Chem 30A

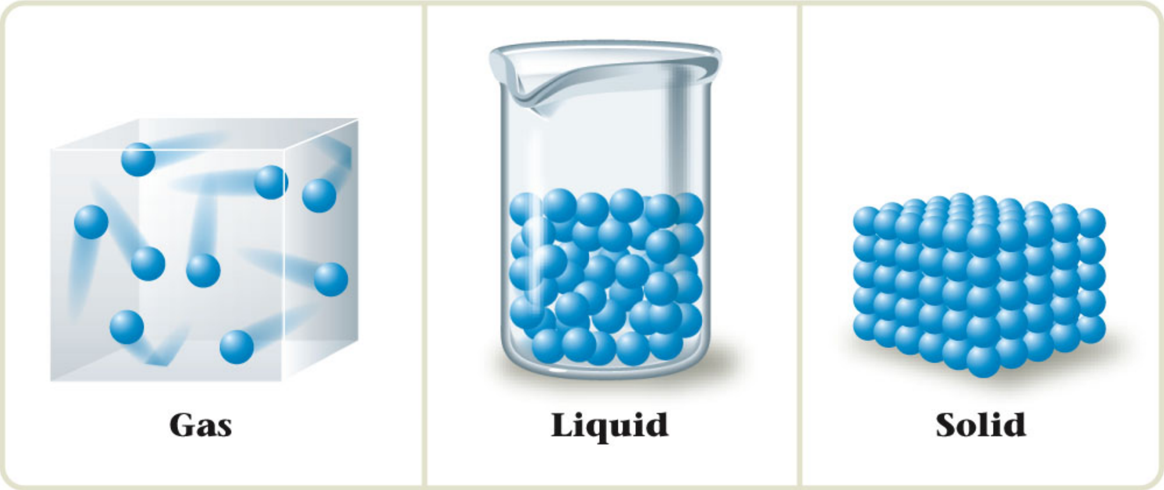
Ch 12. Liquids, Solids, and Intermolecular Forces

Introduction

Introduction

What holds particles together in liquids and solids?

- Gas: widely spaced, rapid random motion, low density
- Liquid: closer together, randomly arranged
- Solid: Closely packed, fixed position, rigid, high density

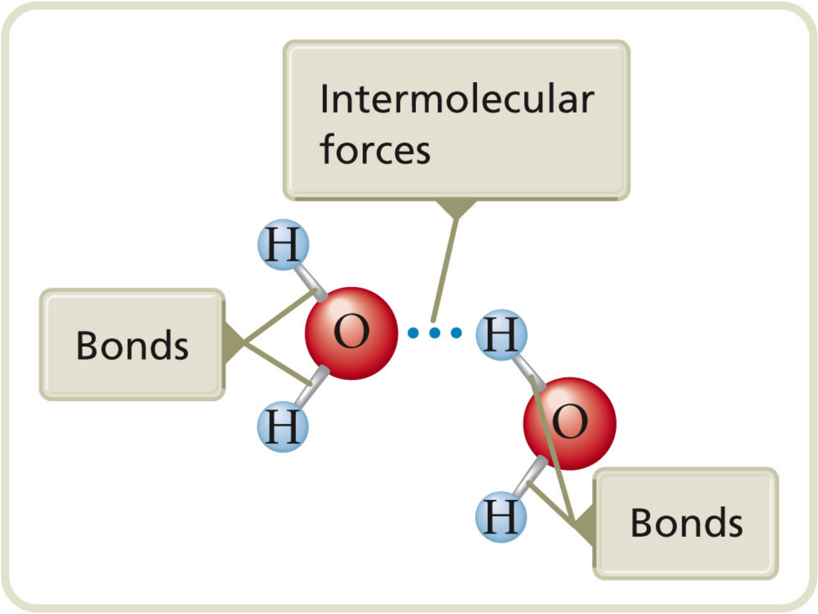


Intermolecular Forces

Intermolecular Forces

Intermolecular Forces

- Intermolecular forces: Forces between molecules that cause them to aggregate and form solids or liquids.



Intermolecular vs. Intramolecular forces (bonds)

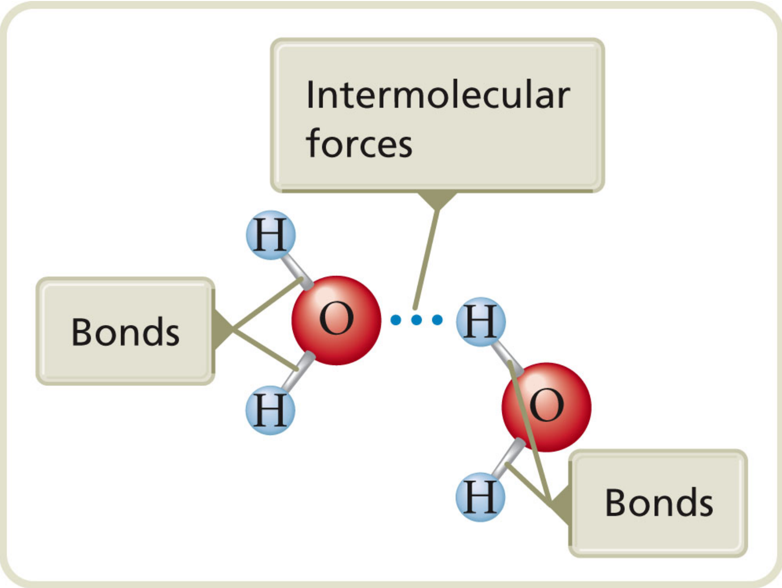
"inter": between molecules

"intra": within a molecule

INTRAmolecular Forces

Intramolecular Forces = Bonds

1. Ionic bond
2. Covalent bond, nonpolar
3. Covalent bond, polar



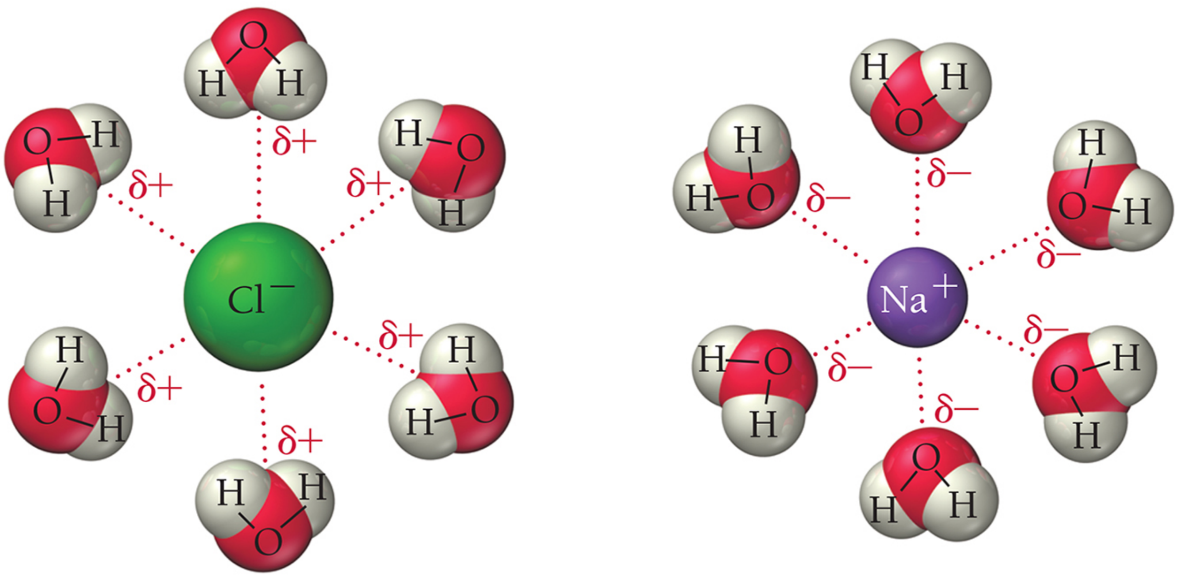
Bonds are much stronger than intermolecular forces.

