Intermolecular Forces

Increasing intermolecular attractions
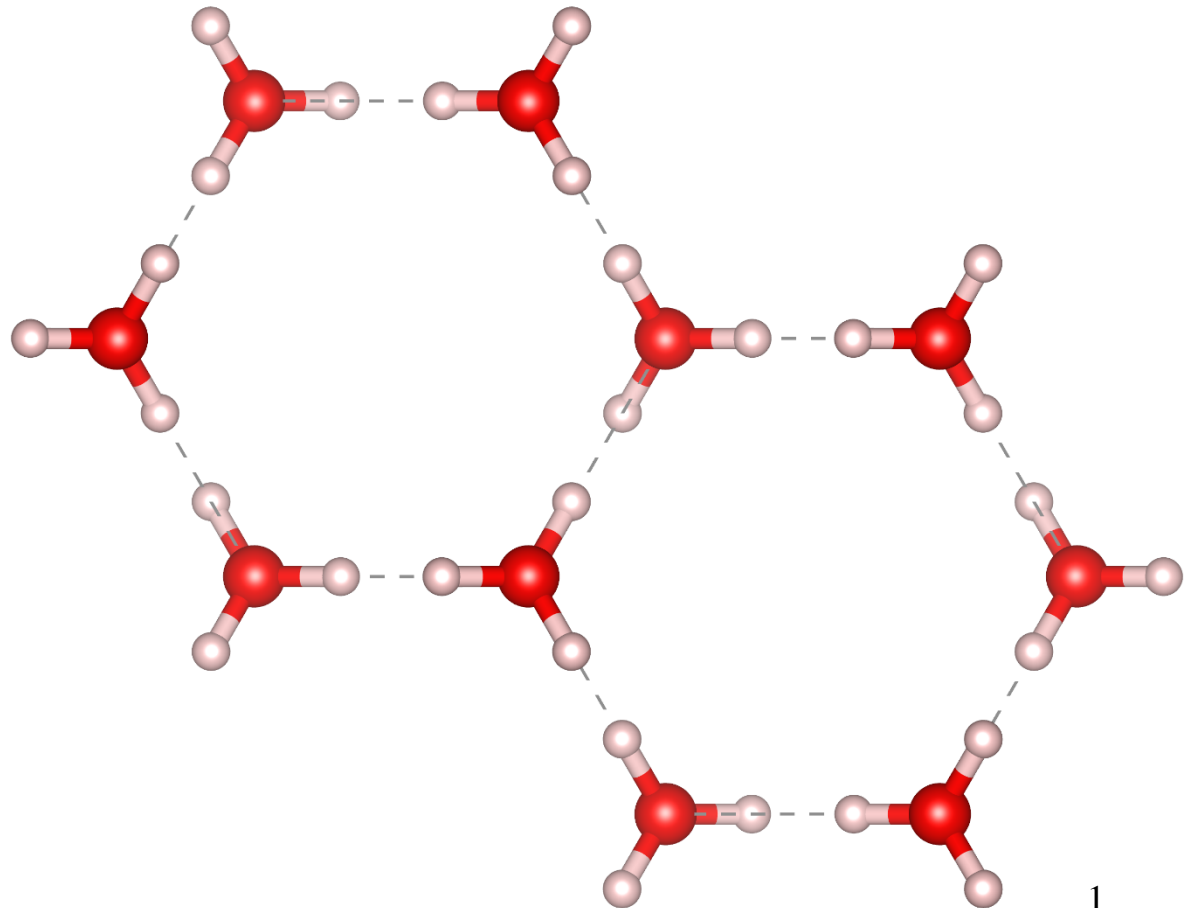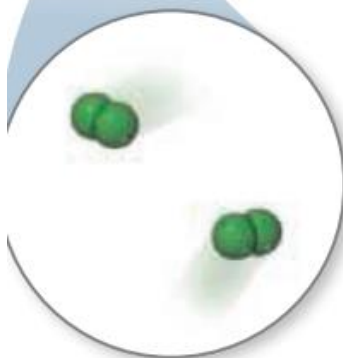

Gas

Liquid

Crystalline solid

Chlorine, Cl$_2$

Bromine, Br$_2$

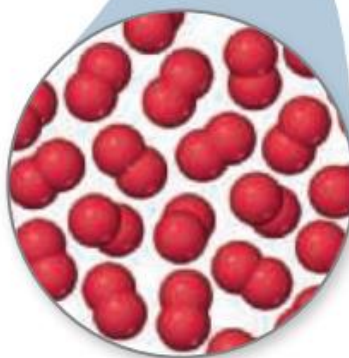Iodine, I$_2$

Particles are far apart; possess complete freedom of motion; kinetic energies of particles >> energies of particle–particle attraction.
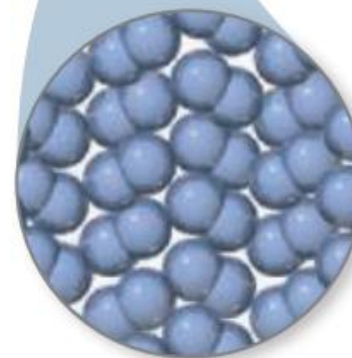
Particles are closely packed but randomly oriented; retain freedom of motion; kinetic energies of particles similar to energies of particle–particle attraction.

Particles are closely packed in an ordered array; positions are essentially fixed; energies of particle–particle attraction >> kinetic energies of particles.

2

Intermolecular Forces

Intermolecular forces are attractive forces **between** molecules.

***Intra*molecular forces** hold atoms together in a molecule.

Intermolecular vs Intramolecular

* 41 kJ to vaporize 1 mole of water (**inter**)

* 930 kJ to break all O-H bonds in 1 mole of water (**intra**)

Generally, **inter**molecular forces are much weaker than **intra**molecular forces.

"Measure" of intermolecular force

boiling point

melting point

ΔH_{vap}

ΔH_{fus}

ΔH_{sub}

3

Intermolecular Forces

<u>Dispersion Forces</u> (London forces, induced dipole-induced dipole forces, London dispersion forces)

Attractive forces that arise as a result of **temporary dipoles induced** in atoms or molecules

In a nonpolar molecule, the charge is uniformly distributed over time. But in any one instant, the charge is not uniformly distributed. In that instant, there is an **instantaneous dipole**.
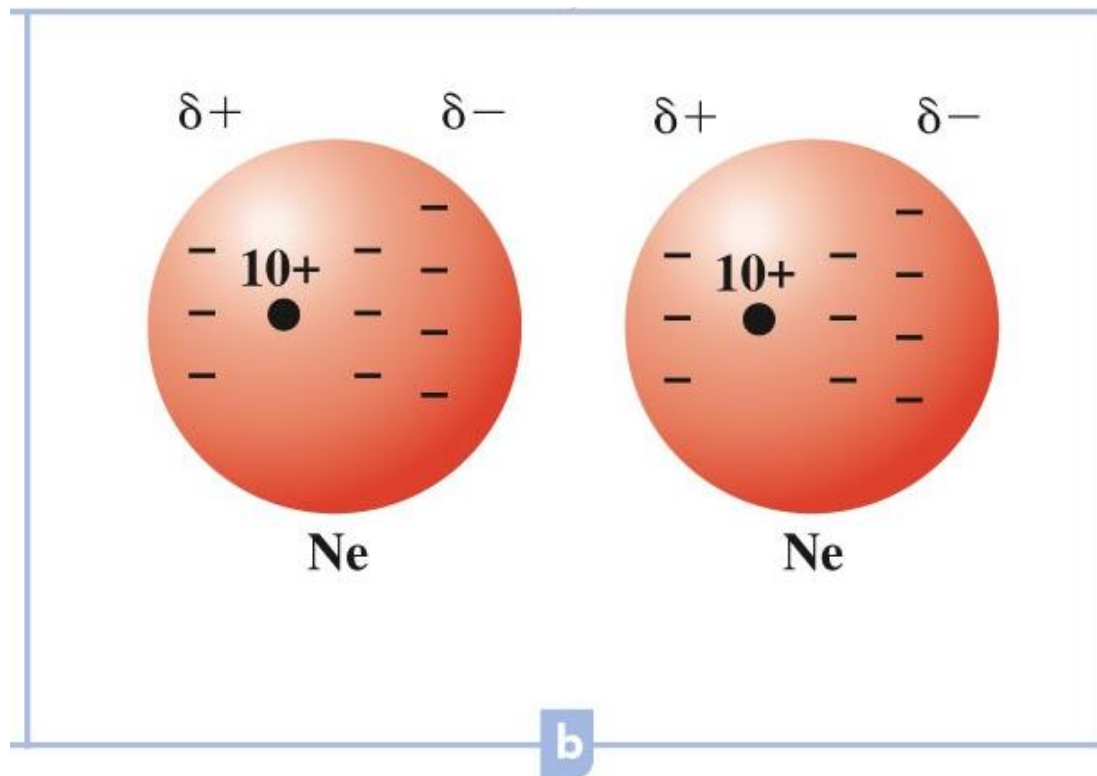
All molecules exhibit London forces.

