

Chapter 9

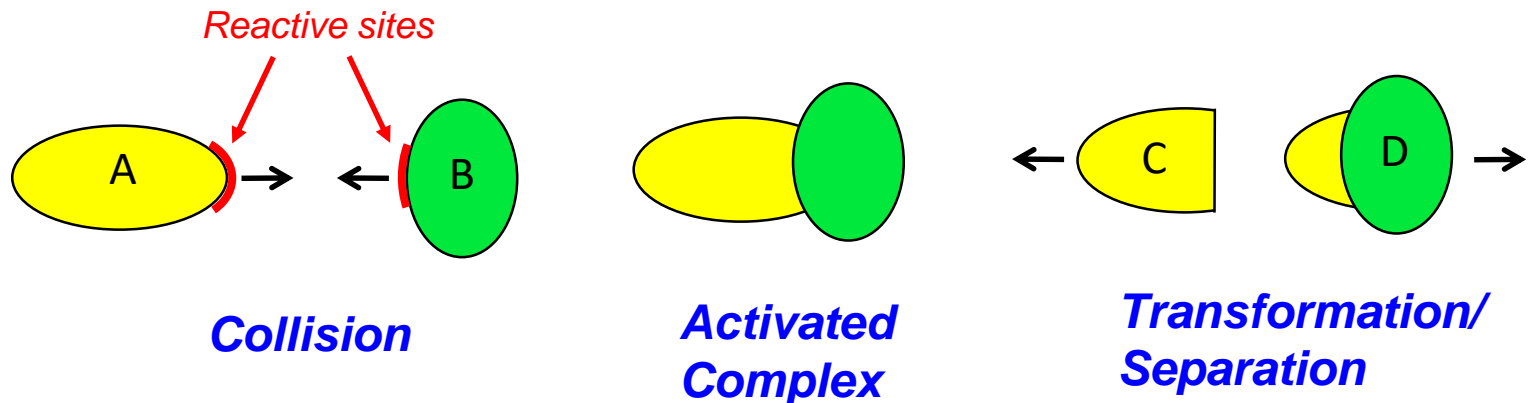
Reaction Engineering



Reaction Rate

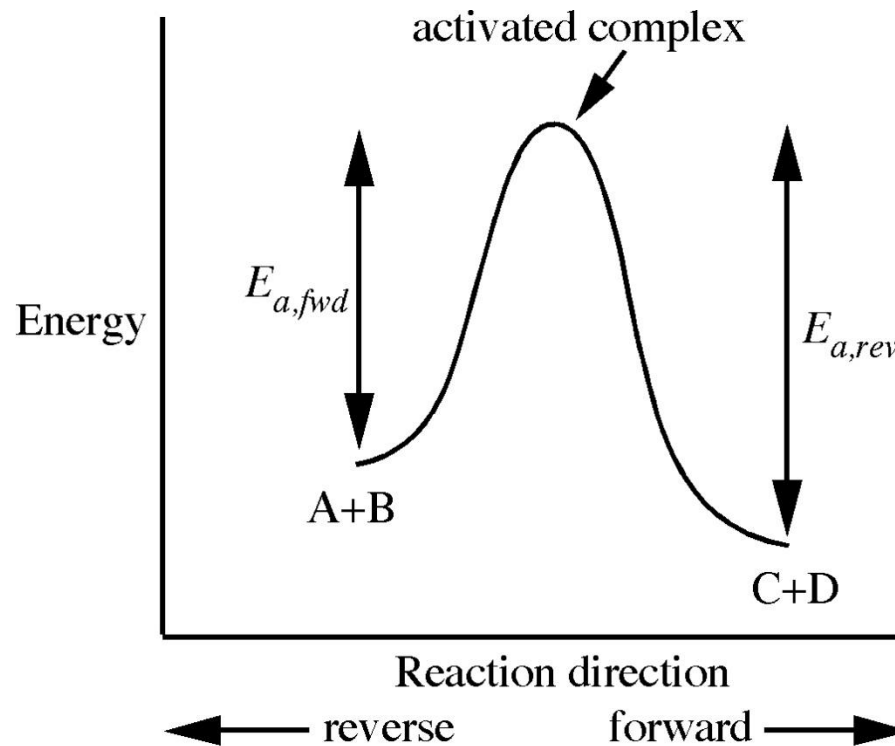


- Frequency of Molecular Collision
 - Depends on **concentrations**
 - Depends on velocity of moving molecules
 - The velocity depends on **the temperature**.
- Orientation and Force of the Collision
 - Not all collisions lead to reaction