INTERmolecular Forces

1. Ion-Dipole force
2. Dipole-dipole force
3. Hydrogen bonding (a special type of dipole-dipole force)
4. London dispersion force (induced dipole-induced dipole force)

1. Ion-Dipole Force

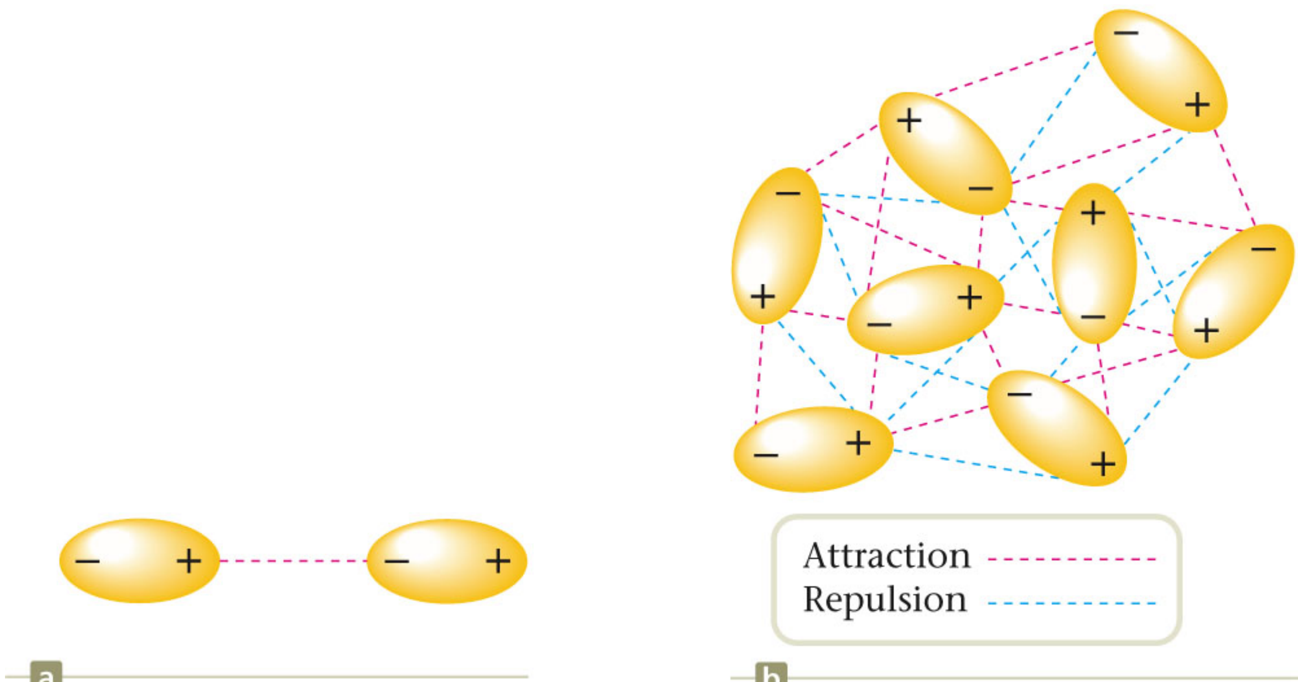
The positive sodium ions interact with the negative ends of water molecules, while the negative chloride ions interact with the positive ends of water molecules.



Strongest intermolecular force (although not as strong as bonds)

2. Dipole-Dipole Force

Occurs between polar molecules (dipoles).

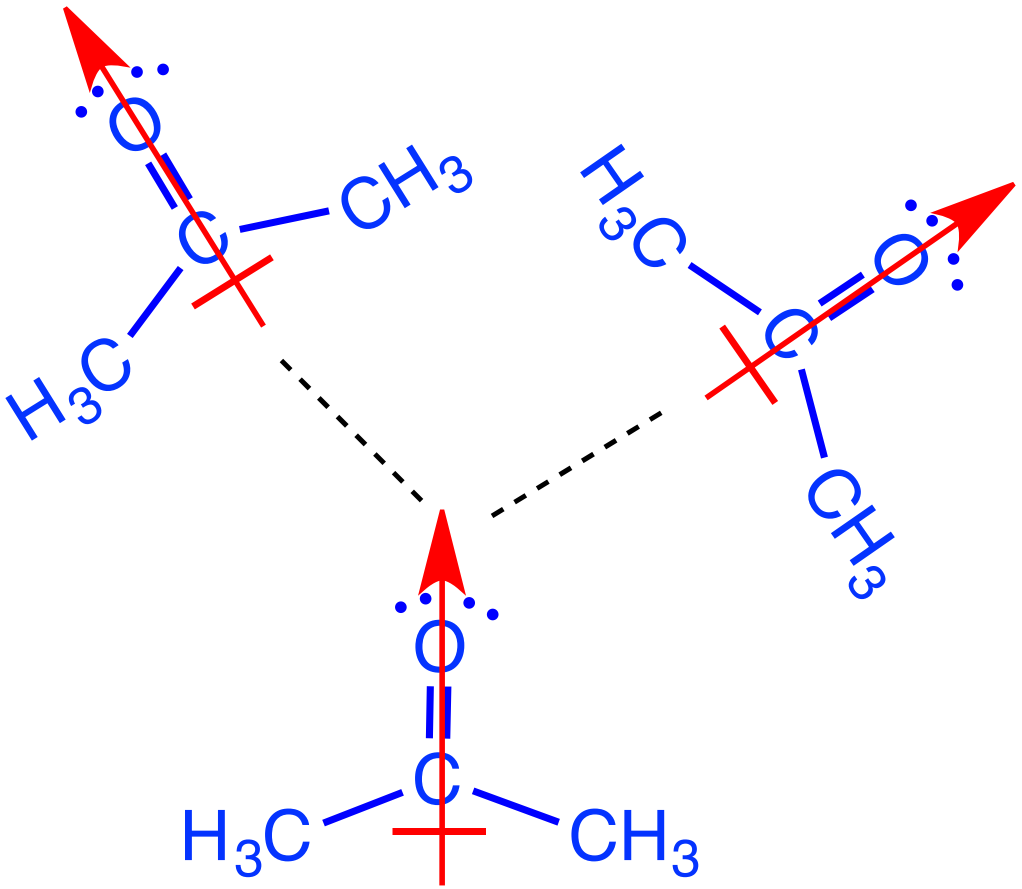


a The interaction of two polar molecules.

b The interaction of many dipoles in a liquid.

Not as strong as ion-dipole force.