$\delta+$ $\delta-$

10+

Ne

a
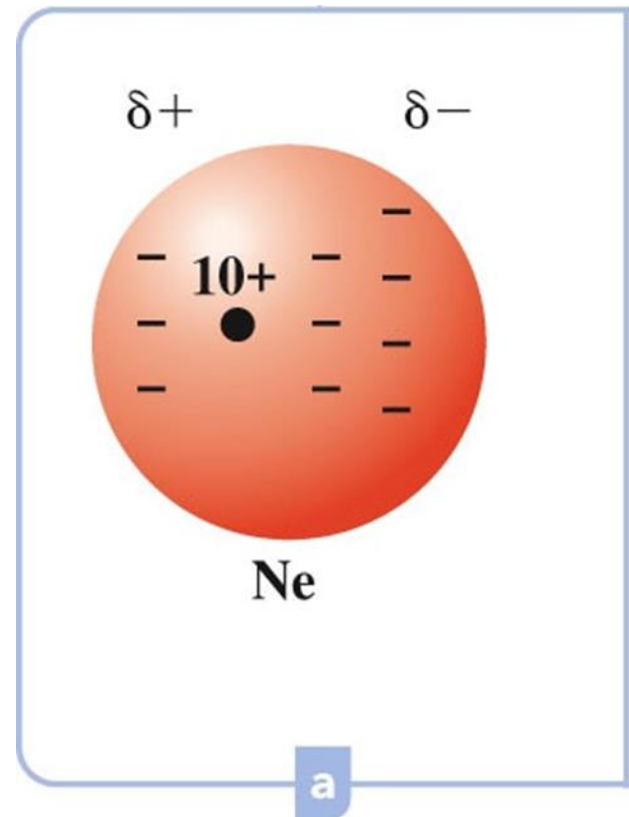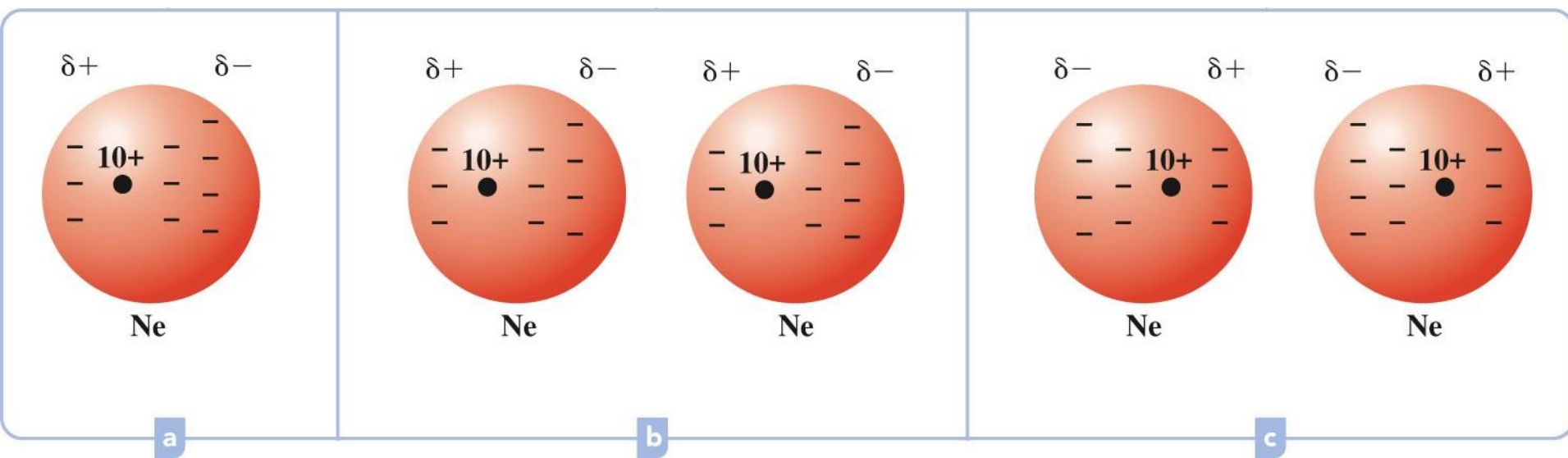
Intermolecular Forces

Dispersion Forces

The instantaneous dipole of the neon atom induces an instantaneous dipole in adjacent atoms, resulting in an attractive force between them.

Intermolecular Forces

Dispersion Forces

In the next moments, the electrons move, and the instantaneous dipoles change. However, the instantaneous dipoles tend to change *together,* maintaining the attractive force between them.

Intermolecular Forces

Dispersion Forces: size

Polarizability is the ease with which the electron distribution in the atom or molecule can be distorted.

Polarizability increases with:

- greater number of electrons

- more diffuse electron cloud

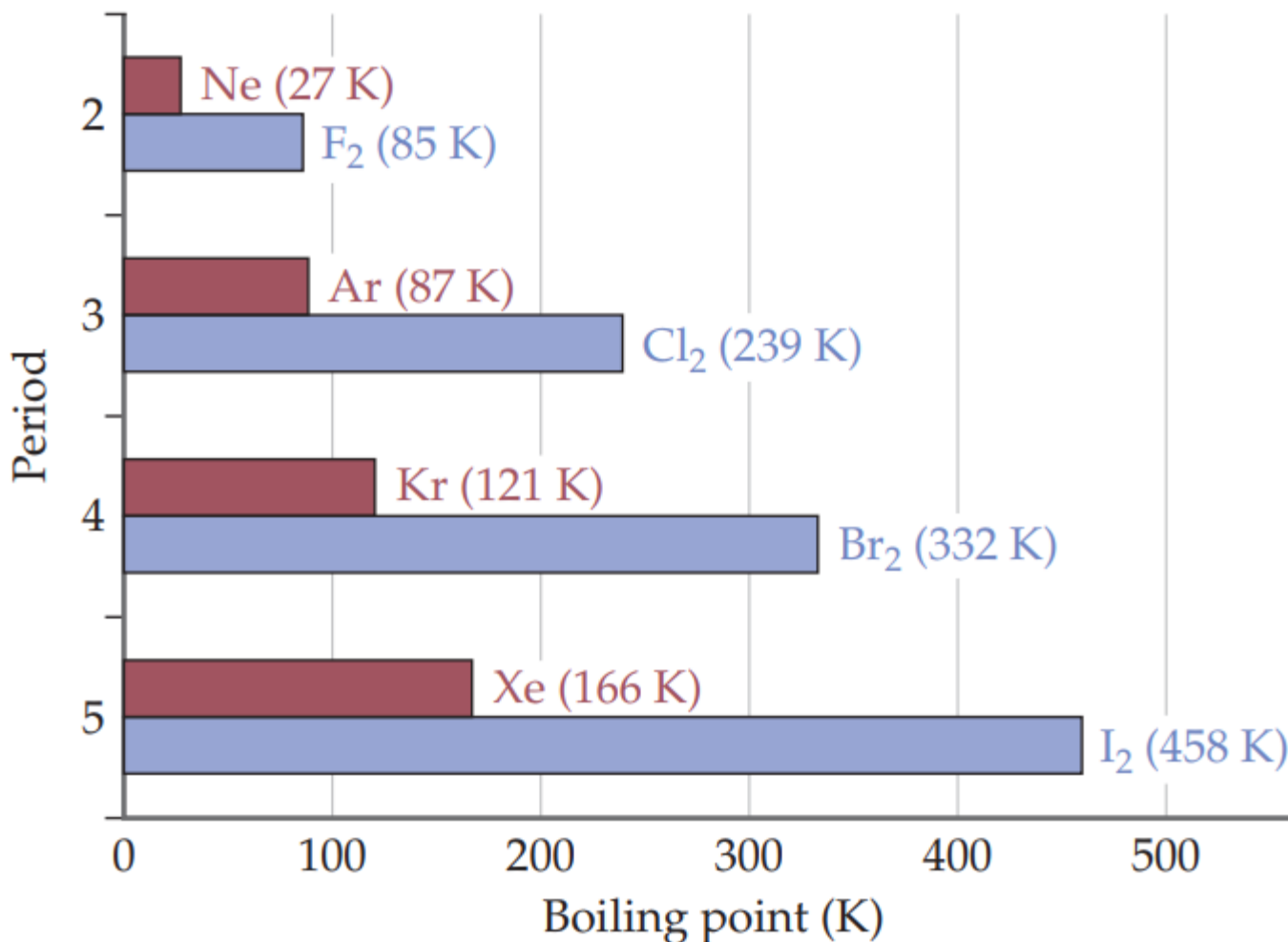Dispersion forces usually increase with molar mass.