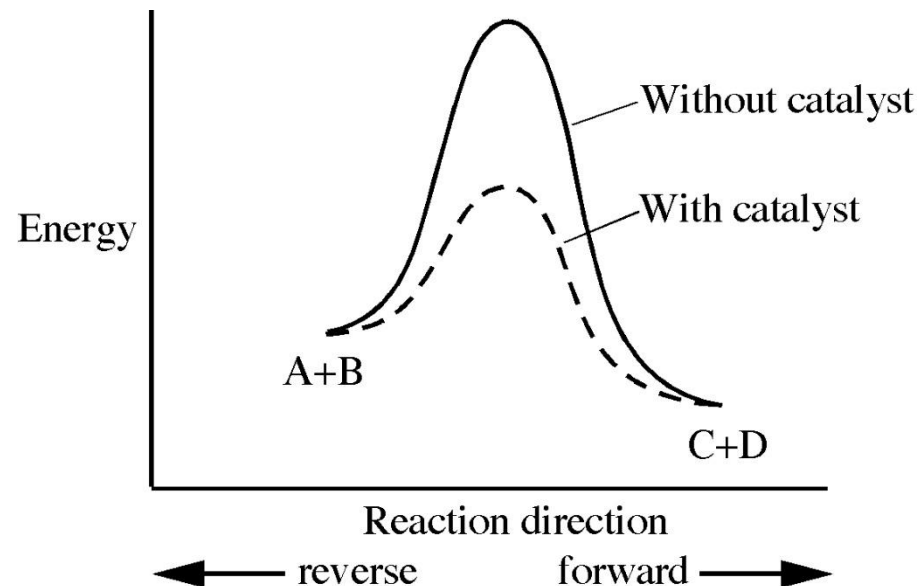
Reaction Rate

- 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)

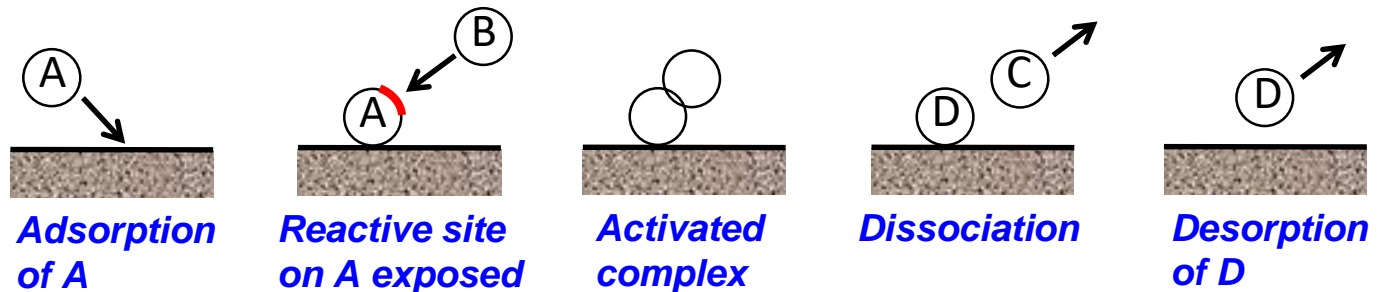


Catalyst

- Catalysts are porous.



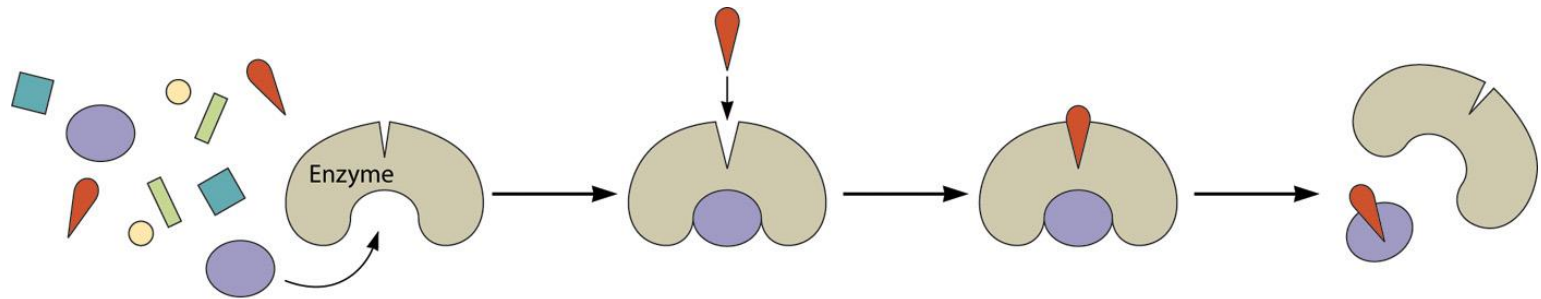
1. Reactants diffuse into the pores.
2. Reaction proceeds.



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



- Reversible Reaction
 - if the reverse reaction rate is significant



Reaction Rate



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

$$r_{\text{reaction,A}} = k_r C_A^n C_B^m$$

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

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

Reaction Rate



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

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

(p = partial pressure)