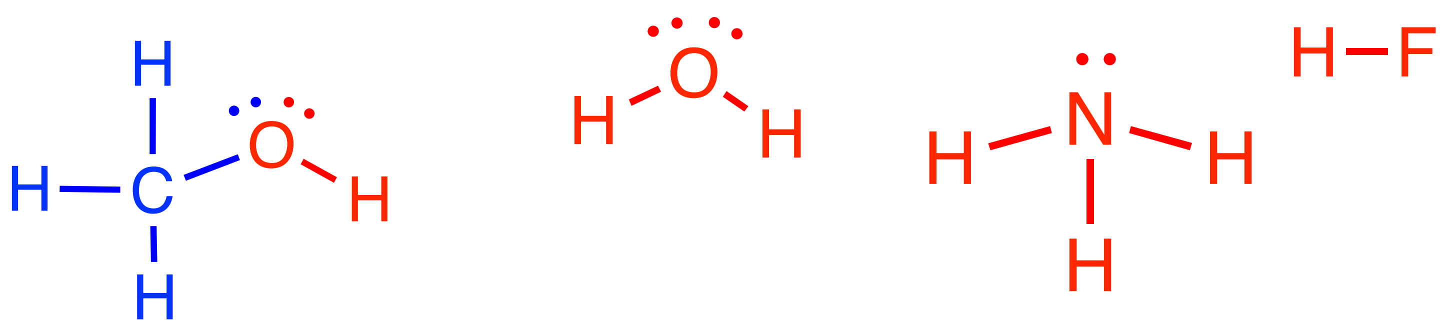
Dipole-Dipole Force



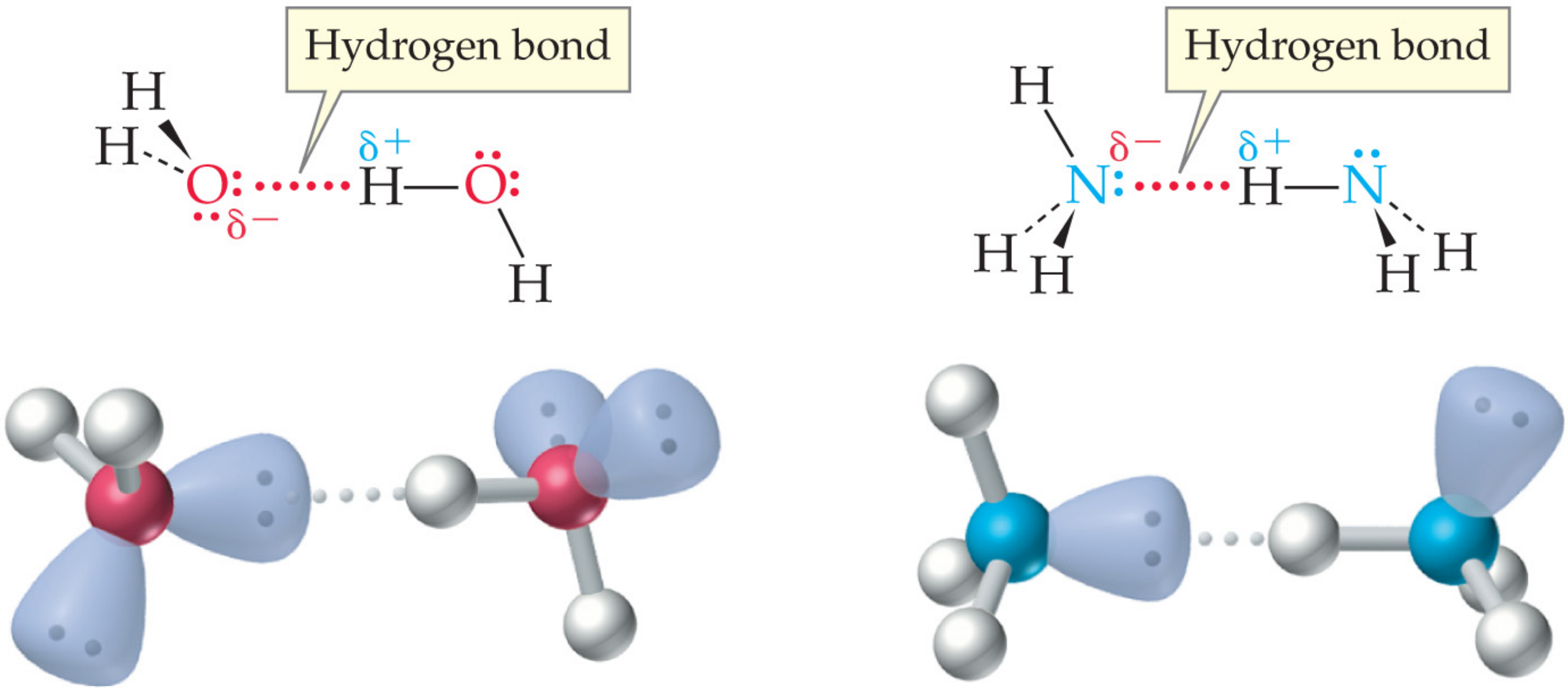
Ex Probs

3. Hydrogen Bonding

- A particularly strong type of dipole-dipole force
- Occurs between polar molecules that have a H bound to a highly electronegative atom (-N-H, -O-H, H-F)
- Examples:



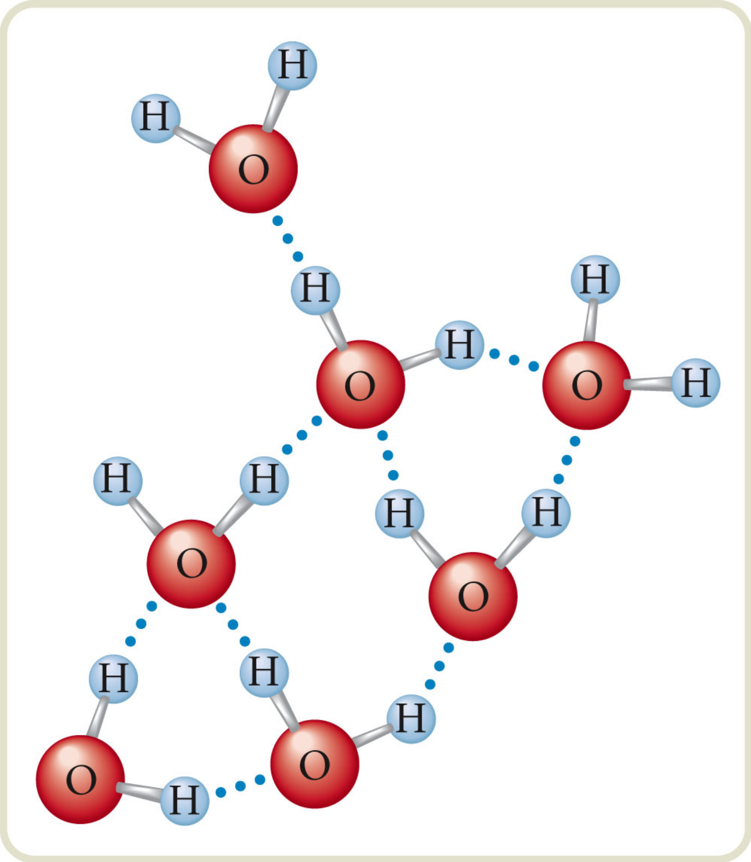
Hydrogen Bonding



The hydrogen bond occurs between:

1) lone pairs on electronegative atom of one molecule, &
2) H on electronegative atom of another molecule.