TABLE 11.2

Melting Points of Similar Nonpolar Compounds

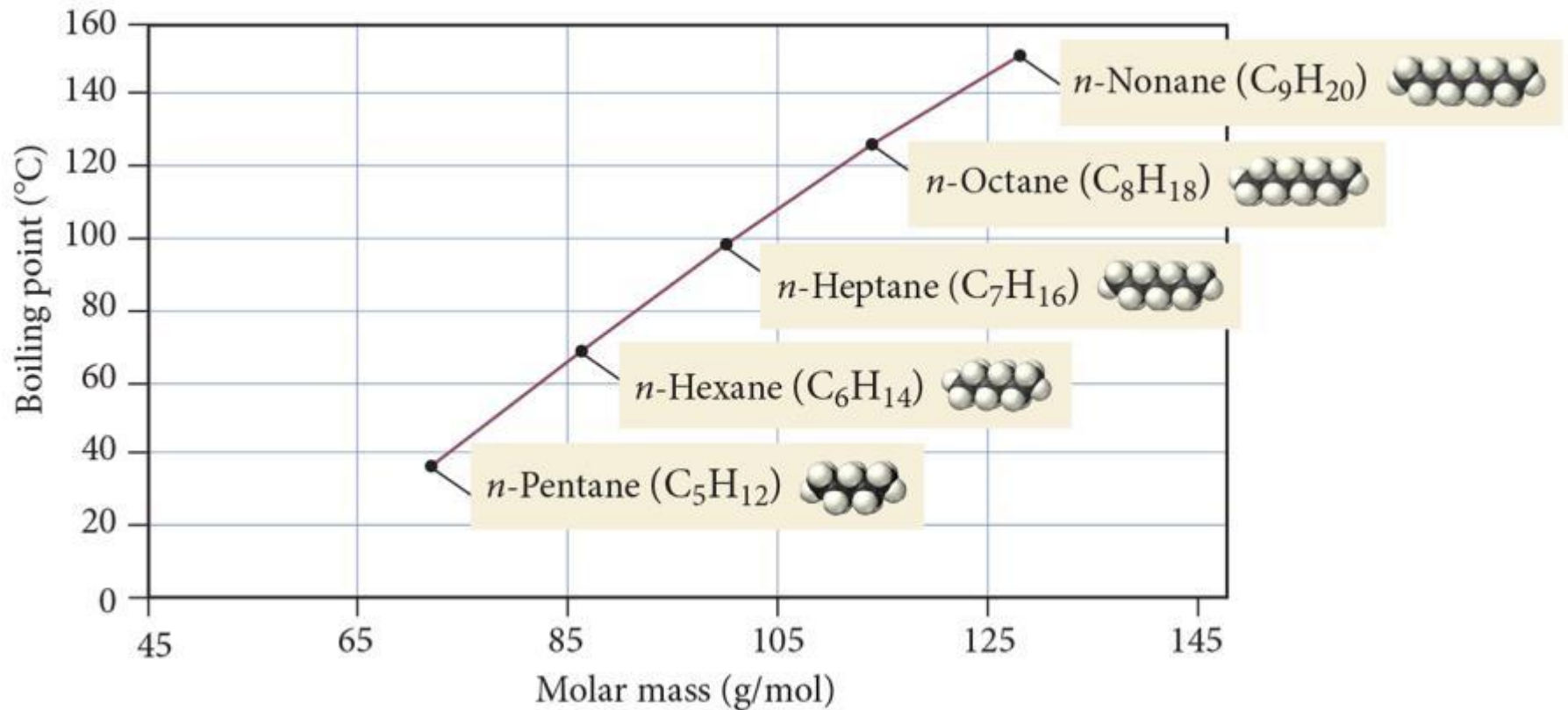| Compound	Melting Point (°C)
CH_4	−182.5
CF_4	−150.0
CCl_4	−23.0
CBr_4	90.0
CI_4	171.0

Intermolecular Forces

Dispersion Forces: size

Intermolecular Forces

Dispersion Forces: size

Intermolecular Forces

Dispersion Forces: shape

Name: pentane
Boiling Point: 36°C
ΔH_{vap}: 25.8 kJ/mol
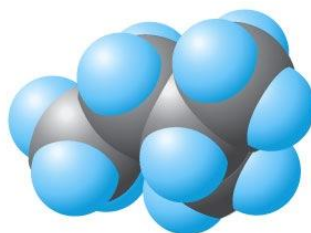
Name: 2-methylbutane
Boiling Point: 28°C
ΔH_{vap}: 24.7 kJ/mol

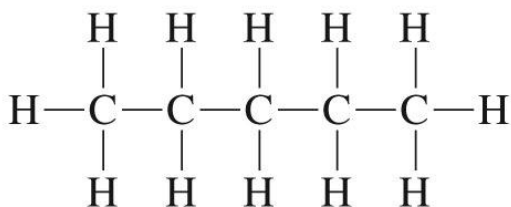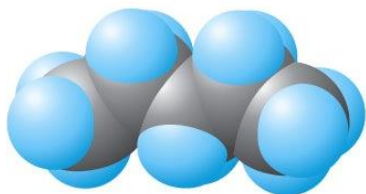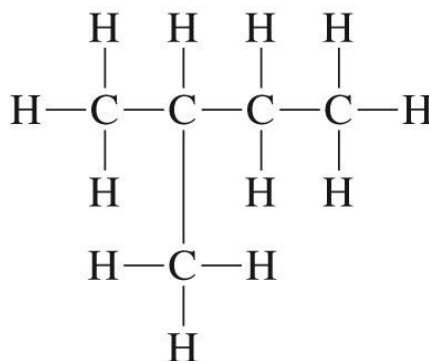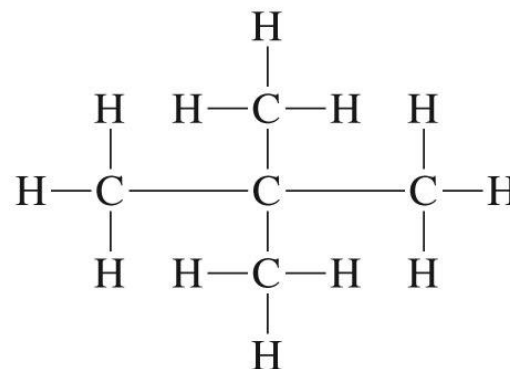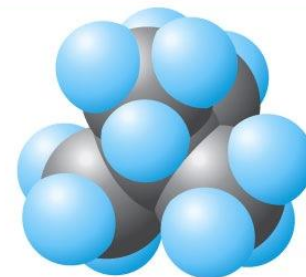Name: 2,2-dimethylpropane
Boiling Point: 9.5°C
ΔH_{vap}: 22.8 kJ/mol

Intermolecular Forces

Dispersion Forces: shape

Linear molecule—larger surface area enhances intermolecular contact and increases dispersion force.