- Reaction Rate Constant

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

- k_0 : frequency factor
- E_a : activation energy

Arrhenius Equation

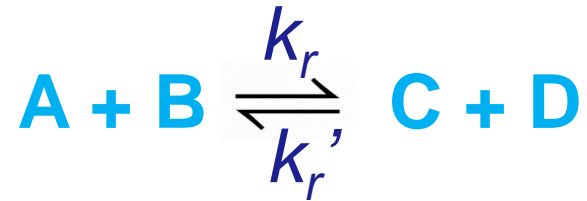
- Reaction Rate Constant

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

- 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



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

Reactor

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

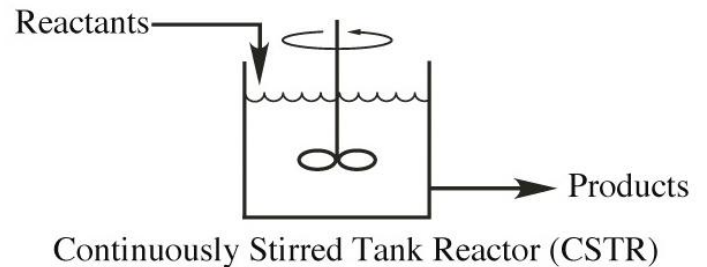
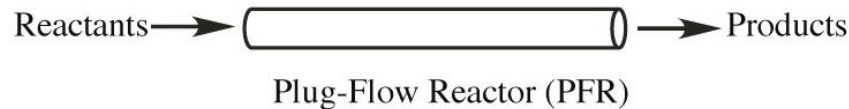
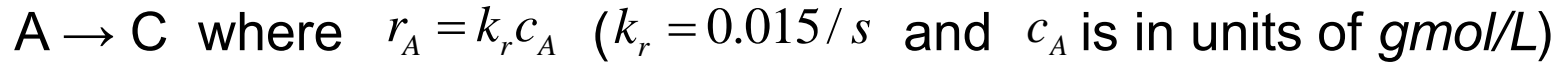


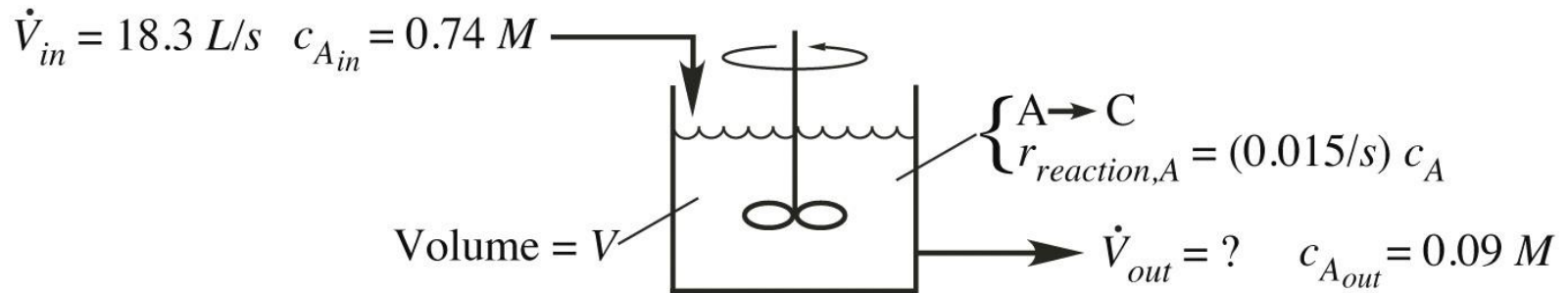
Figure 9.4

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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



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

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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:



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

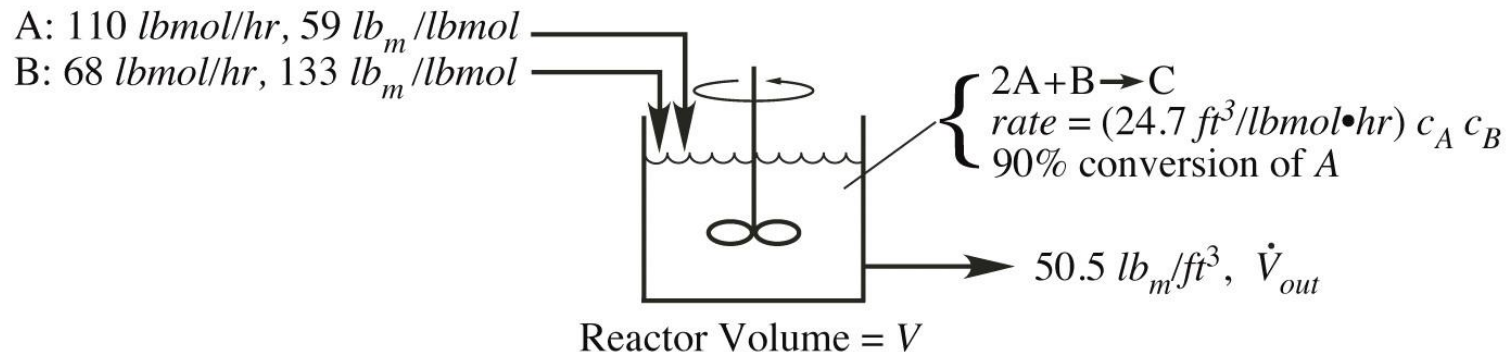
$$\square$$

$$\text{species A: } n_A = 110 \text{ lbmol} / \text{hr} \quad (\text{MW} = 59 \text{ lb}_m / \text{lbmol})$$

$$\square$$

$$\text{species B: } n_B = 68 \text{ lbmol} / \text{hr} \quad (\text{MW} = 133 \text{ lb}_m / \text{lbmol})$$

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



HCl: 0.014 gmol/L, 11600 L/hr
 NaOH: 0.025 gmol/L, ~6500 L/hr

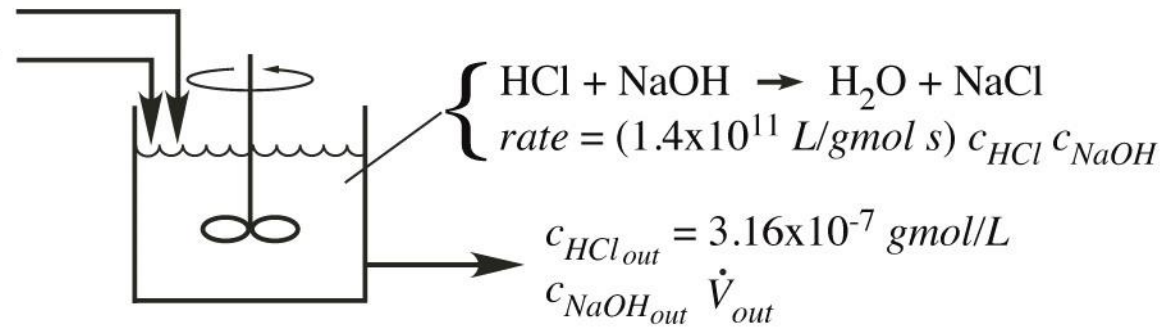


Figure 9.6
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State law: the lowest pH allowable for water added to a lake or river is 6.5