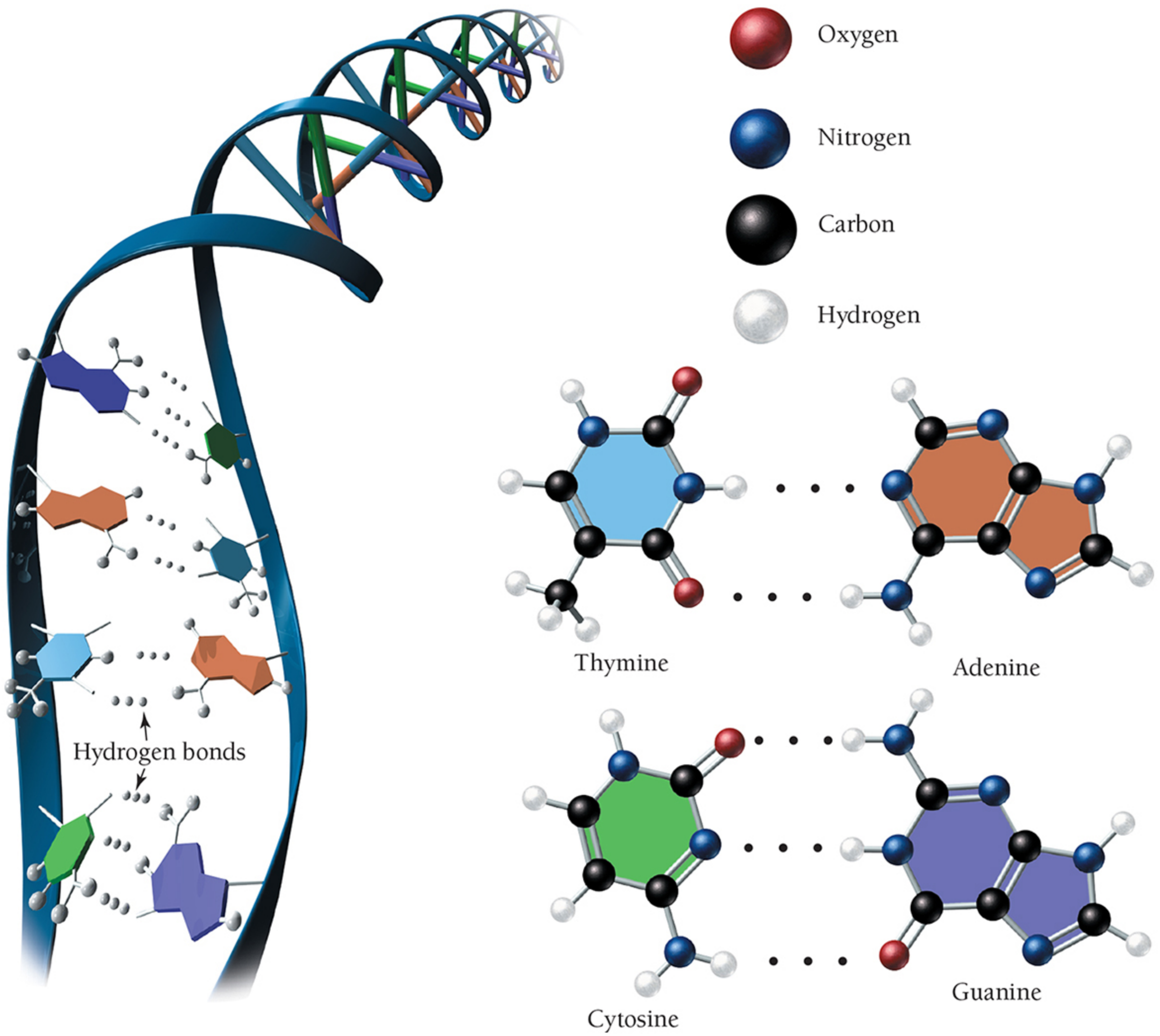
Hydrogen Bonding in Water



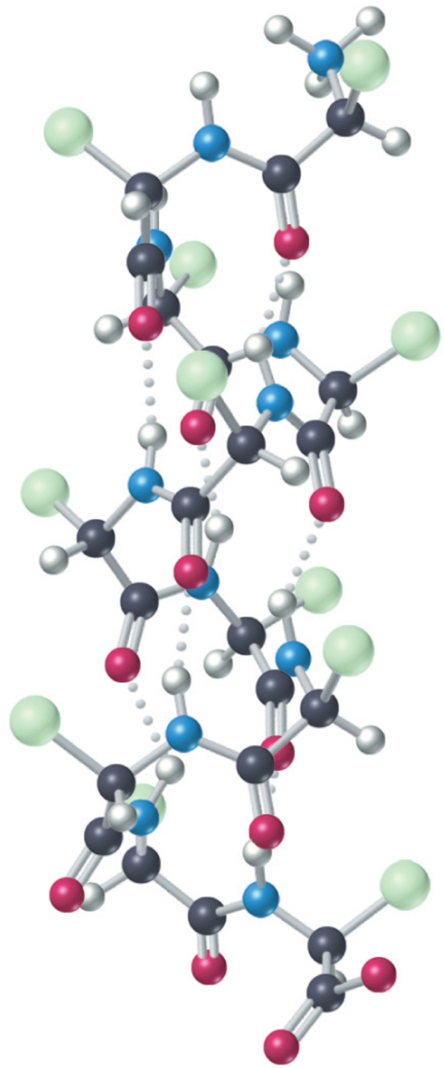
b

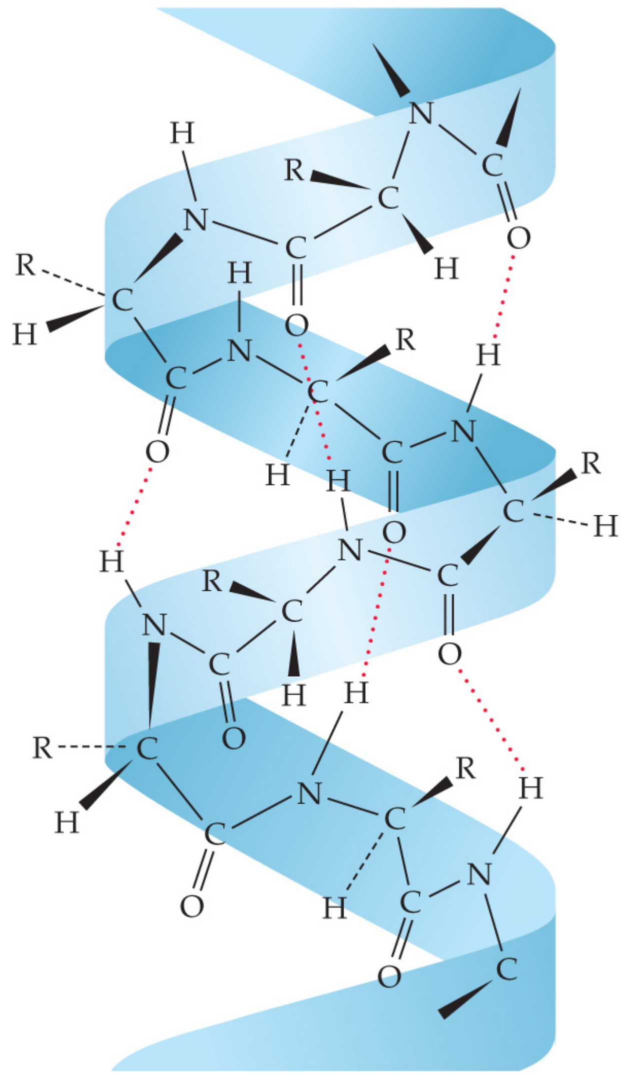
Water has two H atoms and 2 lone pairs → forms a vast network.

Hydrogen Bonding in DNA



Hydrogen Bonding in Peptide (Keratin)

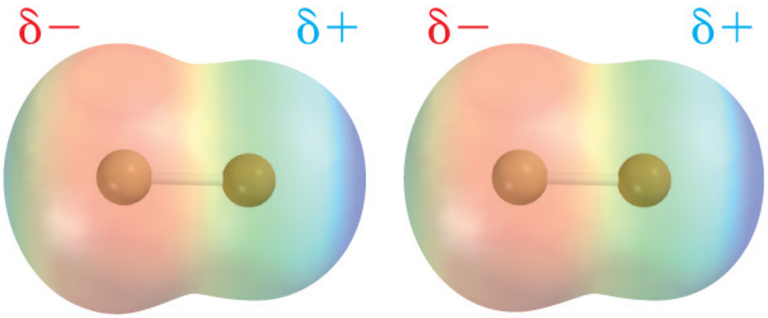




Ex Probs

4. London Dispersion Force (induced dipole-induced dipole)

- London dispersion force occurs when temporary, instantaneous dipole in one molecule induces a similar dipole in a neighboring molecule (temporary, random rearrangement of charge).