Spherical molecule—smaller surface area diminishes intermolecular contact and decreases dispersion force.

n-Pentane (C_5H_{12})
bp = 309.4 K

Neopentane (C_5H_{12})
bp = 282.7 K

Intermolecular Forces

Dipole-Dipole Forces

Attractive forces between **polar molecules**

Orientation of Polar Molecules in a Solid

Intermolecular Forces

Dipole-Dipole Forces

Attractive forces between **polar molecules**

Solid
HCl

Liquid
HCl
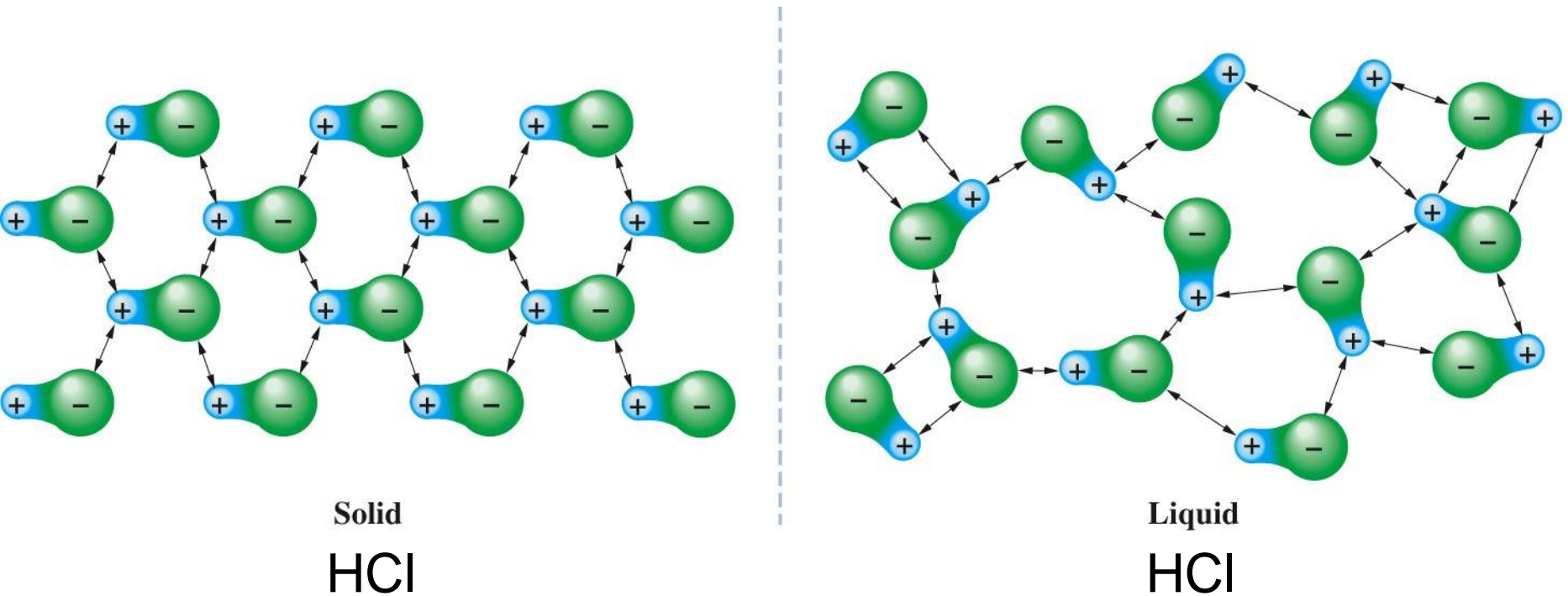
Intermolecular Forces

Dipole-Dipole Forces

Intermolecular Forces

Ion-Dipole Forces

Attractive forces between an **ion** and a **polar molecule**

Ion-Dipole Interaction
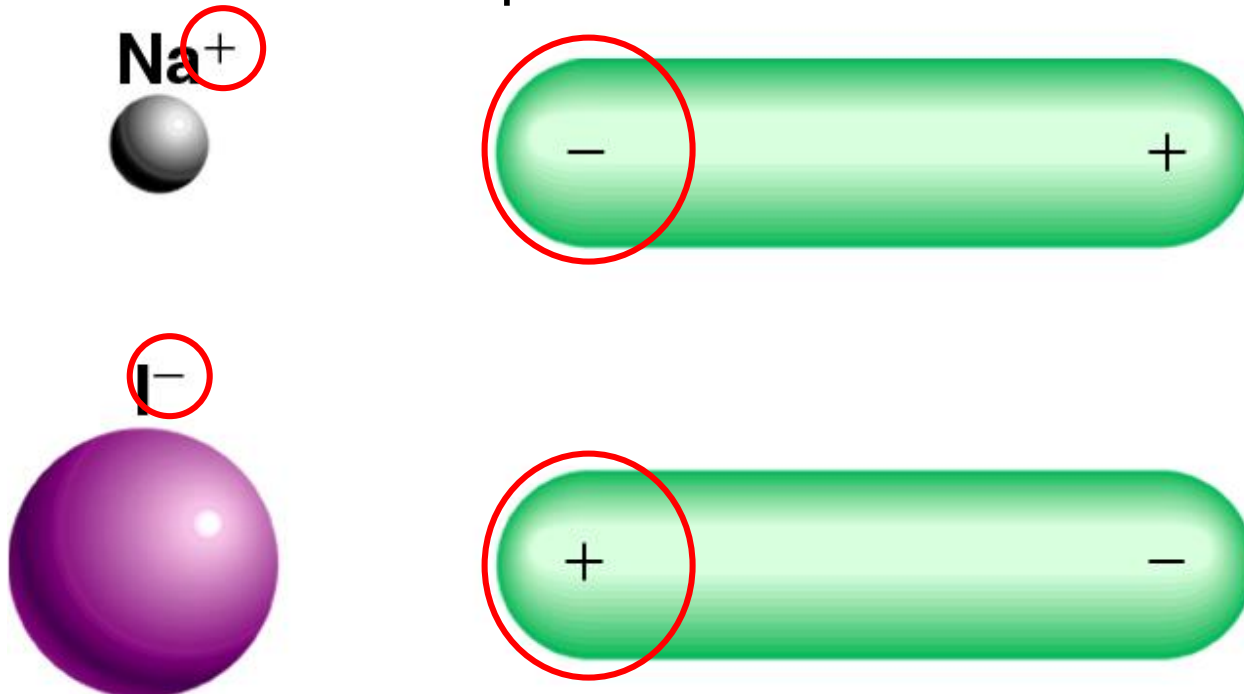
Interaction Between Water and Cations

Na⁺ — Weak interaction — (water molecule)

