Chapter 5:

Stereochemistry – Part 3 Optical Purity

Today! Chapter 5 (5.4, 5.9-5.11)

Resolving Enantiomers

Wednesday Chapter 6:
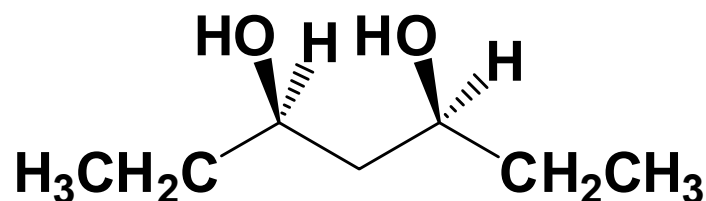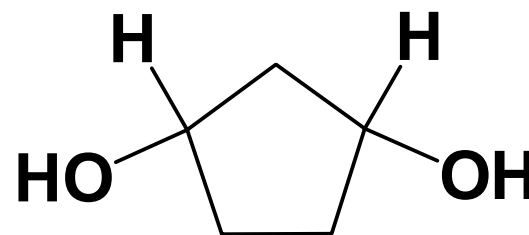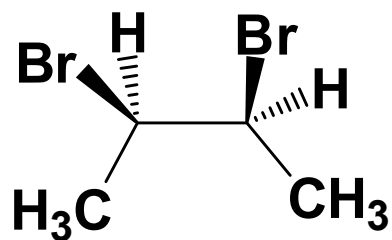**Kinetics and Thermodynamics (6.1-6.6)**

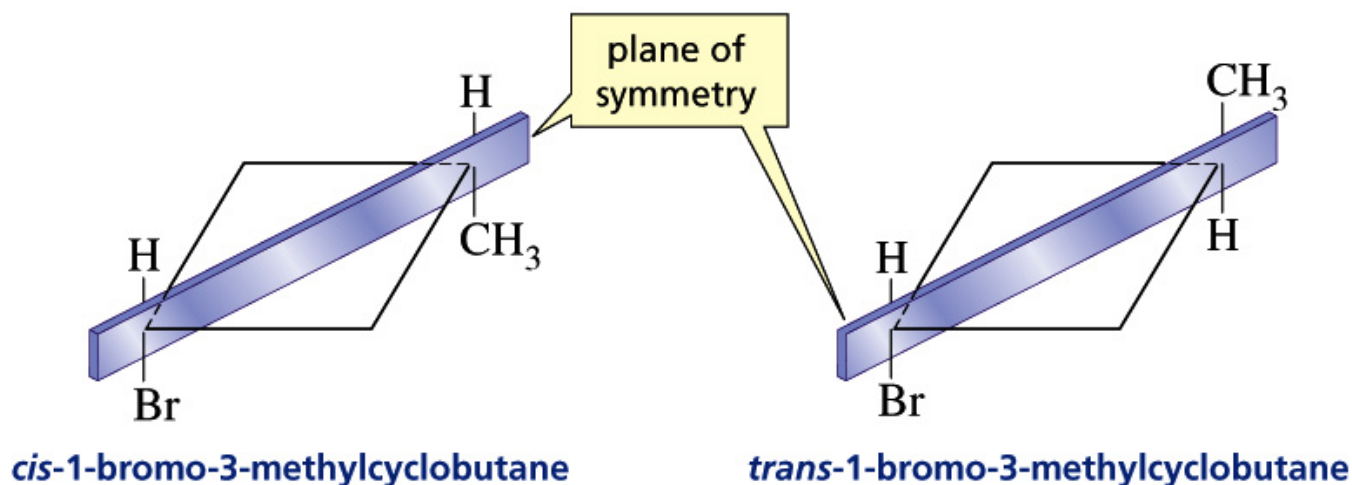**Friday Chapter 6: Mechanisms (6.7 - 6.10, 6.12)**
(We'll come back to 6.11 later.)