Br_2 At any given instant

London Dispersion Force

- Occurs between all molecules, but especially important in nonpolar molecules b/c it's the only intermolecular force available to them.

- Examples
  - I_2, H_2, CH_4, $CH_3CH_2CH_3$
  - Noble gases like He, Ne, Ar in very cold temp

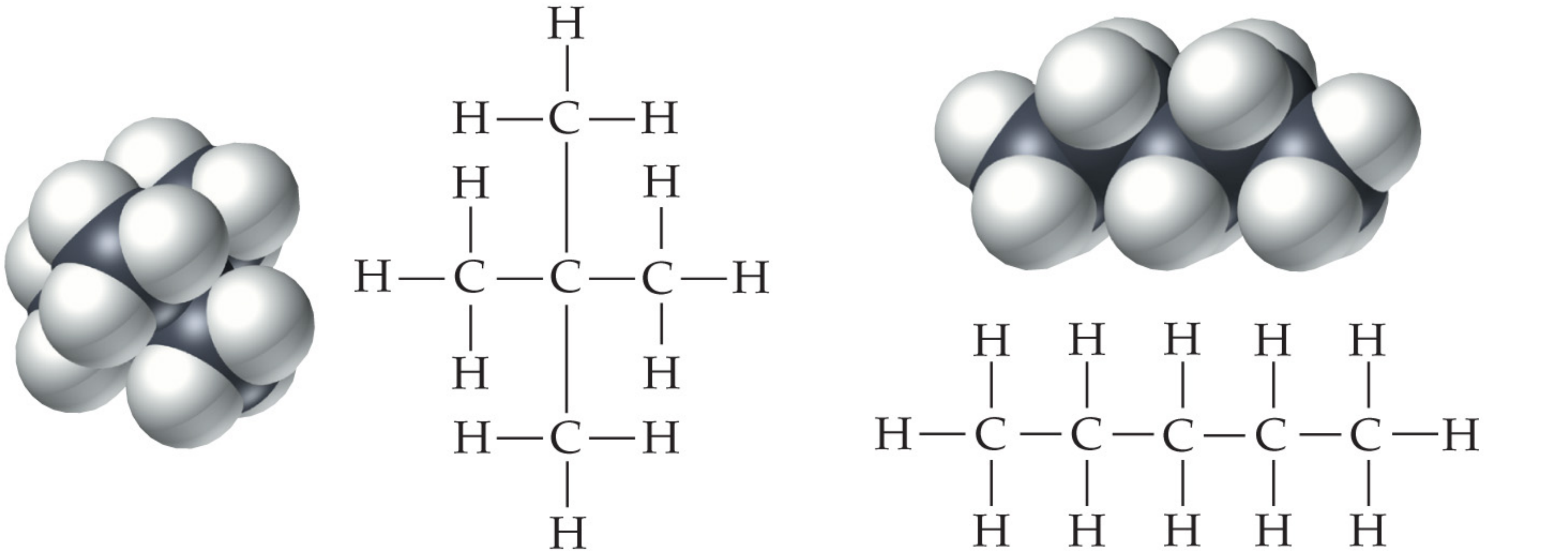
Strength of London Dispersion Forces

- London dispersion force is the weakest intermolecular force.

- London dispersion force increases with:

1) Greater molar mass (due to larger, more polarizable electron cloud)
2) Greater surface area of molecule

London Dispersion Force: Effect of Surface Area



(a) 2,2-Dimethylpropane (bp = 9.5 °C)

(b) Pentane (bp = 36 °C)

Smaller surface area
Smaller total London dispersion force

Larger surface area
Larger total London dispersion force

Strengths of Intermolecular Forces

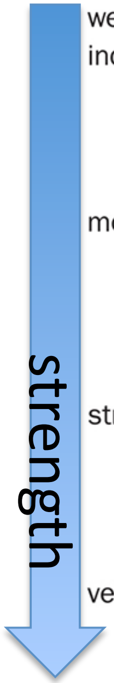
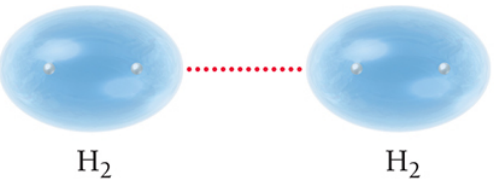
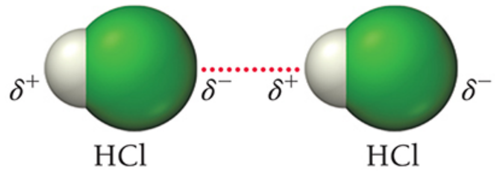
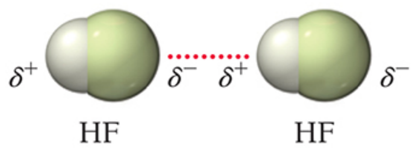
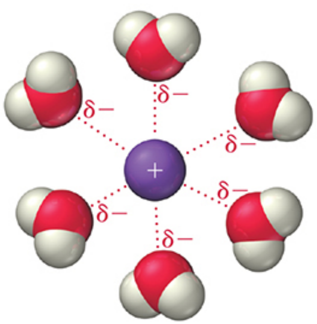


TABLE 12.5 Types of Intermolecular Forces

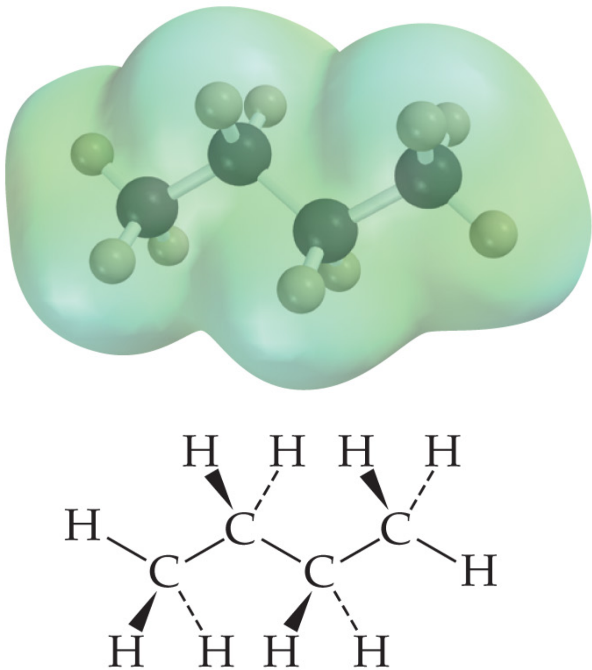
Type of Force	Relative Strength	Present in	Example
dispersion force (or London force)	weak, but increases with increasing molar mass	all atoms and molecules	
dipole–dipole force	moderate	only polar molecules	
hydrogen bond	strong	molecules containing H bonded directly to F, O, or N	
ion–dipole force	very strong	mixtures of ionic compounds and polar compounds	

Intermolecular Forces and Boiling Point

- Greater the intermolecular force between the molecules of a substance, higher the boiling point of that substance.
- i.e., More heat is required to break the intermolecular forces to change liquid to gas.