Mg²⁺ — Strong interaction — (water molecule)
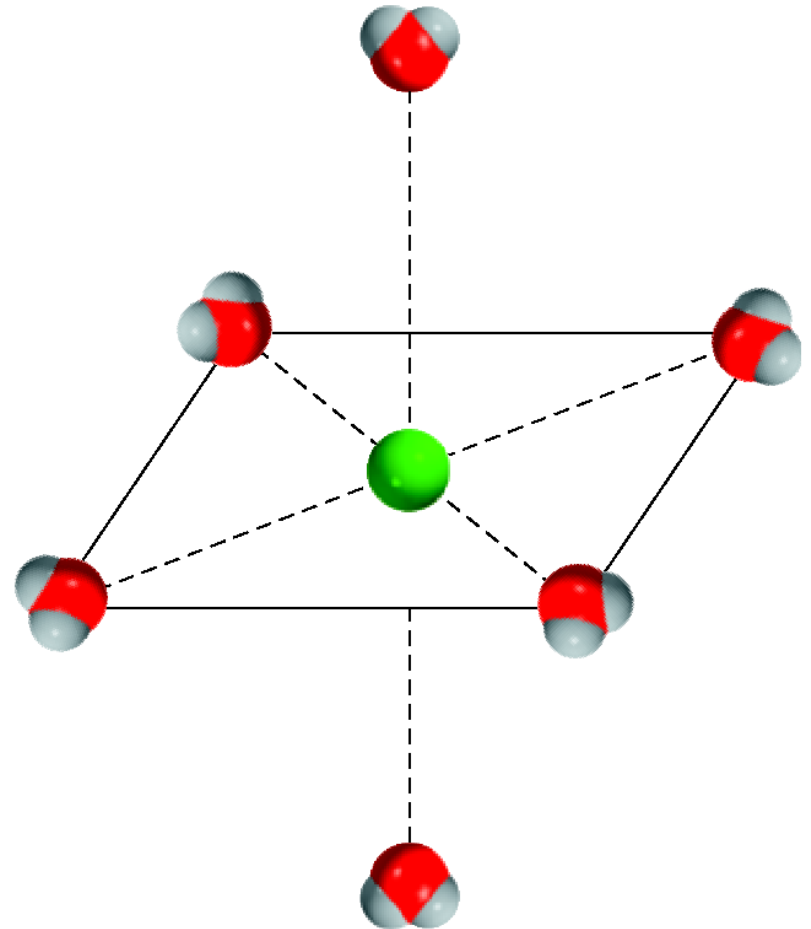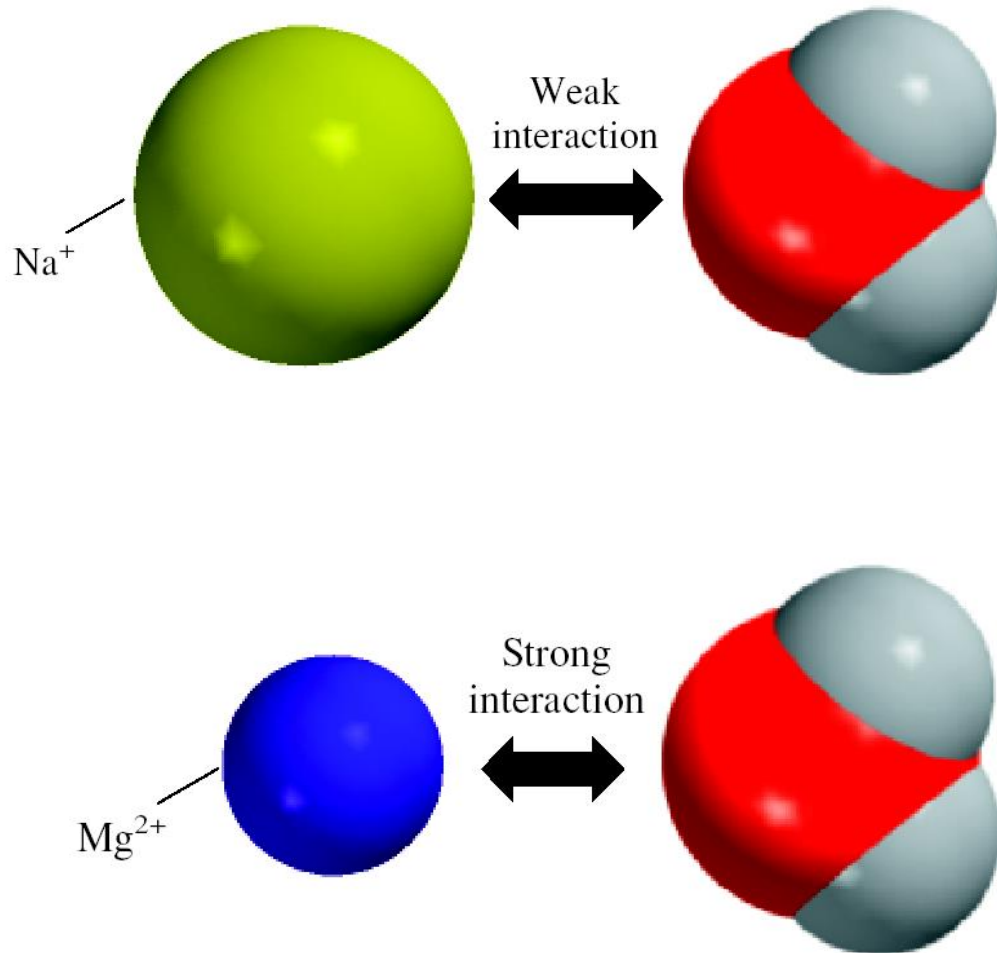
in solution

What type(s) of intermolecular forces exist between each of the following molecules?

HBr

HBr is a polar molecule: dipole-dipole forces. There are also dispersion forces between HBr molecules.

CH_4

CH_4 is nonpolar: dispersion forces.
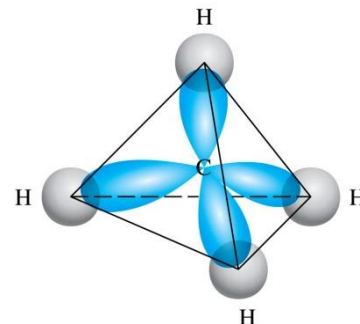
SO_2
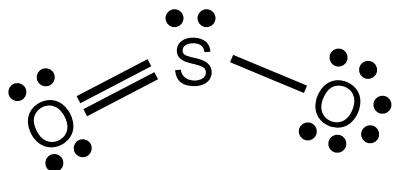
SO_2 is a polar molecule: dipole-dipole forces. There are also dispersion forces between SO_2 molecules.

Intermolecular Forces

Hydrogen Bond

The **hydrogen bond** is a special dipole-dipole interaction between they hydrogen atom in a polar N-H, O-H, or F-H bond and an electronegative O, N, or F atom.

$$A \text{—} H \cdots B \qquad \text{or} \qquad A \text{—} H \cdots A$$

A & B are N, O, or F: smallest, most electronegative
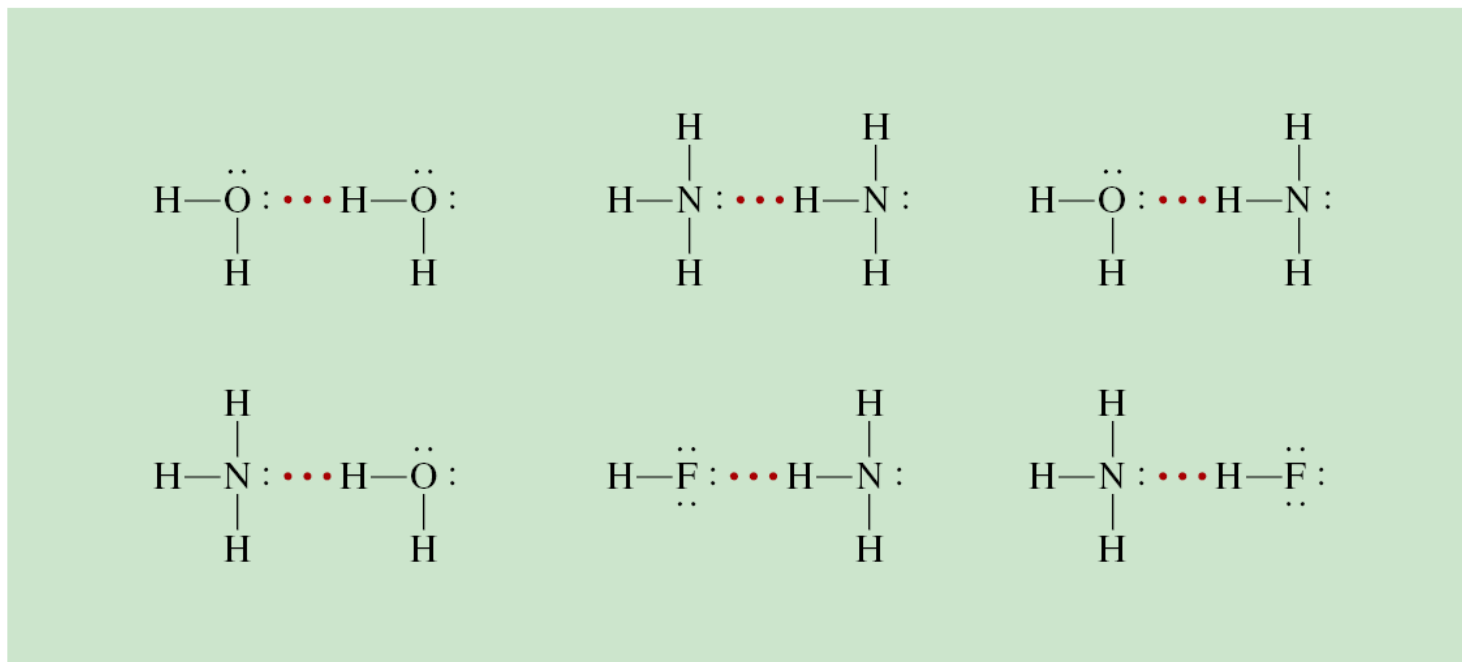
Hydrogen Bond