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

Mole balance on HCl

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

Mole balance on NaOH

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

Total mass balance

$$\dot{V}_{\text{HCl},in} + \dot{V}_{\text{NaOH},in} = \dot{V}_{out}$$

Stoichiometry

$$r_{\text{consumption,HCl}} = r_{\text{consumption,NaOH}}$$

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.

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

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

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

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

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

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)

$$\Delta E = Q + W \quad (10.1)$$

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

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

\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)

Energy Balance for an Open System

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

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

$$\sum_{\substack{\text{output} \\ \text{streams}}} \dot{m} \left[\hat{U} + \frac{1}{2}\alpha v^2 + gz \right]_{out} - \sum_{\substack{\text{input} \\ \text{streams}}} \dot{m} \left[\hat{U} + \frac{1}{2}\alpha v^2 + gz \right]_{in} = \dot{Q} + \dot{W} \quad (10.4)$$

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

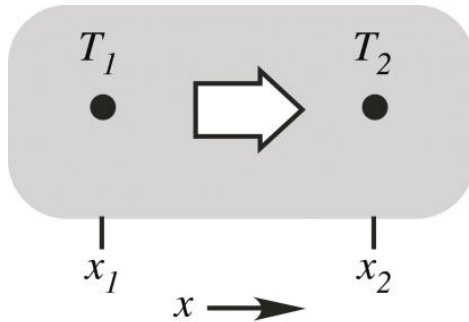


Figure 10.1
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$$\dot{Q}_{cond,x} = -k A \frac{T_2 - T_1}{x_2 - x_1}$$

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)

<i>k (W/m °C) @25 °C</i>	
<i>air</i>	<i>.026</i>
<i>water</i>	<i>.61</i>
<i>glass</i>	<i>1.4</i>
<i>aluminum</i>	<i>237</i>

Which has the lowest k, gas or solid?

What are the best insulations?

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

Convection

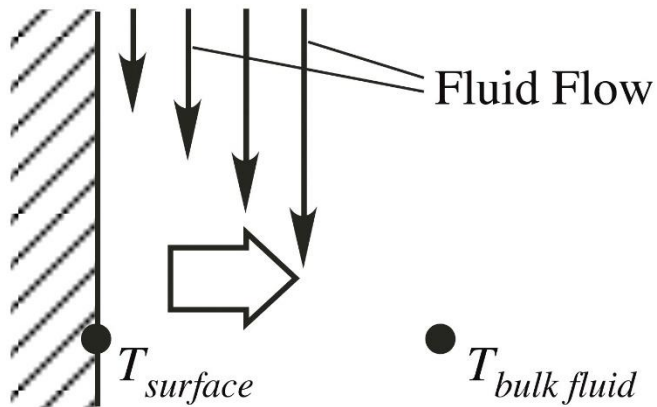


Figure 10.2
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$$\dot{Q}_{conv} = h A (T_{surface} - T_{bulk\ fluid})$$

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

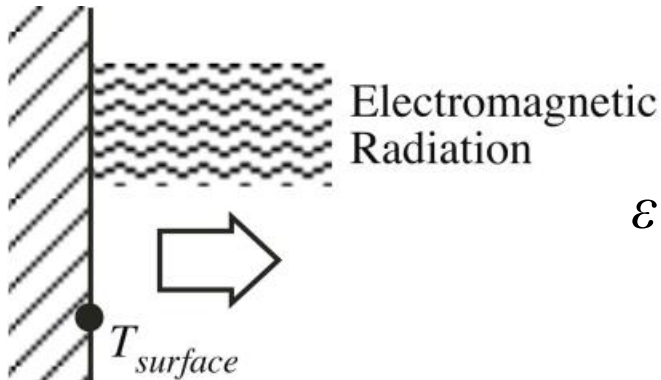


Figure 16.3
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$$\dot{Q}_{rad} = \varepsilon \sigma A (T_{surface})^4$$

ε = emissivity, which indicates how well the surface emits radiation compared with a “perfect” radiator (unit-less)