Meso Compounds

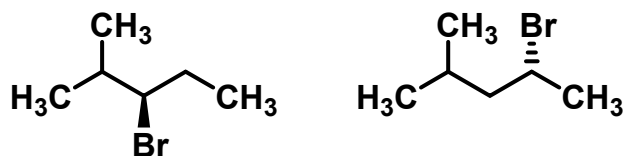Have two or more asymmetric carbons and a plane of symmetry

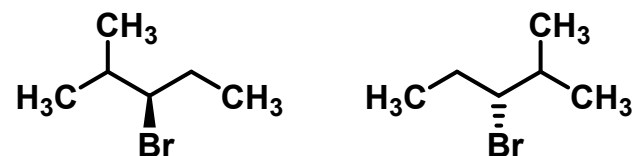As long as any one conformer of a compound has a plane of symmetry, the compound will be achiral

cis-1-bromo-3-methylcyclobutane   trans-1-bromo-3-methylcyclobutane

- For each of the following pairs of compounds – Are they Enantiomers, Diasteriomers, Constitutional Isomers, the Same or Other?

a.

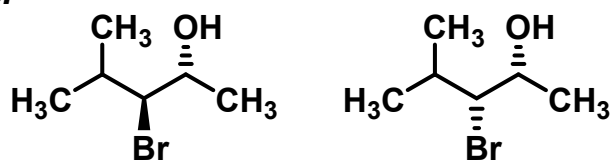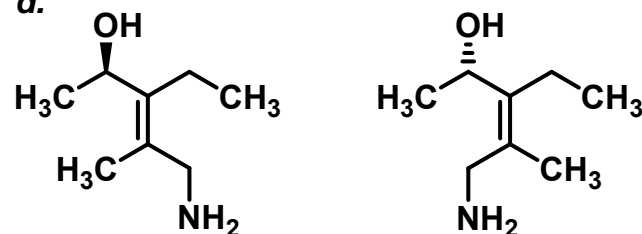constitutional

b.

same

c.

diastereomers

d.
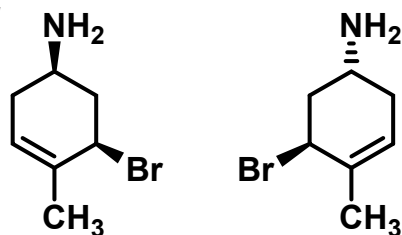

diastereomers

e.

diastereomers

f.

diastereomers

Configuration

- *Relative configuration* compares the arrangement of atoms in space of one compound with those of another.

- Until the 1950s, all configurations were relative.

- *Absolute configuration* is the precise arrangement of atoms in space.

- We can now determine the absolute configuration of almost any compound

Pasteur's Discovery of Enantiomers

- In 1847, Pasteur performed the first resolution of enantiomers from his racemic mixture of tartaric acid salts Louis Pasteur discovered that sodium ammonium salts of tartaric acid crystallize into right handed and left handed forms
- The solutions contain mirror image isomers, called **enantiomers** and they crystallized in distinctly different shapes – such an event is rare

$$CO_2^- \ Na^+$$
$$H-C-OH$$
$$HO-C-H$$
$$CO_2^- \ NH_4^+$$
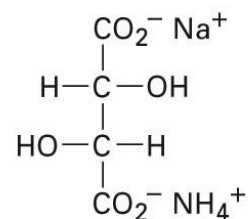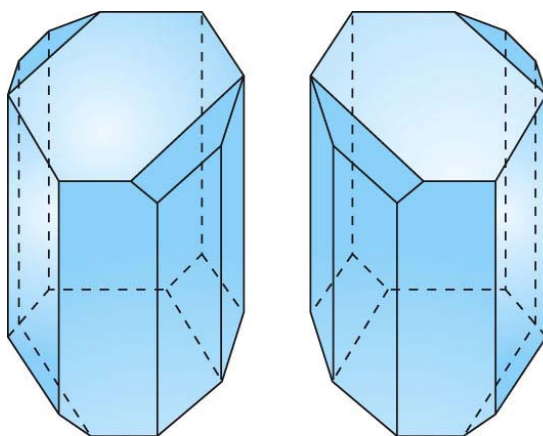
Sodium ammonium tartrate