Hydrogen bonding in water is illustrated here in three different formats: ball-and-stick model, electrostatic map showing electron density distributions, and Lewis formula.
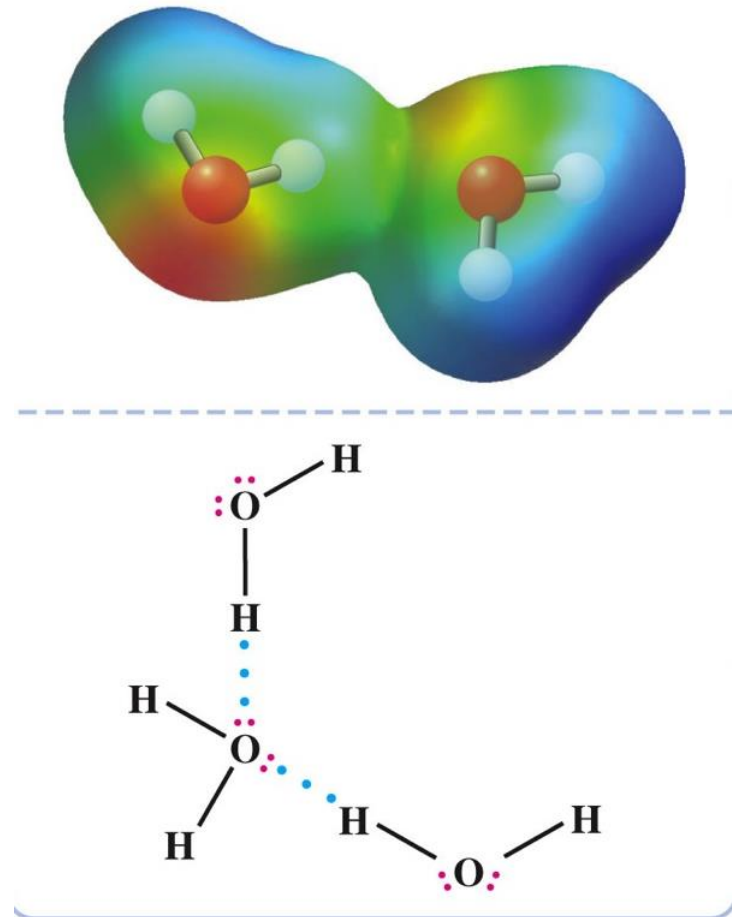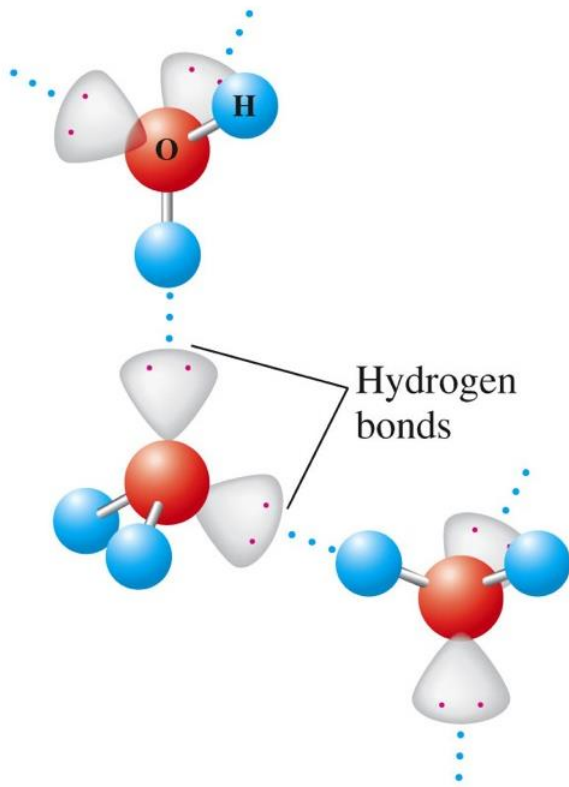
Hydrogen bonds

Why is the hydrogen bond considered a "special" dipole-dipole interaction?

Decreasing molar mass
Decreasing boiling point
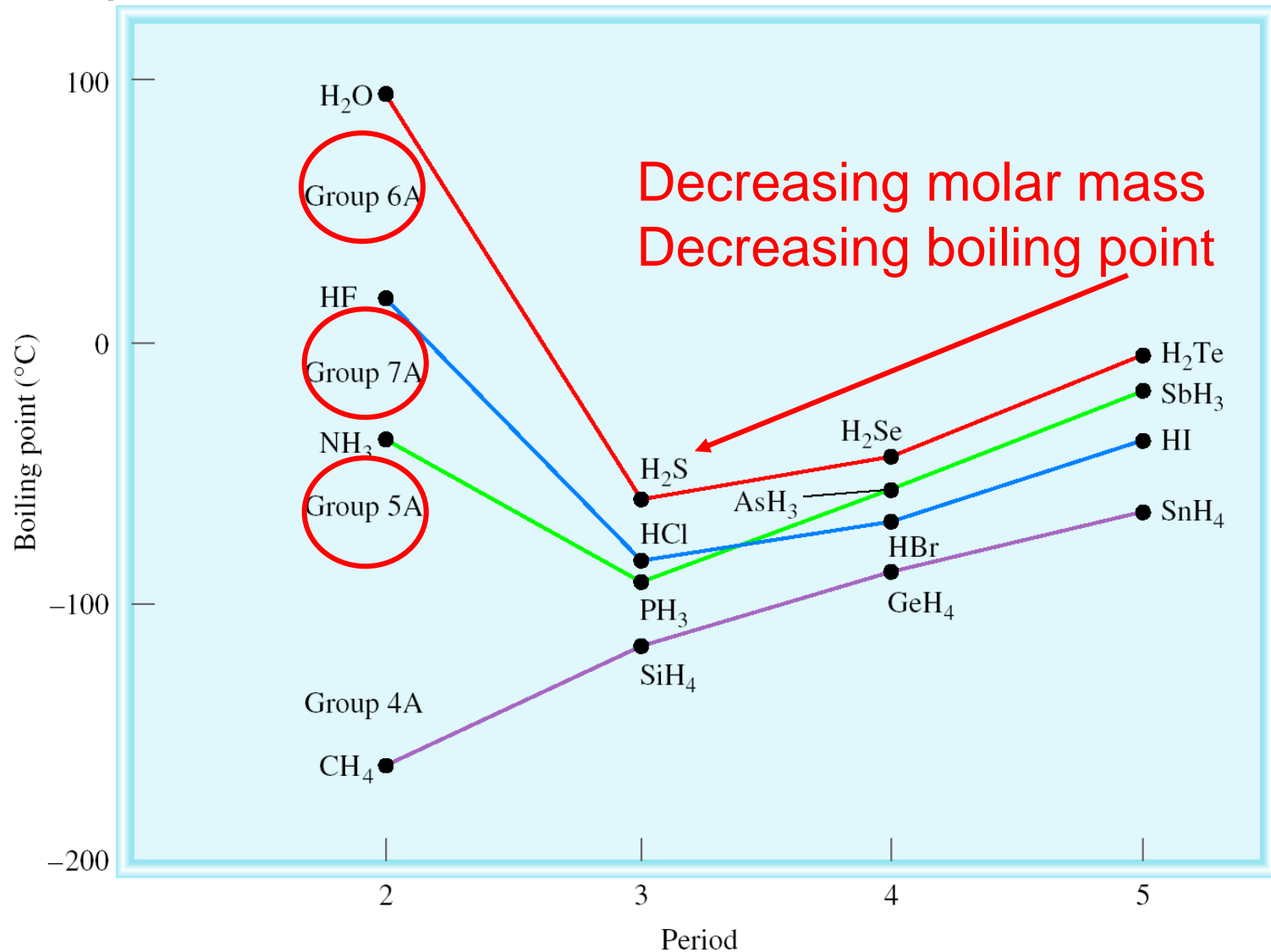
? Identify the intermolecular forces that you would expect for each of the following substances:

  a. O_2
  b. H_2O_2
  c. $CHBr_3$

a. Nonpolar molecule: London forces
b. Polar molecule with O—H bond: London forces, dipole-dipole forces, hydrogen bonding
c. Polar molecule: London forces, dipole-dipole forces

Intermolecular Forces

Type of intermolecular interaction	Atoms Examples: Ne, Ar	Nonpolar molecules Examples: BF_3, CH_4	Polar molecules without OH, NH, or HF groups Examples: HCl, CH_3CN	Polar molecules containing OH, NH, or HF groups Examples: H_2O, NH_3	Ionic solids dissolved in polar liquids Examples: NaCl in H_2O
Dispersion forces (0.1–30 kJ/mol)	√	√	√	√	√
Dipole–dipole interactions (2–15 kJ/mol)			√	√	
Hydrogen bonding (10–40 kJ/mol)				√	
Ion–dipole interactions (>50 kJ/mol)					√

Intermolecular Forces

Exercise 1: In which of these substances is hydrogen bonding likely to play an important role in determining physical properties: methane (CH_4), hydrazine (H_2NNH_2), methyl fluoride (CH_3F), hydrogen sulfide (H_2S)?

Exercise 2: List the substances $BaCl_2$, H_2, CO, HF, and Ne in order of increasing boiling point.