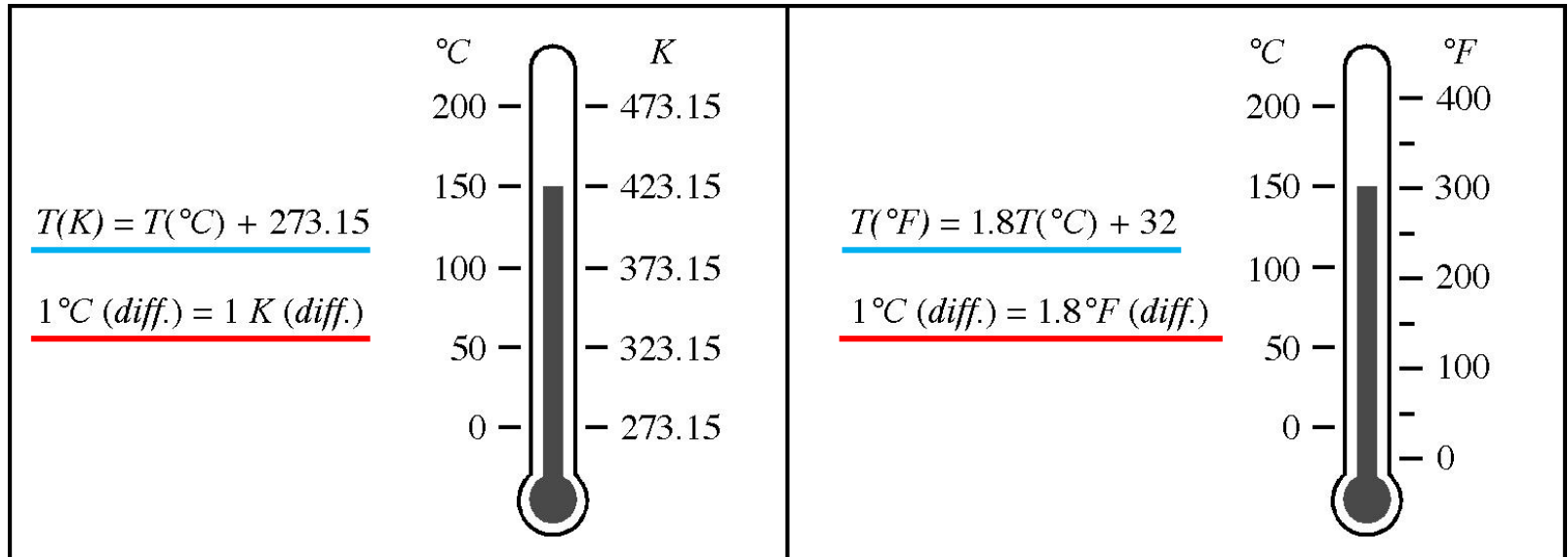
σ = Stefan-Boltzmann constant
($5.67 \times 10^{-8} \text{ W} / \text{m}^2 \text{ K}^4$)

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



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 $\text{Btu/hr ft } ^{\circ}\text{F}$?

ΔT

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 system

Energy Balance

$$\dot{W}_{PV} = \sum_{\substack{\text{input} \\ \text{streams}}} (P\dot{V})_{in} - \sum_{\substack{\text{output} \\ \text{streams}}} (P\dot{V})_{out} = \sum_{\substack{\text{input} \\ \text{streams}}} (\dot{m}P\hat{V})_{in} - \sum_{\substack{\text{output} \\ \text{streams}}} (\dot{m}P\hat{V})_{out} \quad (10.8)$$

$$\dot{W} = \dot{W}_s + \dot{W}_{PV} \quad (10.9)$$

$$\sum_{\substack{\text{output} \\ \text{streams}}} \dot{m} \left[\hat{U} + \frac{1}{2} \alpha v^2 + gz \right]_{out} - \sum_{\substack{\text{input} \\ \text{streams}}} \dot{m} \left[\hat{U} + \frac{1}{2} \alpha v^2 + gz \right]_{in} = \dot{Q} + \dot{W} \quad (10.4)$$

$$\sum_{\substack{\text{output} \\ \text{streams}}} \left\{ \dot{m} \left[\hat{U} + \frac{1}{2} \alpha v^2 + gz \right] \right\}_{out} - \sum_{\substack{\text{input} \\ \text{streams}}} \left\{ \dot{m} \left[\hat{U} + \frac{1}{2} \alpha v^2 + gz \right] \right\}_{in} = \dot{Q} + \dot{W}_s + \dot{W}_{PV} \quad (10.10)$$

Energy Balance

$$\sum_{\substack{\text{output} \\ \text{streams}}} \left\{ \dot{m} \left[\hat{U} + P\hat{V} + \frac{1}{2}\alpha v^2 + gz \right] \right\}_{out} - \sum_{\substack{\text{input} \\ \text{streams}}} \left\{ \dot{m} \left[\hat{U} + P\hat{V} + \frac{1}{2}\alpha v^2 + gz \right] \right\}_{in} = \dot{Q} + \dot{W}_s \quad (10.11)$$

Compare Eq. 10.11 with mechanical energy balance.

$$\left(\frac{P}{\rho} + \frac{1}{2}\alpha v_{ave}^2 + gz \right)_{out} - \left(\frac{P}{\rho} + \frac{1}{2}\alpha v_{ave}^2 + gz \right)_{in} = w_s - w_f \quad (7.8a)$$

Energy Balance

$$\hat{H} = \hat{U} + P\hat{V} \quad (10.12)$$

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

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

$$(10.13)$$

Energy Balance

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

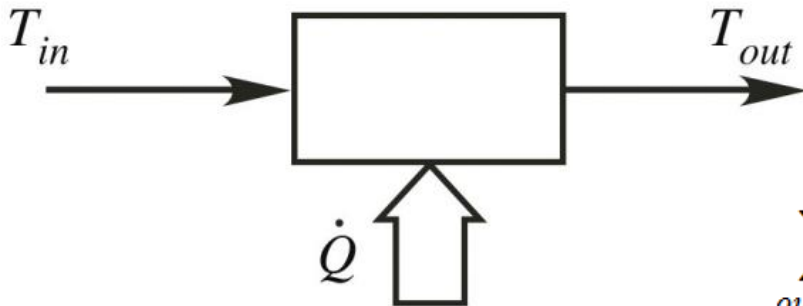
$$\sum_{\text{output streams}} \left\{ \dot{m} \left[\hat{H} + \frac{1}{2} \alpha v^2 + gz \right] \right\}_{\text{out}} - \sum_{\text{input streams}} \left\{ \dot{m} \left[\hat{H} + \frac{1}{2} \alpha v^2 + gz \right] \right\}_{\text{in}} = \dot{Q} + \dot{W}_s$$