Effect of Dipole-Dipole Force on Boiling Point

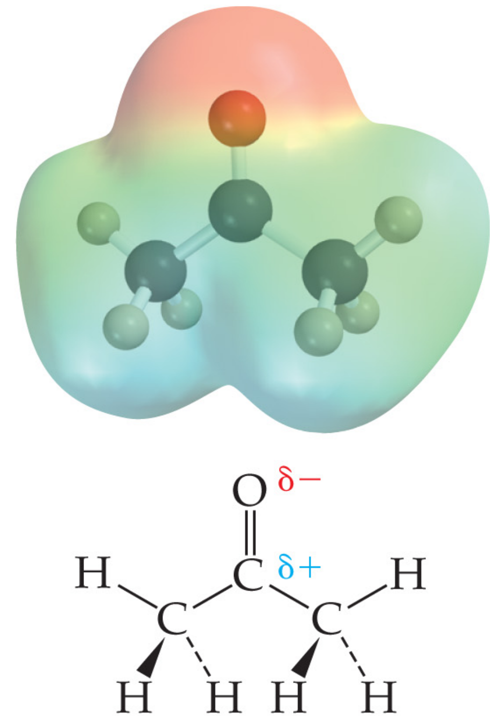
NO dipole-dipole force



Butane (C_4H_{10})

Mol wt = 58 amu
bp = −0.5 °C

Has dipole-dipole force

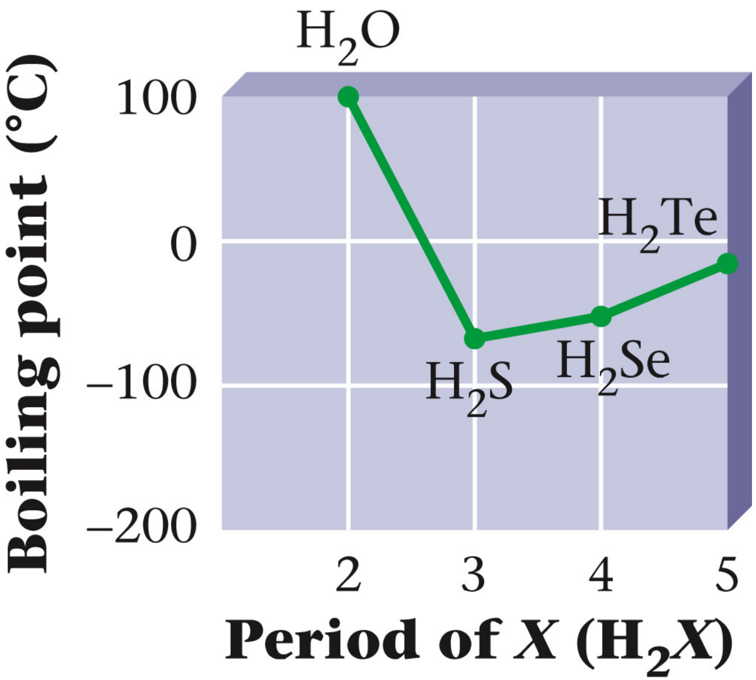


Acetone (C_3H_6O)

Mol wt = 58 amu
bp = 56.2 °C

Effect of Hydrogen Bonding on Boiling Point

- Hydrogen bonding makes the boiling point of water very high, relative to hydrides of other group 6 elements.



Ex Probs

Phase Changes

Phase Changes

Phase Changes

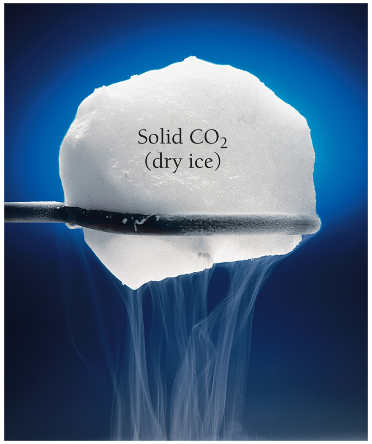
- Phase change: Change in the physical state of matter (gas, liquid, solid)

Phase Changes

- Melting (Fusion): solid to liquid
- Freezing: liquid to solid

- Vaporization: liquid to gas
- Condensation: gas to liquid

- Sublimation: solid to gas
- Deposition: gas to solid



Heat in Phase Changes

- Energy is transferred as heat during phase changes.

- Heat (q) absorbed or released by a process* =

  Enthalpy change (ΔH) = $H_{final} - H_{initial}$

- $\Delta H = q$ (*under constant pressure)

Exothermic vs. Endothermic Process

- Exothermic process ($-\Delta H$): a process that releases heat

- Endothermic process ($+\Delta H$): a process that absorbs heat

Enthalpy Change of Phase Changes

- Melting (Fusion): solid to liquid → endothermic +ΔH
- Freezing: liquid to solid → exothermic -ΔH

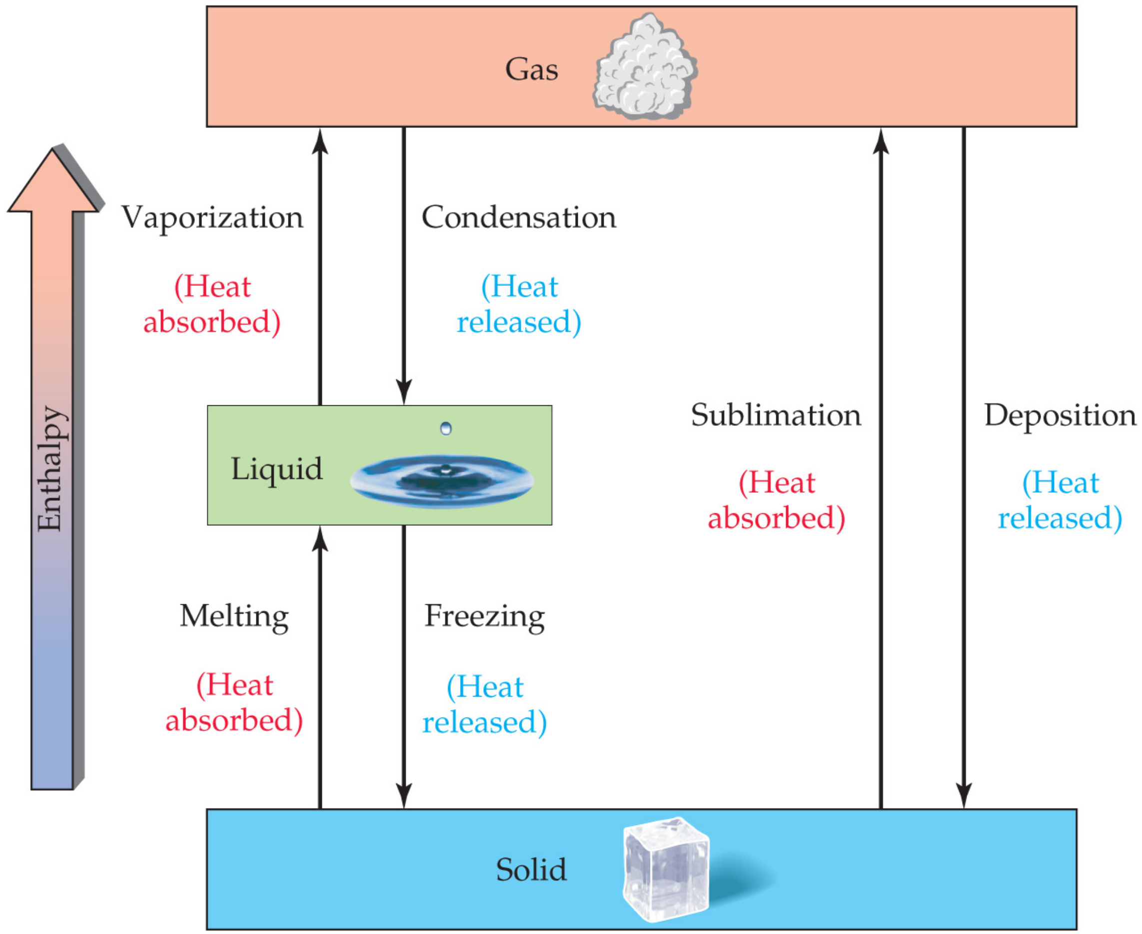
- Vaporization: liquid to gas → endothermic +ΔH
- Condensation: gas to liquid → exothermic -ΔH

- Sublimation: solid to gas → endothermic +ΔH
- Deposition: gas to solid → exothermic -ΔH