Surface Tension

Surface tension is the property that allows insects to walk on the surface of water or a pin to float.
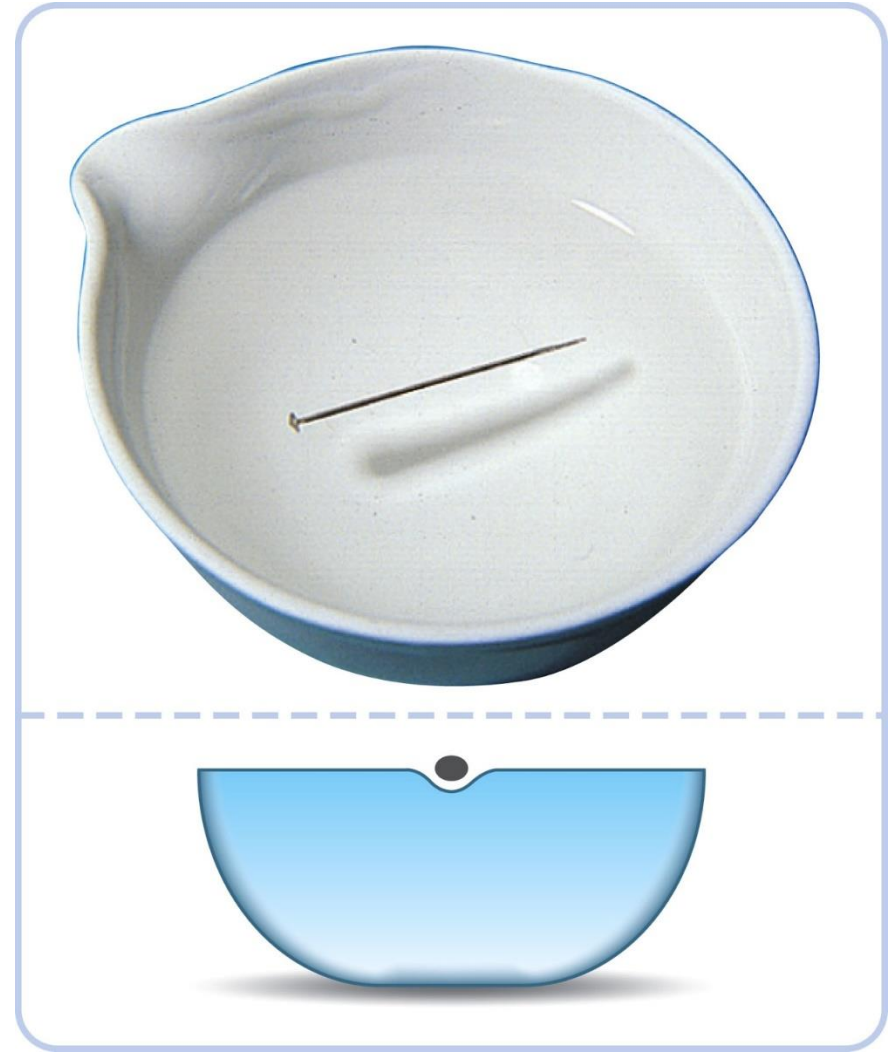
Surface Tension

Surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area.

Strong
intermolecular
forces

High
surface
tension
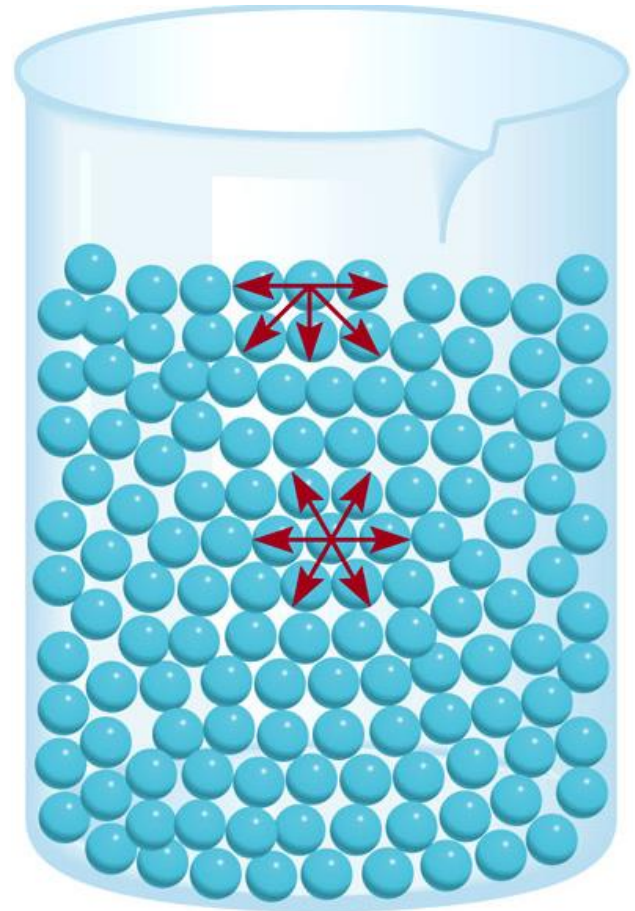
Surface Tension

Cohesion is the intermolecular attraction between like molecules

Adhesion is an attraction between unlike molecules
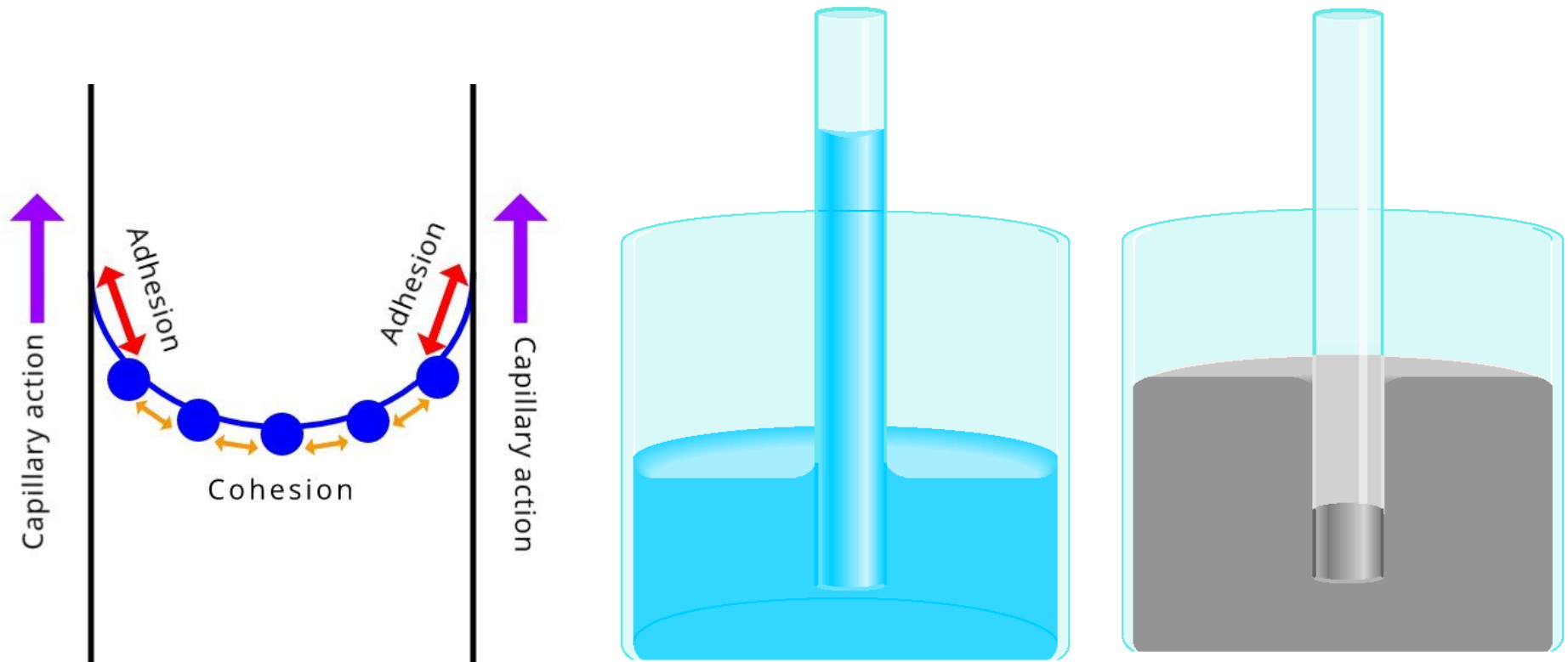
Viscosity

Viscosity is a measure of a fluid's resistance to flow.