(10.13)

$$\sum_{\text{output streams}} (\dot{m} \hat{H})_{\text{out}} - \sum_{\text{input streams}} (\dot{m} \hat{H})_{\text{in}} = \dot{Q}$$

(10.14)

Energy Balance



$$\sum_{\text{output streams}} (\dot{m} \hat{H})_{out} - \sum_{\text{input streams}} (\dot{m} \hat{H})_{in} = \dot{Q} \quad (10.14)$$

Figure 10.5
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(i) **Sensible Heating/Cooling:** $\sum_{out} \dot{m} \bar{C}_p (T - T_{ref}) - \sum_{in} \dot{m} \bar{C}_p (T - T_{ref}) = \dot{Q}$
 $T_{out} > T_{in}$ (No phase change) (10.16)

(ii) **Phase Change:** $\dot{m}_{\text{phase change}} \Delta \hat{H}_{\text{phase change}} = \dot{Q}$
 $T_{out} = T_{in}$ (Phase change) (10.18)

(iii) **Chemical Reaction:** $r_{\text{consumption},A} \Delta \tilde{H}_{\text{reaction},A} = \dot{Q}$
 $T_{out} = T_{in}$ (10.20)

Heat-Exchangers

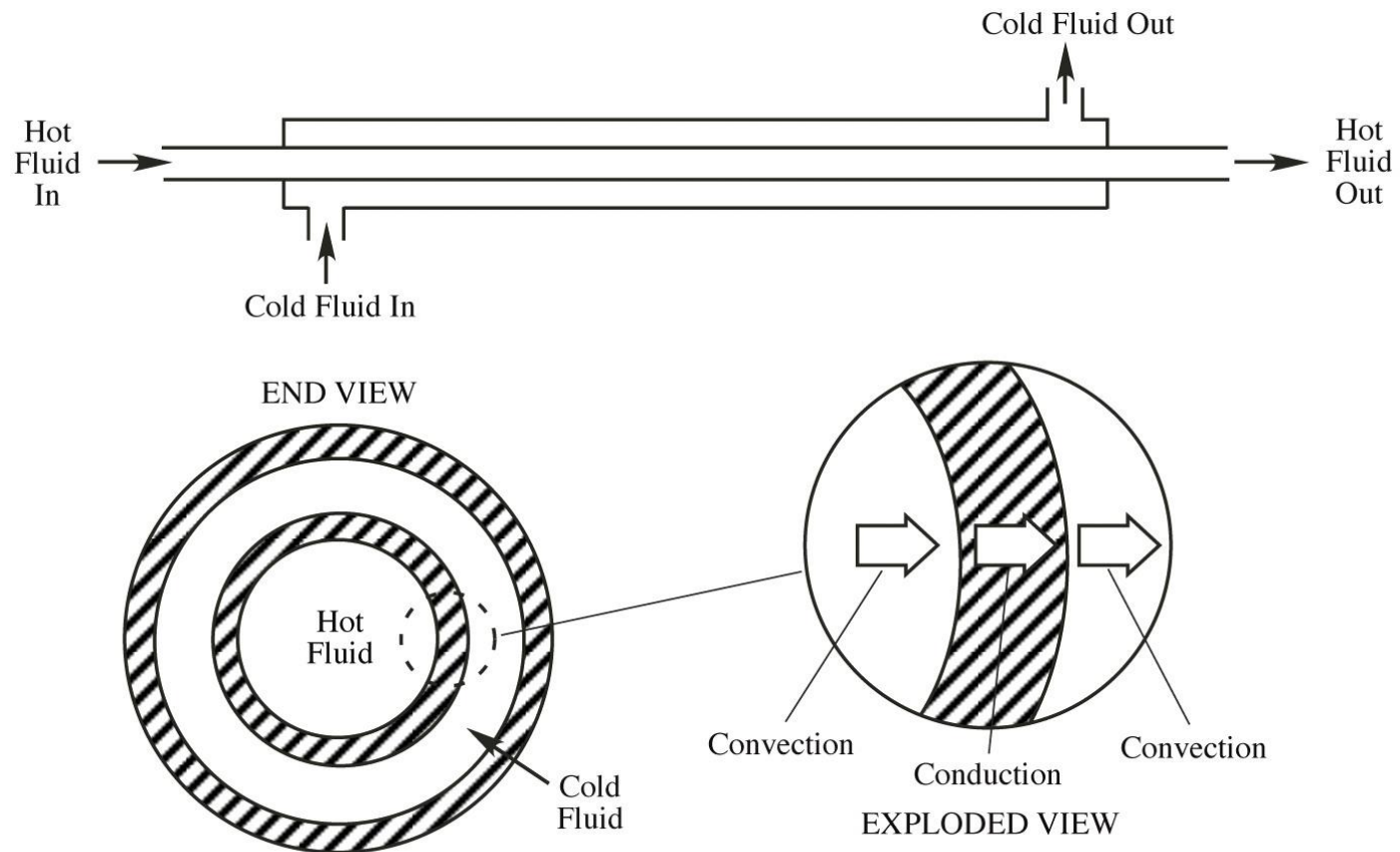


Figure 10.10
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Concentric-Cylinder Heat Exchanger