The optical rotations of equal concentrations of these forms have opposite optical rotations
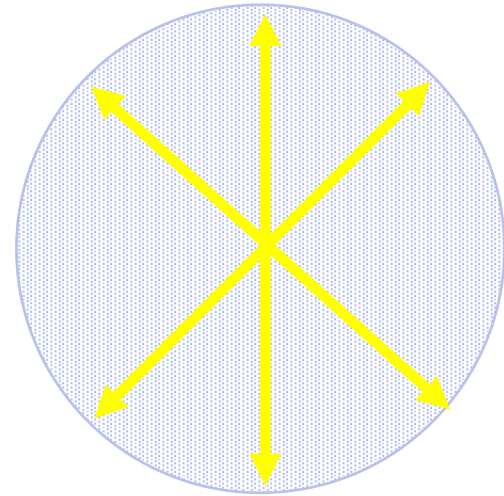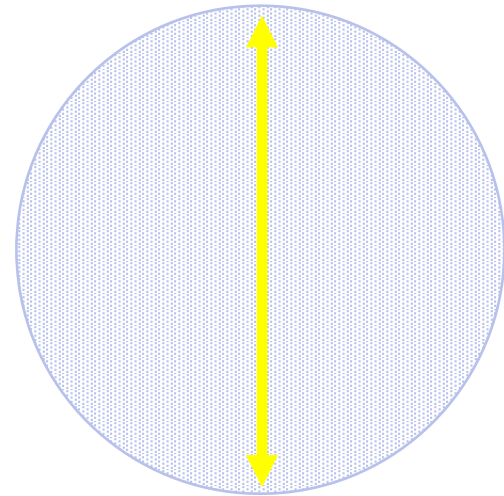
Light
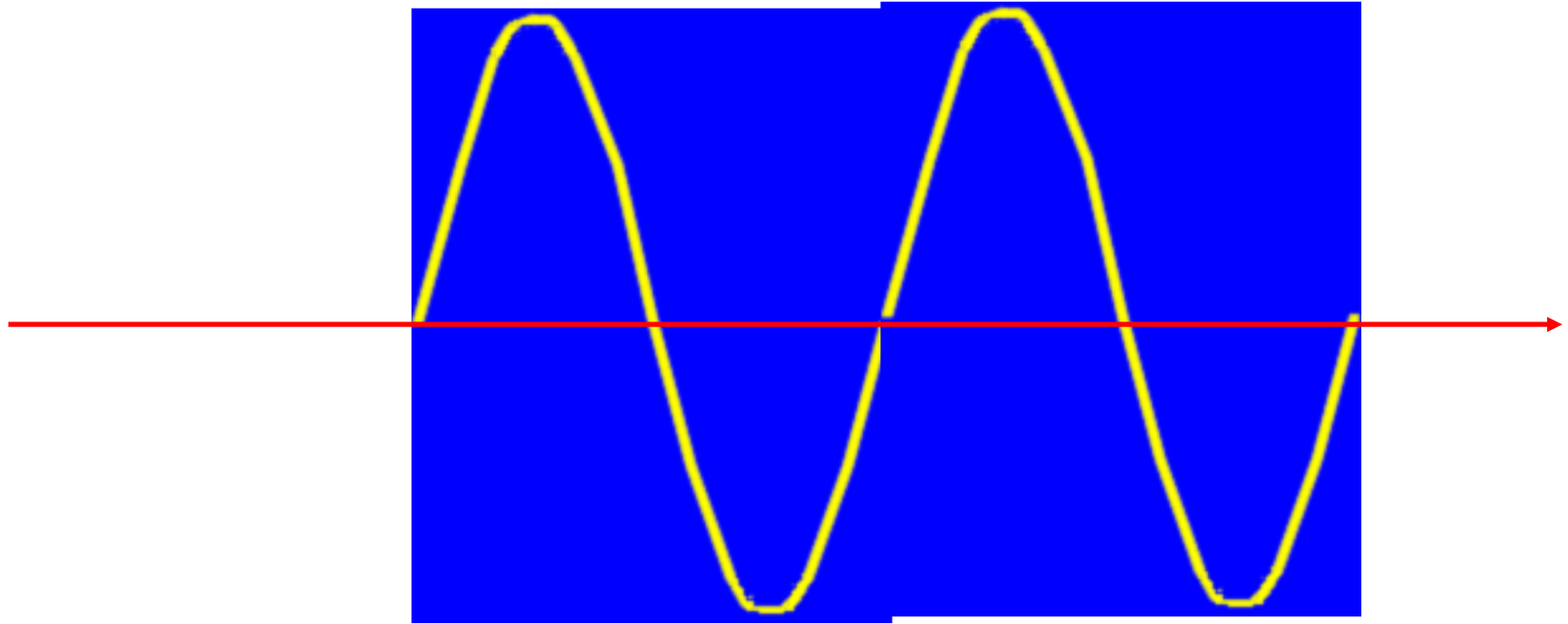
has wave properties