Strong
intermolecular
forces

High
viscosity

TABLE 11.3	Viscosity of Some Common Liquids at 20°C
Liquid	**Viscosity (N s/m^2)***
Acetone (C_3H_6O)	3.16×10^{-4}
Benzene (C_6H_6)	6.25×10^{-4}
Blood	4×10^{-3}
Carbon tetrachloride (CCl_4)	9.69×10^{-4}
Diethyl ether ($C_2H_5OC_2H_5$)	2.33×10^{-4}
Ethanol (C_2H_5OH)	1.20×10^{-3}
Glycerol ($C_3H_8O_3$)	1.49
Mercury (Hg)	1.55×10^{-3}
Water (H_2O)	1.01×10^{-3}

*The SI units of viscosity are newton-second per meter squared.

Viscosity

- **Viscosity** is the resistance of a liquid to flow.
  - 1 poise = 1 P = 1 g/cm · s
  - Often given in centipoise, cP
    - H_2O = 1 cP at room temperature
- Larger intermolecular attractions = higher viscosity

TABLE 11.3 Viscosities of a Series of Hydrocarbons at 20 °C

Substance	Formula	Viscosity (kg/m-s)
Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	3.26×10^{-4}
Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	4.09×10^{-4}
Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	5.42×10^{-4}
Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	7.11×10^{-4}
Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	1.42×10^{-3}

Viscosity

- Raising the temperature of a liquid reduces its viscosity.
  - Raising the temperature of the liquid increases the average kinetic energy of the molecules.
  - The increased molecular motion makes it easier to overcome the intermolecular attractions and flow.

TABLE 11.6 Viscosity of Liquid Water at Several Temperatures	
Temperature (°C)	Viscosity (cP)
20	1.002
40	0.653
60	0.467
80	0.355
100	0.282

Heat of Vaporization

- The amount of heat energy required to vaporize one mole of the liquid is called the **heat of vaporization, ΔH_{vap}.**
  - Sometimes called the enthalpy of vaporization
- It is always endothermic; therefore, ΔH_{vap} is +.
- It is somewhat temperature dependent.
- $\Delta H_{condensation} = -\Delta H_{vaporization}$

TABLE 11.7 Heats of Vaporization of Several Liquids at Their Boiling Points and at 25 °C

| Liquid	Chemical Formula	Normal Boiling Point (°C)	ΔH_{vap}(kJ/mol) at Boiling Point	ΔH_{vap}(kJ/mol) at 25 °C
Water	H_2O	100	40.7	44.0
Rubbing alcohol (isopropyl alcohol)	C_3H_8O	82.3	39.9	45.4
Acetone	C_3H_6O	56.1	29.1	31.0
Diethyl ether	$C_4H_{10}O$	34.6	26.5	27.1

Effect of Intermolecular Forces on Evaporation and Condensation

- The weaker the attractive forces among molecules, the less energy they will need to vaporize.

- Also, weaker attractive forces means that more energy will need to be removed from the vapor molecules before they can condense.

- The net result will be more molecules in the vapor phase and a liquid that evaporates faster; *the weaker the attractive forces, the faster the rate of evaporation.*

- Liquids that evaporate easily are said to be **volatile**.
  – For example, gasoline, fingernail polish remover

- Liquids that do not evaporate easily are called **nonvolatile**.
  – For example, motor oil

Temperature Dependence of Vapor Pressure

- Increasing the temperature increases the number of molecules able to escape the liquid.

- The net result is that *as the temperature increases, the vapor pressure increases*.

- Small changes in temperature can make big changes in vapor pressure.
  - The rate of growth depends on the strength of the intermolecular forces.

Vapor Pressure Curves
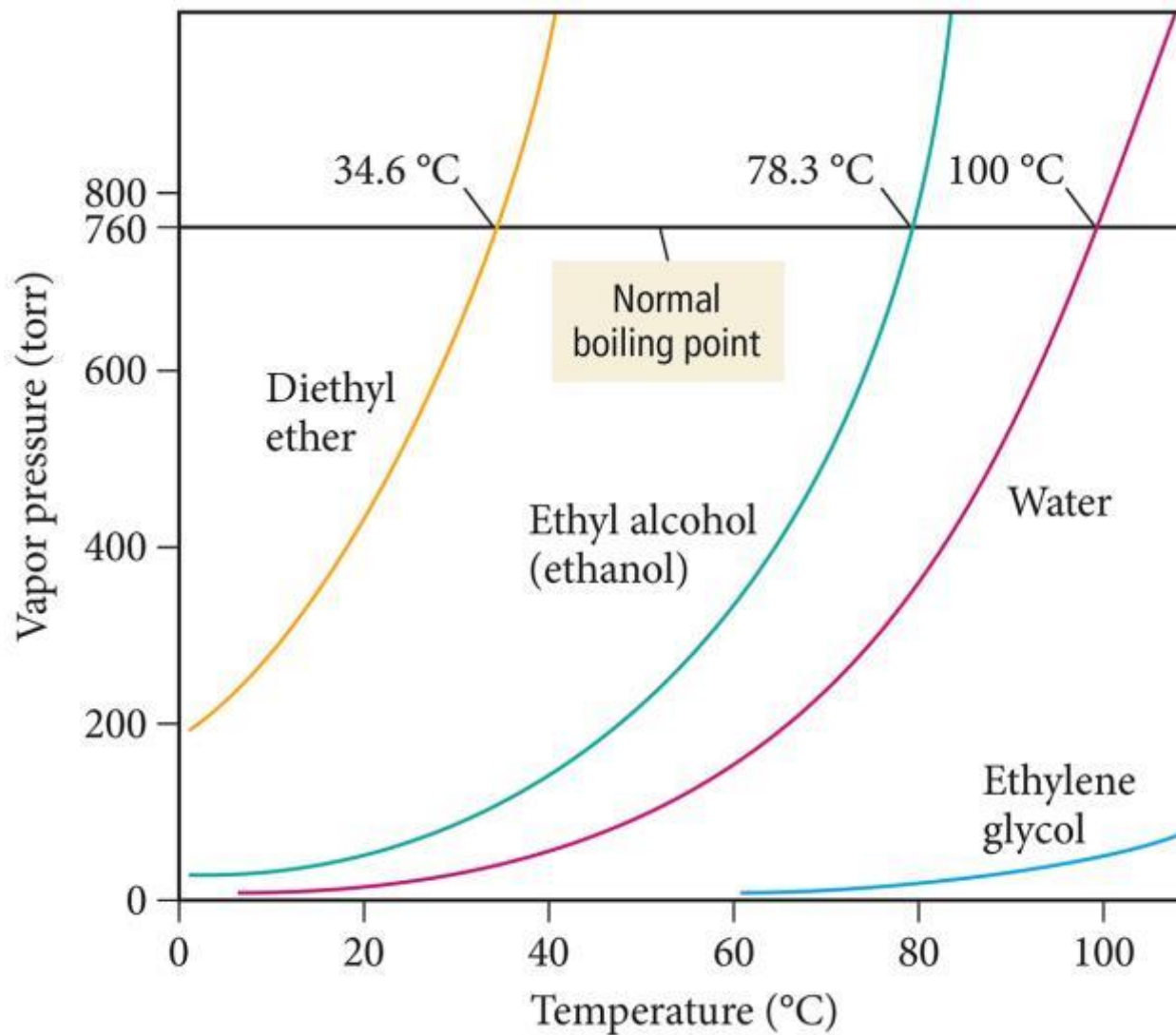
Attractive Forces and Solubility

- Solubility depends, in part, on the attractive forces of the solute and solvent molecules.
  - *Like dissolves like.*
  - *Miscible liquids will always dissolve in each other.*
- Polar substances dissolve in polar solvents.
  - **Hydrophilic groups = OH, CHO, C=O, COOH, NH$_2$, Cl**
- Nonpolar molecules dissolve in nonpolar solvents.
  - **Hydrophobic groups = C—H, C—C**
- Many molecules have both hydrophilic and hydrophobic parts; solubility in water becomes a competition between the attraction of the polar groups for the water and the attraction of the nonpolar groups for their own kind.

Immiscible Liquids

Pentane, C_5H_{12}, is a nonpolar molecule.

Water is a polar molecule.

The attractive forces among the water molecules are much stronger than their attractions for the pentane molecules. The result is that the liquids are immiscible.

$C_5H_{12}(l)$

$H_2O(l)$