Heat-Exchangers

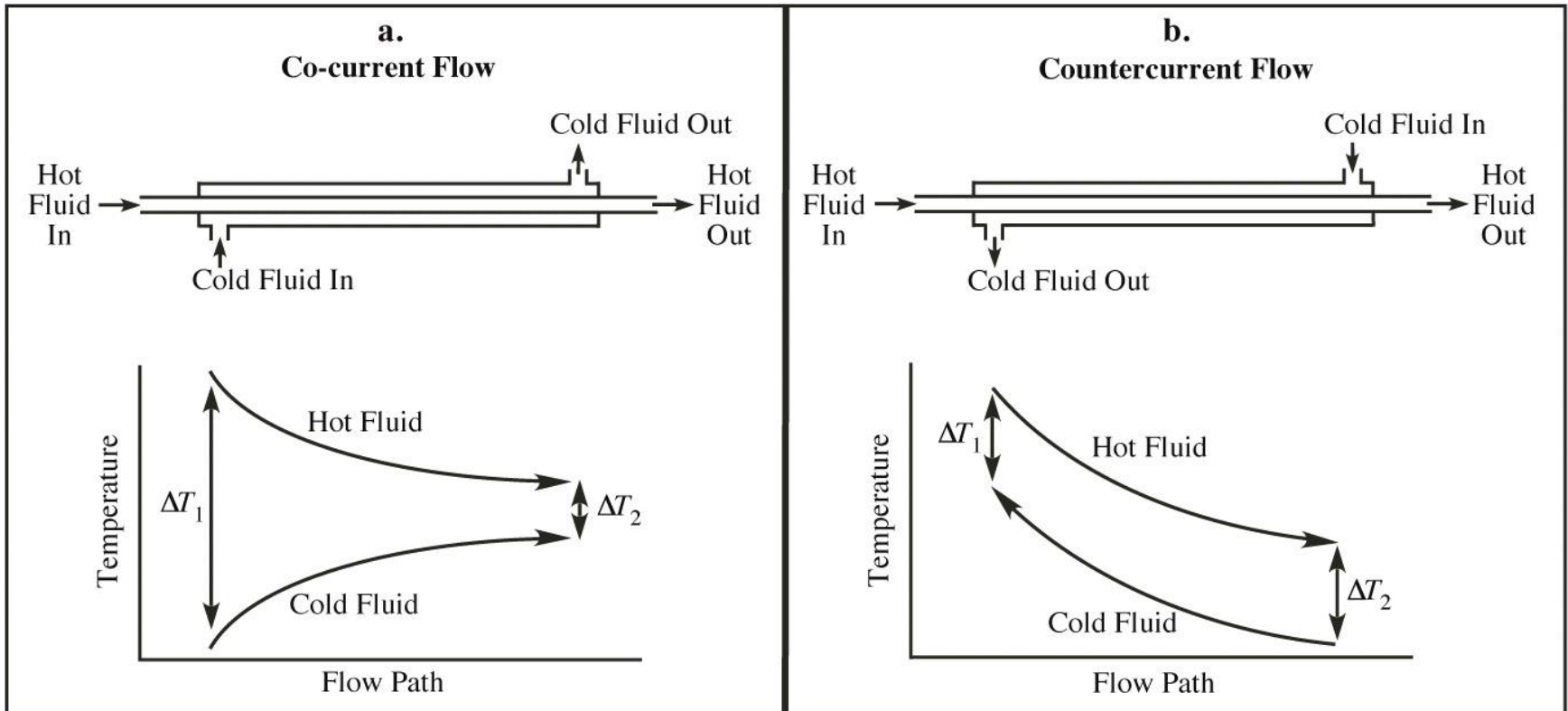


Figure 10.11

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Heat-Exchangers

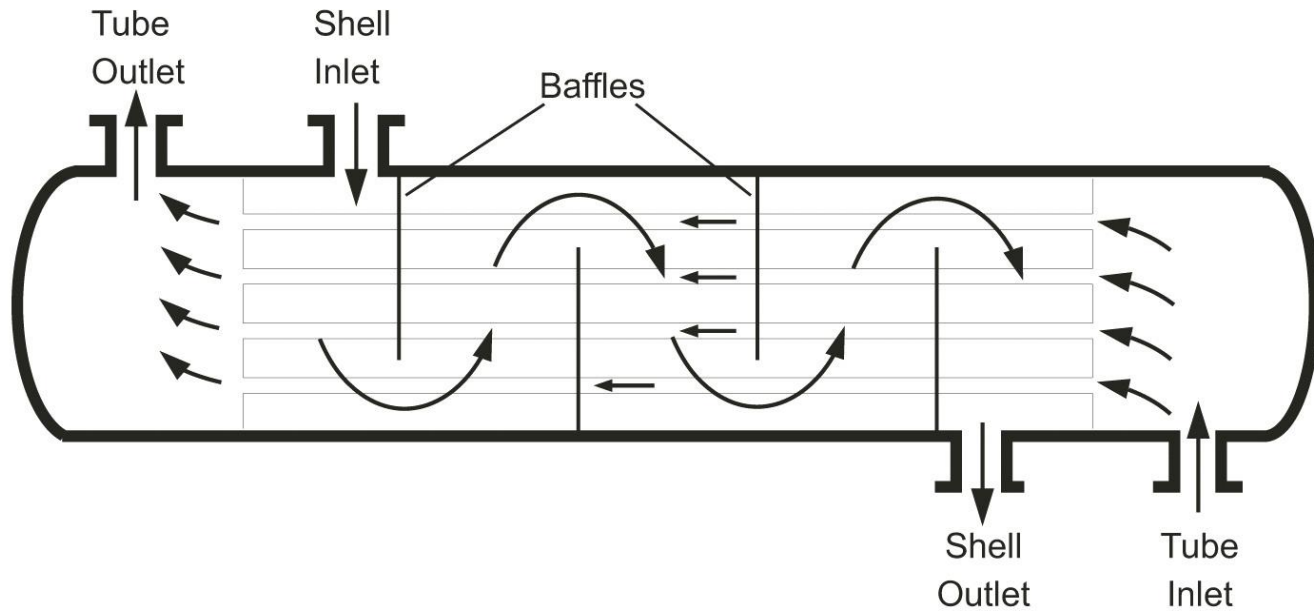


Figure 10.12
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Shell-and-Tube Heat Exchanger

Heat-Exchangers

(i) Sensible Heating/Cooling:

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

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

(ii) Phase Change:

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

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

(iii) Chemical Reaction:

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

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

