)
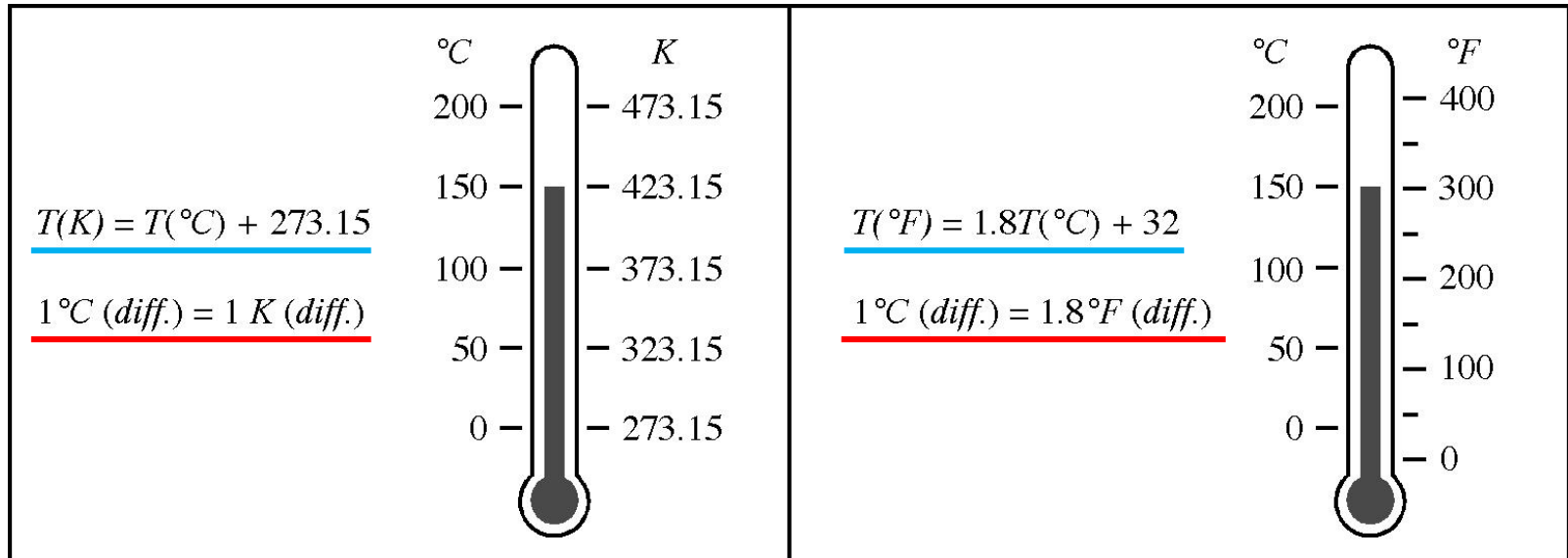
σ = Stefan-Boltzmann constant

$(5.67 \times 10^{-8}\ W / m^2\ K^4)$

A = area of the radiating surface

T = absolute surface temperature (K)

$$\dot{Q}_{rad,net} = \varepsilon_1\, \sigma\, A_1\, (T_{surface,1})^4 - \varepsilon_2\, \sigma\, A_2\, (T_{surface,2})^4$$

Temperature & Temp. Difference

°C   K

200	473.15
150	423.15
100	373.15
50	323.15
0	273.15

$T(K) = T(°C) + 273.15$

$1°C \ (diff.) = 1 \ K \ (diff.)$

°C   °F

200	400
150	300
100	200
50	100
0	0

$T(°F) = 1.8T(°C) + 32$

$1°C \ (diff.) = 1.8°F \ (diff.)$

Ex. 10.1. A typical value for the thermal conductivity of steel is 53 *W/m K*. What is the corresponding value in unit of *Btu/hr ft °F*?
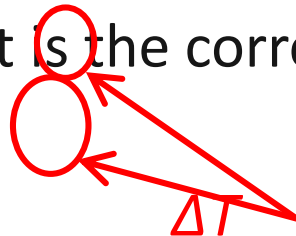
Rate of Work

- ## Rate of shaft work ($\dot{W}_s$)