Enthalpy Changes of Phase Changes

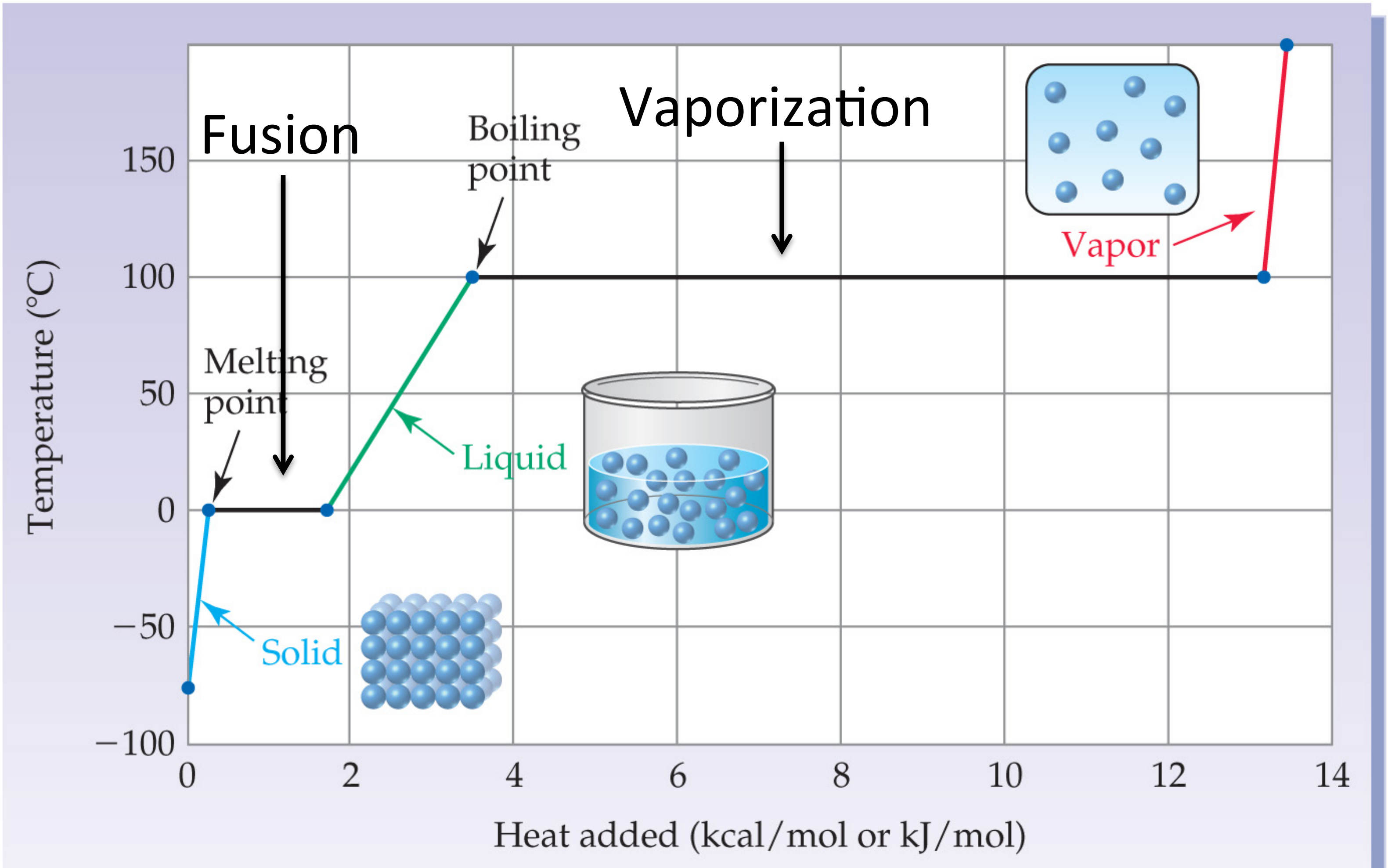
- Phase changes from Solid → Liquid → Gas are endothermic because heat is needed to break the intermolecular forces.

Enthalpy Changes of Phase Changes



Every change of state is reversible.

Heating Curve for Water



——— Phase change

Temperature of Phase Change

- Melting point (mp): the temperature at which solid turns into liquid (temperature of transition between solid and liquid) = freezing point

- Boiling point (bp): the temperature at which liquid turns into gas (the temperature of transition between liquid and gas)

Heating Curve for Water

- Within a single phase: temperature increases when heat is added, b/c…

- the heat increases the kinetic energy (energy of motion) of the particles.

$$KE_{avg} \propto T$$

- Can calculate the temperature change through $q = mC\Delta T$.

Heating Curve for Water

- During a phase change: temperature remains constant till phase change is completed for the whole sample as heat is added, because…

  the added heat is breaking apart the intermolecular forces (attractive forces between particles).

Heats of Phase Changes

- Heat of fusion (ΔH_{fus}): quantity of heat required to completely melt one mole of a substance once it has reached its melting point

$$q = \text{moles} \times \Delta H_{fus}$$

- Heat of vaporization (ΔH_{vap}): quantity of heat required to completely vaporize one mole of a liquid once it has reached its boiling point.

$$q = \text{moles} \times \Delta H_{vap}$$

Heats of Phase Changes

TABLE 12.3 Heats of Fusion of Several Substances

Liquid	Chemical Formula	Melting Point (°C)	Heat of Fusion (kJ/mol)
water	H_2O	0.00	6.02
isopropyl alcohol (rubbing alcohol)	C_3H_8O	−89.5	5.37
acetone	C_3H_6O	−94.8	5.69
diethyl ether	$C_4H_{10}O$	−116.3	7.27

TABLE 12.2 Heats of Vaporization of Several Liquids at Their Boiling Points and at 25 °C

Liquid	Chemical Formula	Normal Boiling Point (°C)	Heat of Vaporization (kJ/mol) at Boiling Point	Heat of Vaporization (kJ/mol) at 25 °C
water	H_2O	100.0	40.7	44.0
isopropyl alcohol (rubbing alcohol)	C_3H_8O	82.3	39.9	45.4
acetone	C_3H_6O	56.1	29.1	31.0
diethyl ether	$C_4H_{10}O$	34.5	26.5	27.1