periodic increase and decrease in amplitude of wave
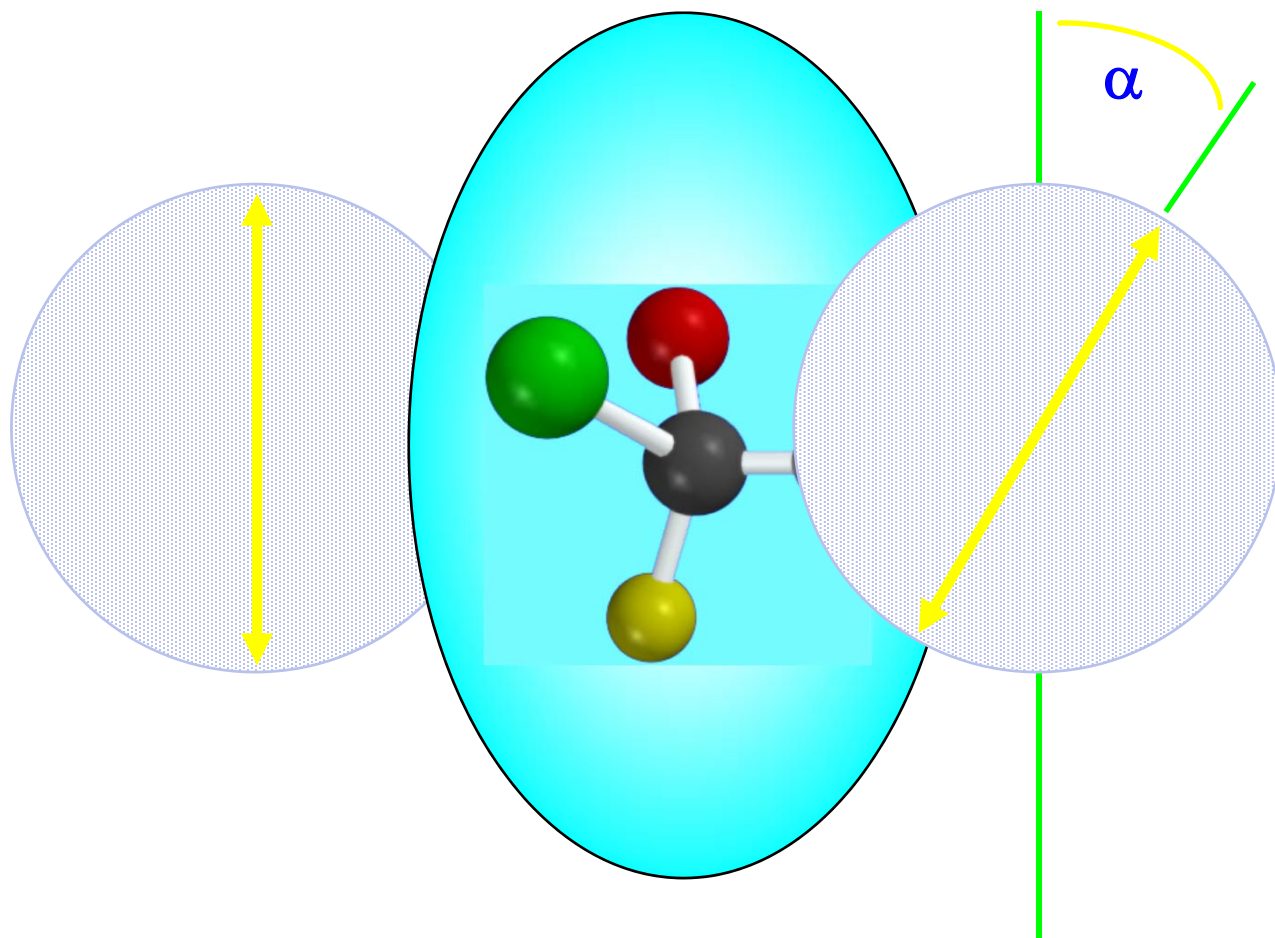
Polarized light