  - Energy per time

  - Positive when work is done on the system (such as in a pump, "push" the fluid)

  - Negative when work is done by the fluid (such as in turbine)

- ## Rate of flow work ($\dot{W}_{PV}$)

  - Work resulting from the displacement of fluid during flow

  - Similar to the pressure-volume work associated with the compression or expansion of a closed

Energy Balance

$$\dot{W}_{PV} = \sum_{\substack{input \\ streams}} (P\dot{V})_{in} - \sum_{\substack{output \\ streams}} (P\dot{V})_{out} = \sum_{\substack{input \\ streams}} (\dot{m}P\hat{V})_{in} - \sum_{\substack{output \\ streams}} (\dot{m}P\hat{V})_{out}$$

(10.8)

$$\dot{W} = \dot{W}_s + \dot{W}_{PV}$$

(10.9)

$$\sum_{\substack{output \\ streams}} \dot{m}\left[\hat{U} + \frac{1}{2}\alpha v^2 + gz\right]_{out} - \sum_{\substack{input \\ streams}} \dot{m}\left[\hat{U} + \frac{1}{2}\alpha v^2 + gz\right]_{in} = \dot{Q} + \dot{W}$$

(10.4)

$$\sum_{\substack{outpu \\ streams}} \left\{\dot{m}\left[\hat{U} + \frac{1}{2}\alpha v^2 + gz\right]\right\}_{out} - \sum_{\substack{input \\ streams}} \left\{\dot{m}\left[\hat{U} + \frac{1}{2}\alpha v^2 + gz\right]\right\}_{in} = \dot{Q} + \dot{W}_s + \dot{W}_{PV}$$

(10.10)

Energy Balance

$$\sum_{\substack{outpu \\ streams}} \left\{ \dot{m} \left[\hat{U} + P\hat{V} + \frac{1}{2}\alpha v^2 + gz \right] \right\}_{out} - \sum_{\substack{input \\ streams}} \left\{ \dot{m} \left[\hat{U} + P\hat{V} + \frac{1}{2}\alpha v^2 + gz \right] \right\}_{in}$$

$$= \dot{Q} + \dot{W}_s \qquad \text{(10.11)}$$

Compare Eq. 10.11 with mechanical energy balance.

$$\left(\frac{P}{\rho} + \frac{1}{2}\alpha v^2_{ave} + gz \right)_{out} - \left(\frac{P}{\rho} + \frac{1}{2}\alpha v^2_{ave} + gz \right)_{in} = w_s - w_f$$

$$\text{(7.8a)}$$

Energy Balance

$$\hat{H} = \hat{U} + P\hat{V}$$

(10.12)

Most common form of
the steady-state open-system energy balance.

$$\sum_{\substack{output \\ streams}} \left\{ \dot{m} \left[\hat{H} + \frac{1}{2}\alpha v^2 + gz \right] \right\}_{out} - \sum_{\substack{input \\ streams}} \left\{ \dot{m} \left[\hat{H} + \frac{1}{2}\alpha v^2 + gz \right] \right\}_{in} = \dot{Q} + \dot{W}_s$$

(10.13)

Energy Balance

Steady-state energy balance
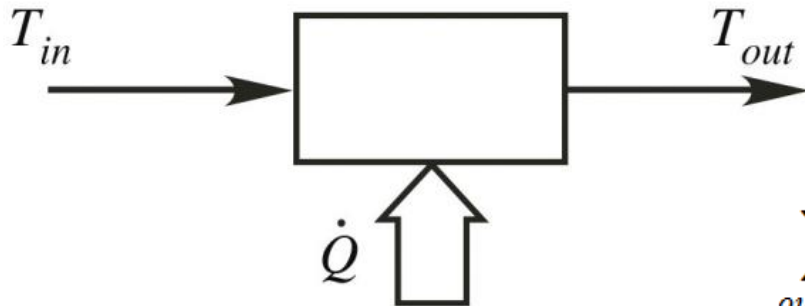with negligible change in kinetic and potential energies
and with no shaft work

$$\sum_{\substack{output \\ streams}} \left\{ \dot{m} \left[\hat{H} + \frac{1}{2}\alpha v^2 + gz \right] \right\}_{out} - \sum_{\substack{input \\ streams}} \left\{ \dot{m} \left[\hat{H} + \frac{1}{2}\alpha v^2 + gz \right] \right\}_{in} = \dot{Q} + \dot{W}_s \qquad (10.13)$$

$$\sum_{\substack{output \\ streams}} \left(\dot{m}\,\hat{H} \right)_{out} - \sum_{\substack{input \\ streams}} \left(\dot{m}\,\hat{H} \right)_{in} = \dot{Q} \qquad (10.14)$$