Heat-Exchangers

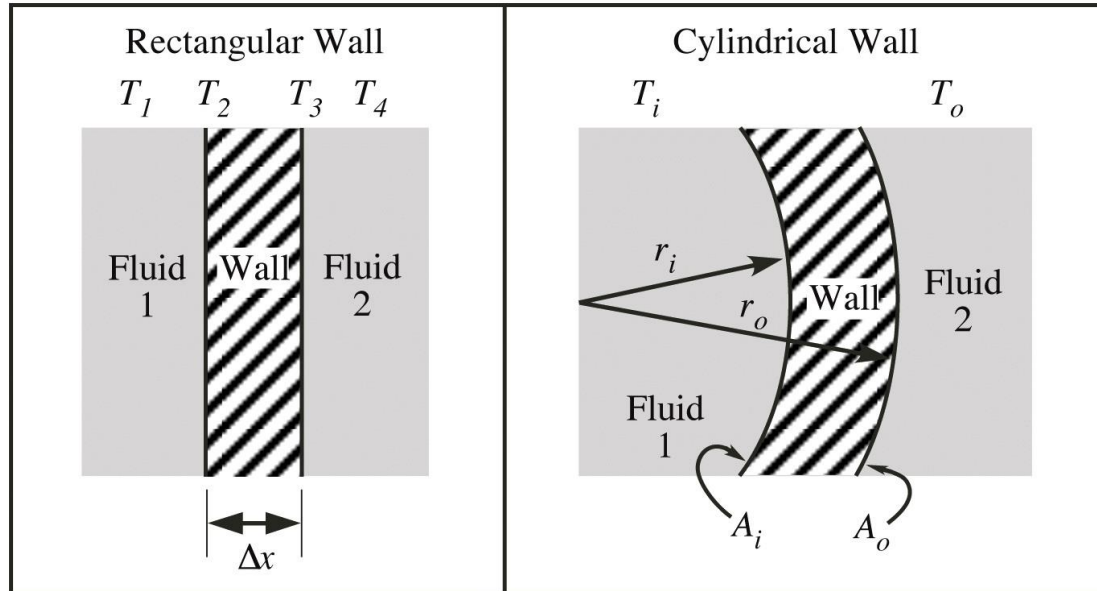


Figure 10.15
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$$\dot{Q} = h_1 A (T_1 - T_2) = kA \frac{T_2 - T_3}{\Delta x} = h_2 A (T_3 - T_4) \quad (10.25)$$

Homework

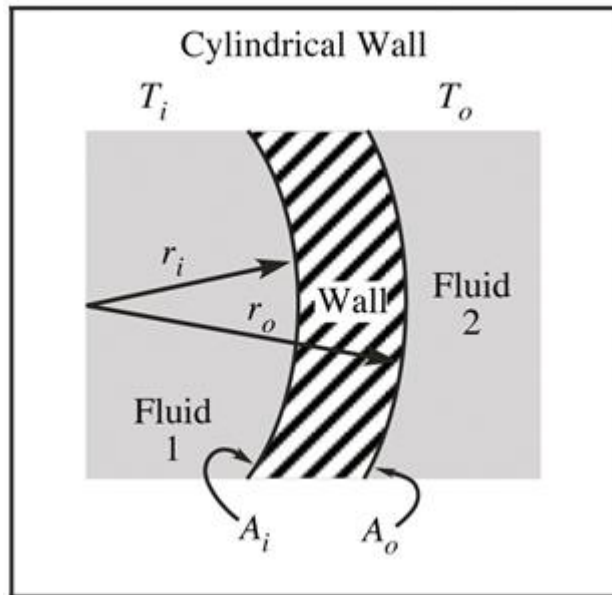
- Derive following equations.

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

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

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 complex.



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

U_o : overall heat transfer coefficient

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

log mean temperature difference