Ordinary (nonpolarized) light consists of many beams vibrating in different planes

Plane-polarized light consists of only those beams that vibrate in the same plane

Rotation of plane-polarized light

A substance is optically active if it rotates the plane of polarized light.

Chiral compounds are optically active; they rotate the plane of polarized light.

the plane of polarization has been rotated

direction of light propagation

light source   normal light   polarizer   plane-polarized light   sample tube containing a chiral compound   plane-polarized light
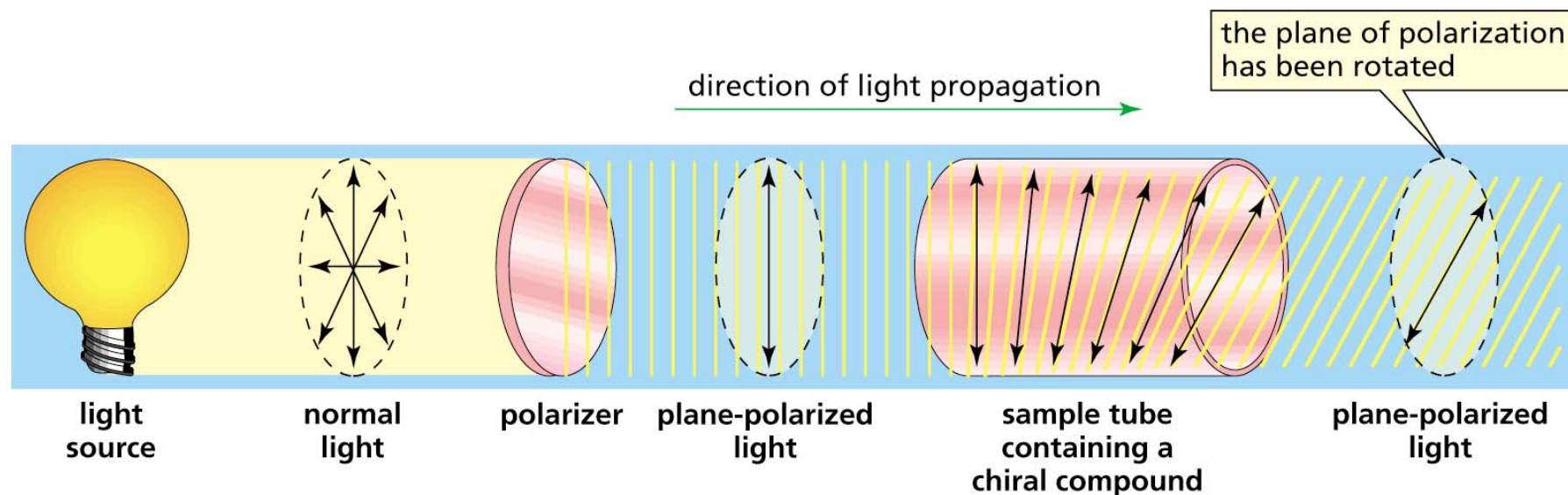
Clockwise (+)   Counterclockwise (-)

Different from *R,S* configuration

Achiral compounds do not rotate the plane of polarized light. They are optically inactive.