Energy Balance

Figure 10.5
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$$\sum_{\substack{output \\ streams}} \left(\dot{m}\,\hat{H} \right)_{out} - \sum_{\substack{input \\ streams}} \left(\dot{m}\,\hat{H} \right)_{in} = \dot{Q}$$

(10.14)

(i) Sensible Heating/Cooling: $\sum\limits_{out} \dot{m}\bar{C}_p(T - T_{ref}) - \sum\limits_{in} \dot{m}\bar{C}_p(T - T_{ref}) = \dot{Q}$

$T_{out} > T_{in}$ (No phase change)

(10.16)

(ii) Phase Change: $\dot{m}_{phase\ change}\,\Delta\hat{H}_{phase\ change} = \dot{Q}$

$T_{out} = T_{in}$ (Phase change)

(10.18)

(iii) Chemical Reaction: $r_{consumption,A}\,\Delta\tilde{H}_{reaction,A} = \dot{Q}$

$T_{out} = T_{in}$

(10.20)

Heat-Exchangers

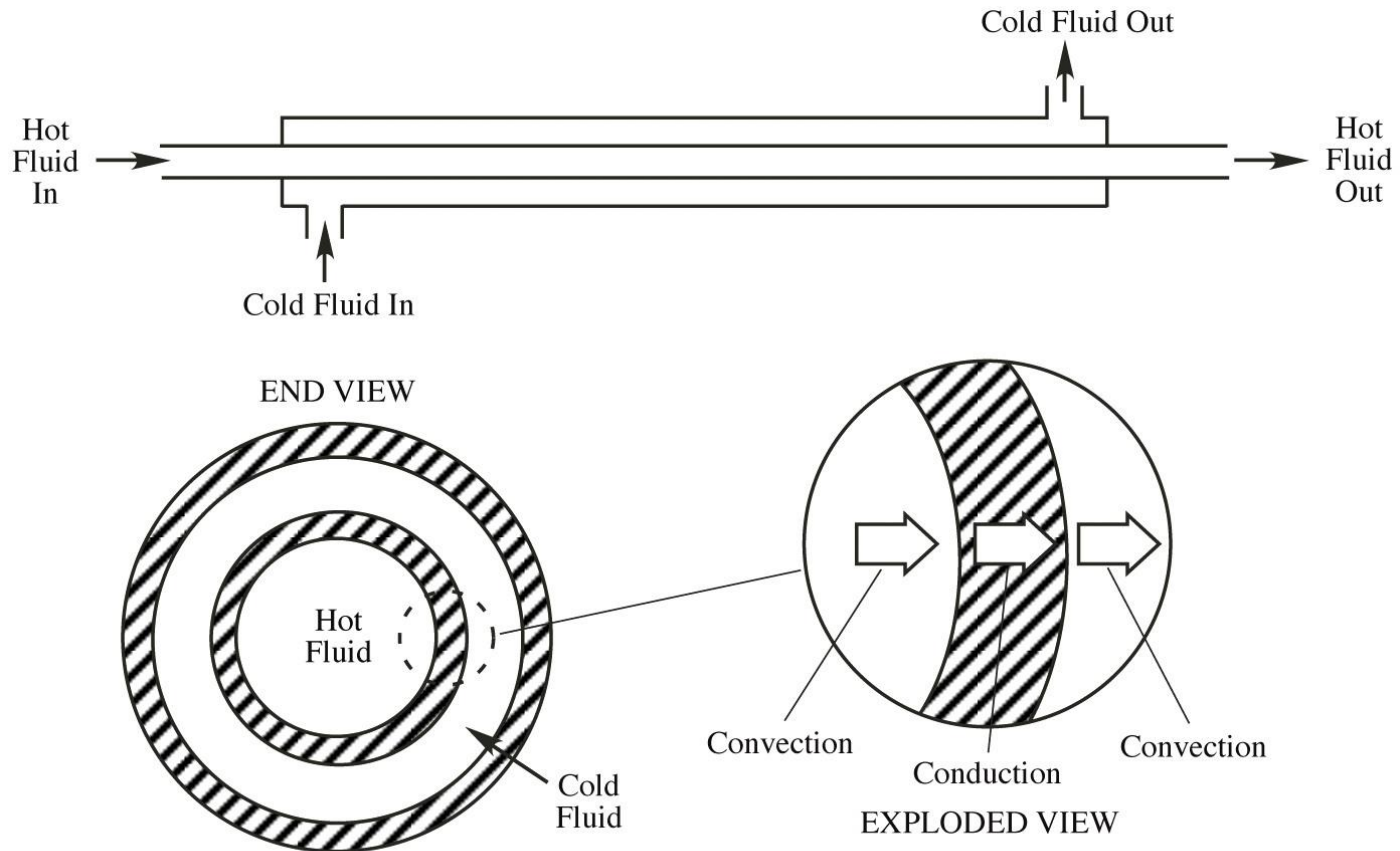**Concentric-Cylinder Heat Exchanger**
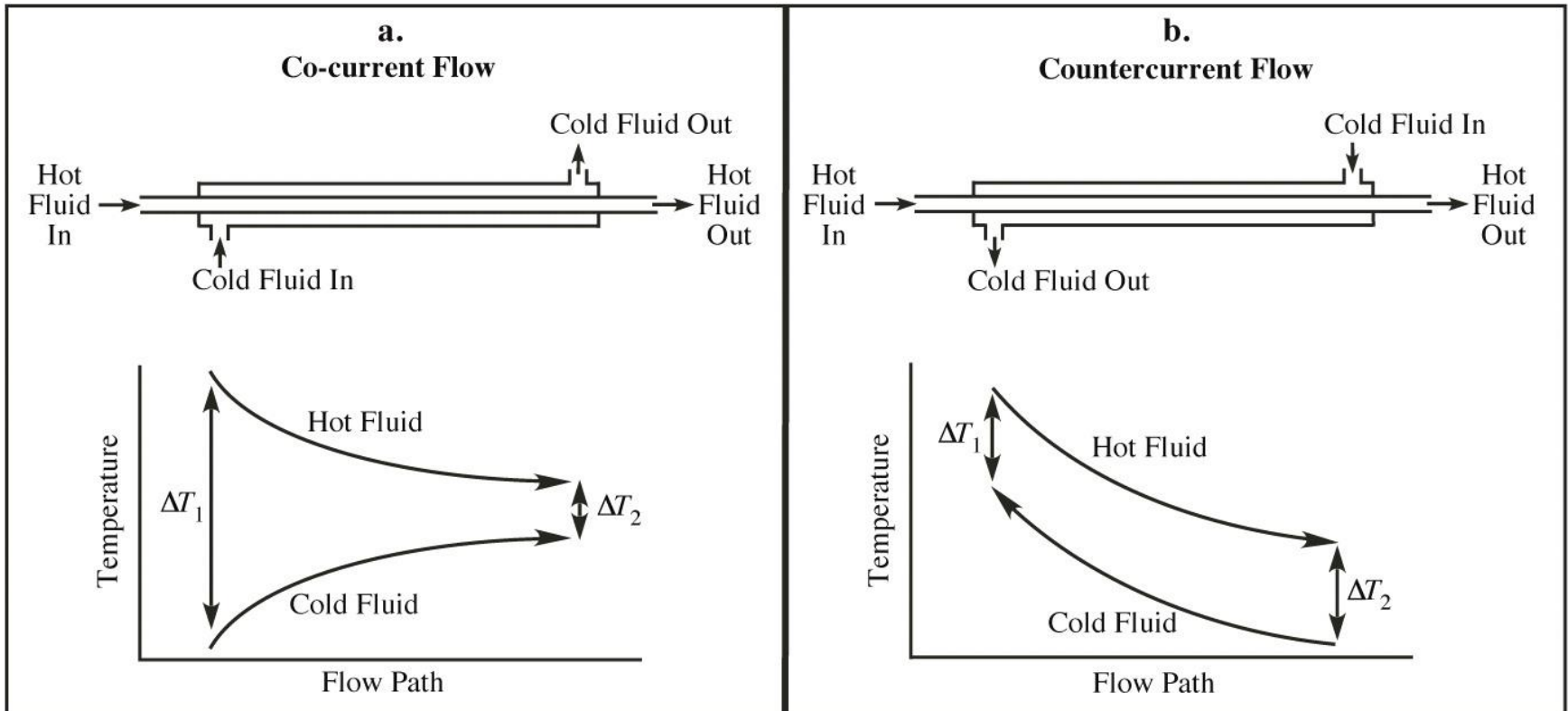
Heat-Exchangers