A polarizer measures the degree of optical rotation of a compound

The observed rotation (α)

$$[\alpha]_\lambda^T = \frac{\alpha}{l \times c}$$

$[\alpha]_\lambda^T$ = *specific rotation*

T is the temp in °C

λ is the wavelength

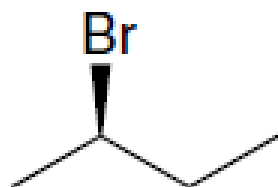α is the measured rotation in degrees

l is the path length in decimeters

c is the concentration in grams per mL

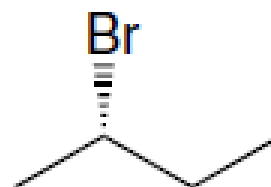Each optically active compound has a characteristic specific rotation

Optical Activity

◆ Consider the enantiomers of 2-bromobutane.

(R)-2-Bromobutane

(S)-2-Bromobutane

$$[\alpha]_{D}^{20} = -23.1$$

$$[\alpha]_{D}^{20} = +23.1$$

- *R* and *S* refer to the configuration of the chiral center.
- (+) and (-) signs refer to the direction that the plane of light is rotated.
- The optical activity was measured at 589 nm, which is the sodium D line wavelength.

Optical Activity

◆ For unequal amounts of enantiomers, the ENANTIOMERIC EXCESS (% ee) can be determined from the optical rotation.

$[\alpha]_D^{20} = -23.1$ $\qquad$ $[\alpha]_D^{20} = +23.1$
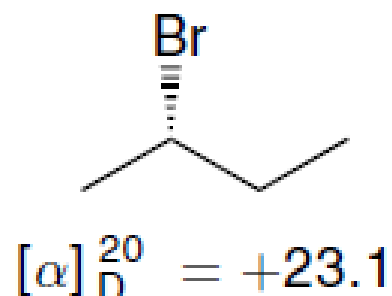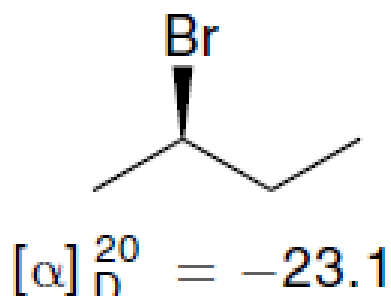
◆ For a mixture of 70% (*R*) and 30% (*S*), what is the % ee?

◆ % ee= 70%- 30%= 40% (excess R over S)

Optical Activity

◈ If the mixture has an optical rotation of +4.6, use the formula to calculate the % ee and the ratio of *R/S.*

Br

$[\alpha]_D^{20} = -23.1$

Br

$[\alpha]_D^{20} = +23.1$
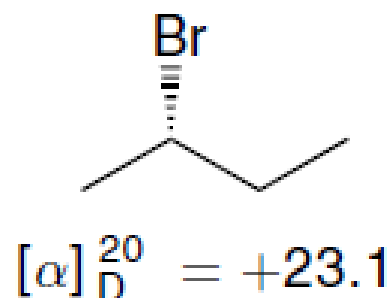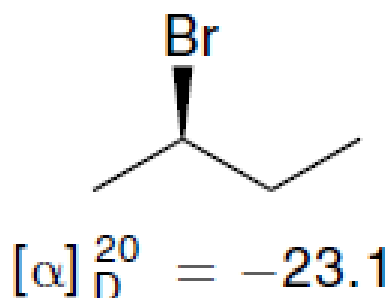
$$\% \ ee = \frac{|\text{observed } [\alpha]|}{|[\alpha] \text{ of pure enantiomer}|} \times 100\%$$

$$\%ee = \frac{4.6}{23.1} \ X100\% = 18.6\%$$

A *racemic* mixture, which contains **equal** amounts of two enantiomers, is optically inactive

$$\text{optical purity} = \frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}}$$

$$\text{enantiomeric excess (e.e.)} = \frac{\text{excess of a single enantiomer}}{\text{entire mixture}}$$

For Next Time….

Wednesday Chapter 6:
Kinetics and Thermodynamics (6.1-6.6)

Friday Chapter 6: Mechanisms (6.7 - 6.10, 6.12)
(We'll come back to 6.11 later.)

Suggested Homework Problems Chapter 5
#4, 9, 19,23,31, 36,38 (a-c), 39 (a-e),45, 55

Suggested Homework Problems Chapter 6
#4, 7, 11, 17, 24, 26, 28, 34-36