Figure 10.11

Heat-Exchangers

Tube Outlet Shell Inlet Baffles Shell Outlet Tube Inlet
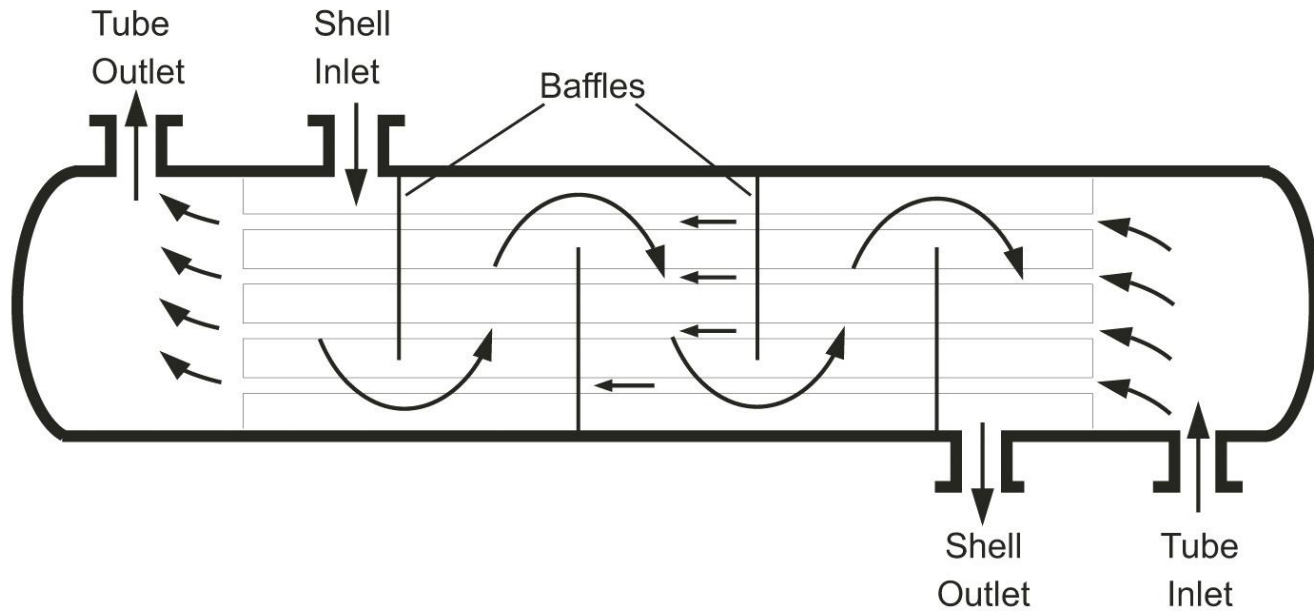
Shell-and-Tube Heat Exchanger

Heat-Exchangers

(i) Sensible Heating/Cooling:

$$\left[\dot{m} C_p (T_{out} - T_{in}) \right]_{hot} = -\dot{Q}_{duty} \qquad (10.24a)$$

$$\left[\dot{m} C_p (T_{out} - T_{in}) \right]_{cold} = \dot{Q}_{duty} \qquad (10.24b)$$

(ii) Phase Change:

$$\left[\dot{m} \Delta \hat{H}_{phase\,change} \right]_{hot} = -\dot{Q}_{duty} \qquad (10.24c)$$

$$\left[\dot{m} \Delta \hat{H}_{phase\,change} \right]_{cold} = \dot{Q}_{duty} \qquad (10.24d)$$

(iii) Chemical Reaction:

$$\left[r_{consumption,A} \Delta \tilde{H}_{reaction,A} \right]_{hot} = -\dot{Q}_{duty} \qquad (10.24e)$$

$$\left[r_{consumption,A} \Delta \tilde{H}_{reaction,A} \right]_{cold} = \dot{Q}_{duty} \qquad (10.24f)$$
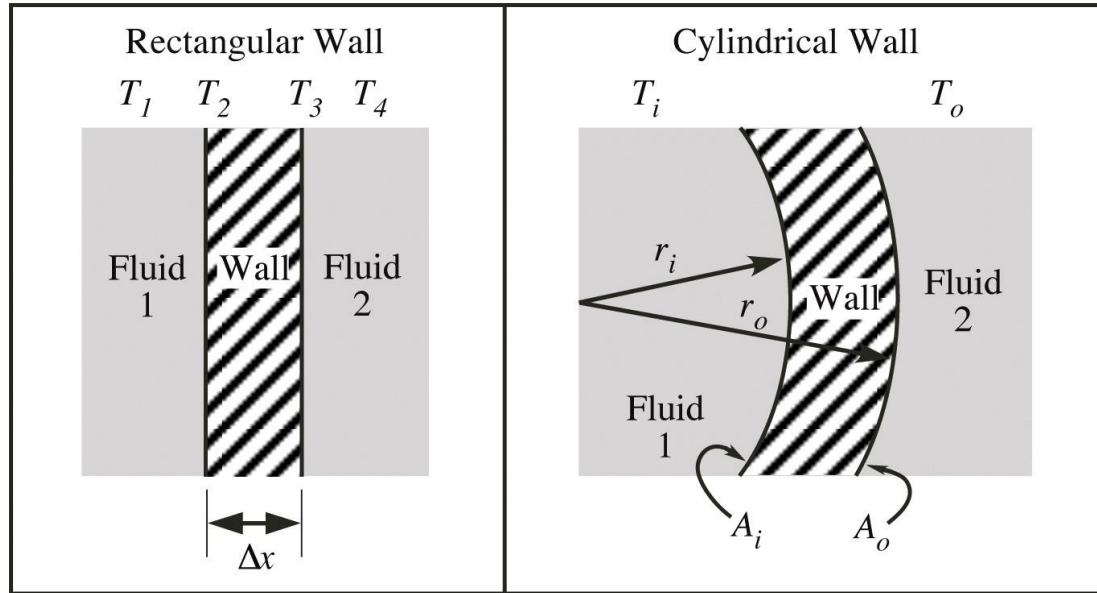
Heat-Exchangers

$$\dot{Q} = h_1 A(T_1 - T_2) = kA \frac{T_2 - T_3}{\Delta x} = h_2 A(T_3 - T_4) \quad (10.25)$$

Homework

- Derive following equations.

$$\dot{Q} = \frac{T_1 - T_4}{\dfrac{1}{h_1 A} + \dfrac{\Delta x}{kA} + \dfrac{1}{h_2 A}}$$ (10.26)

$$\dot{Q} = \frac{T_i - T_o}{\dfrac{1}{h_i A_i} + \dfrac{\ln(r_o / r_i)}{2\pi kL} + \dfrac{1}{h_o A_o}}$$ (10.27)

Heat-Exchangers

- T_i and T_o change along the length of the device.

- The prediction of the values of h_i and h_o is

$$\dot{Q}_{duty} = U_o A \Delta T_{ave} \quad (10.28)$$

U_o : overall heat transfer coefficient

$$\Delta T_{\log mean} = \frac{\Delta T_1 - \Delta T_2}{\ln \dfrac{\Delta T_1}{\Delta T_2}} \quad (10.29)$$

log mean temperature difference