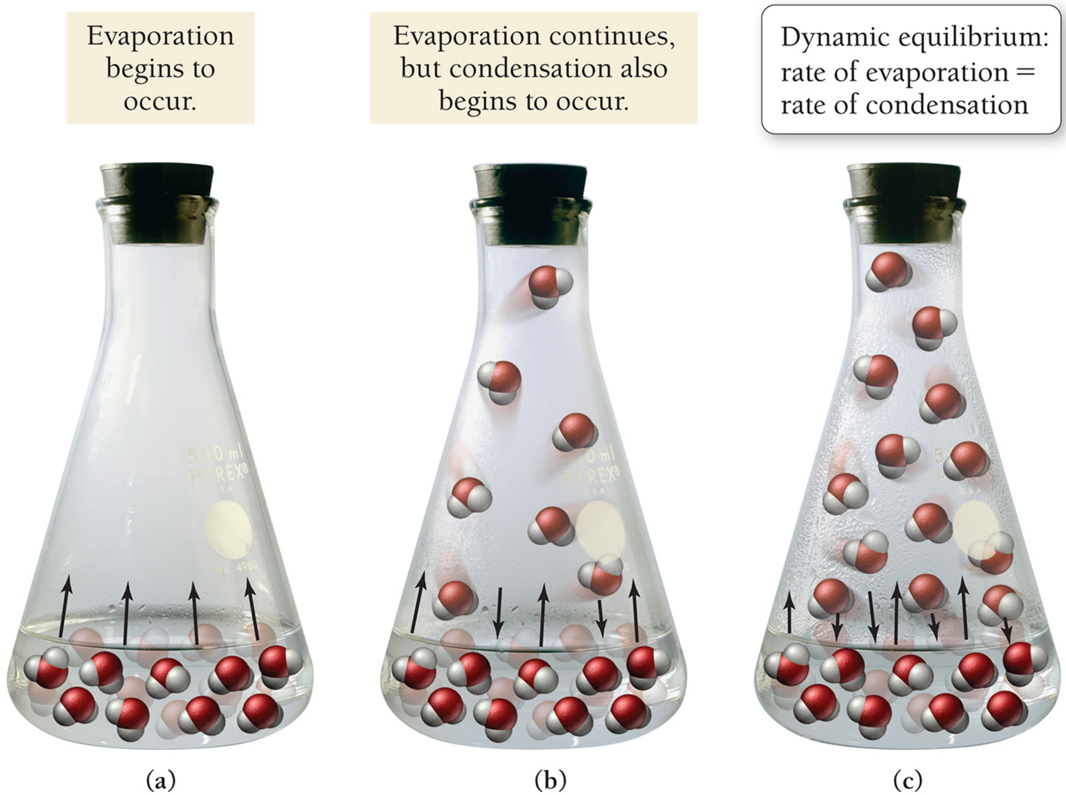
Ex Probs

Vapor Pressure of a Liquid

Vapor: the gaseous state of a substance that is normally liquid (or solid) at room temperature

Vapor pressure: the pressure exerted by a vapor in equilibrium with its liquid phase in a closed system

During evaporation, molecules escape from surface of liquid.



Boiling Point

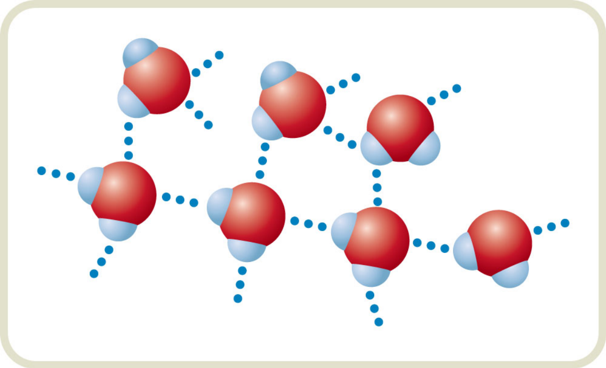
- When temperature reaches boiling point, molecules in *interior* of liquid have enough KE to escape as gas (bubbles).
- **Boiling point:** the temperature at which

  vapor pressure = atmospheric pressure

Bubbles can form and rise since the vapor pressure can overcome the atmospheric pressure.

Water: A Unique Liquid

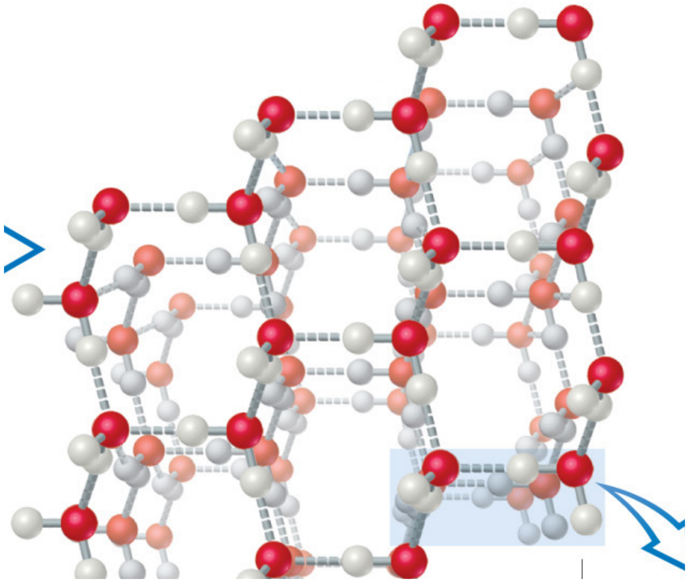
Water is a polar molecule that has strong hydrogen bonding, which causes water to:



- Have highest specific heat capacity of any liquid
- Have unusually high heat of vaporization (540 cal/g)
- Be more dense as a liquid than as a solid (unique)

Why Ice Floats

- In ice, water molecules are locked into position by hydrogen bonding → more open structure than liquid water → less dense than liquid water.
- Explains why ice floats, pipes burst when they freeze



Solids

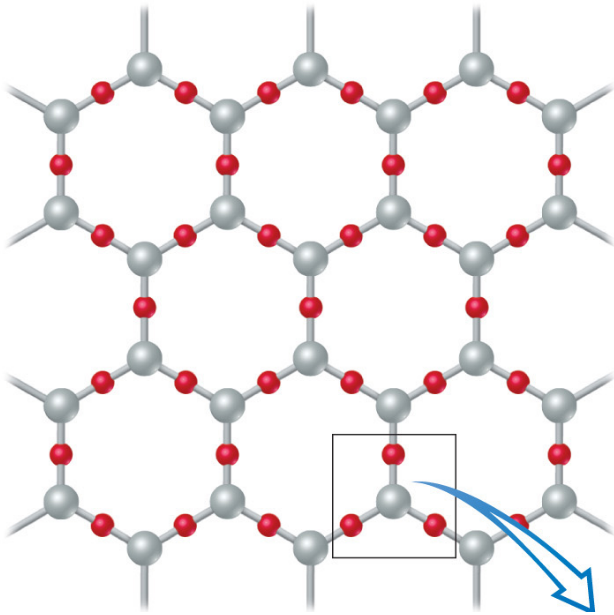
Solids

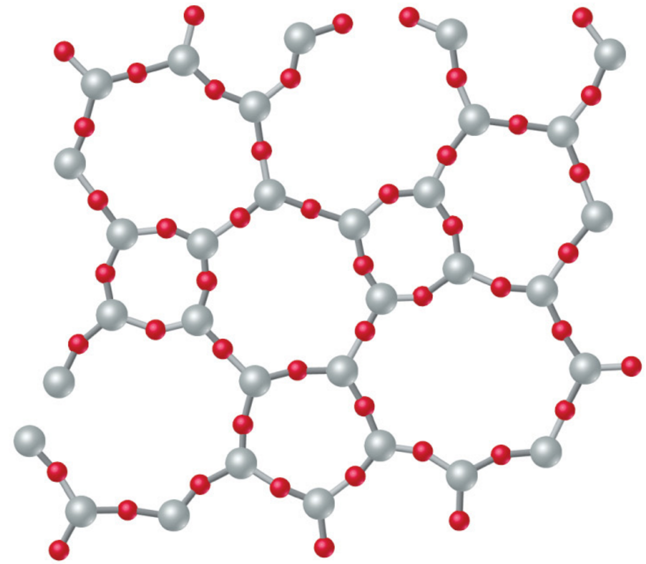
Structures of Solids

Two Major Categories of Solid Structures

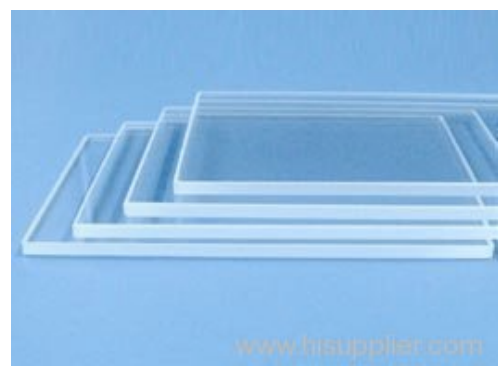
1. Crystalline: Atoms, ions, or molecules are ordered in well-defined 3D arrangements
2. Amorphous: Particles have no orderly structure.

Crystalline and Amorphous SiO_2





Crystalline
(quartz)

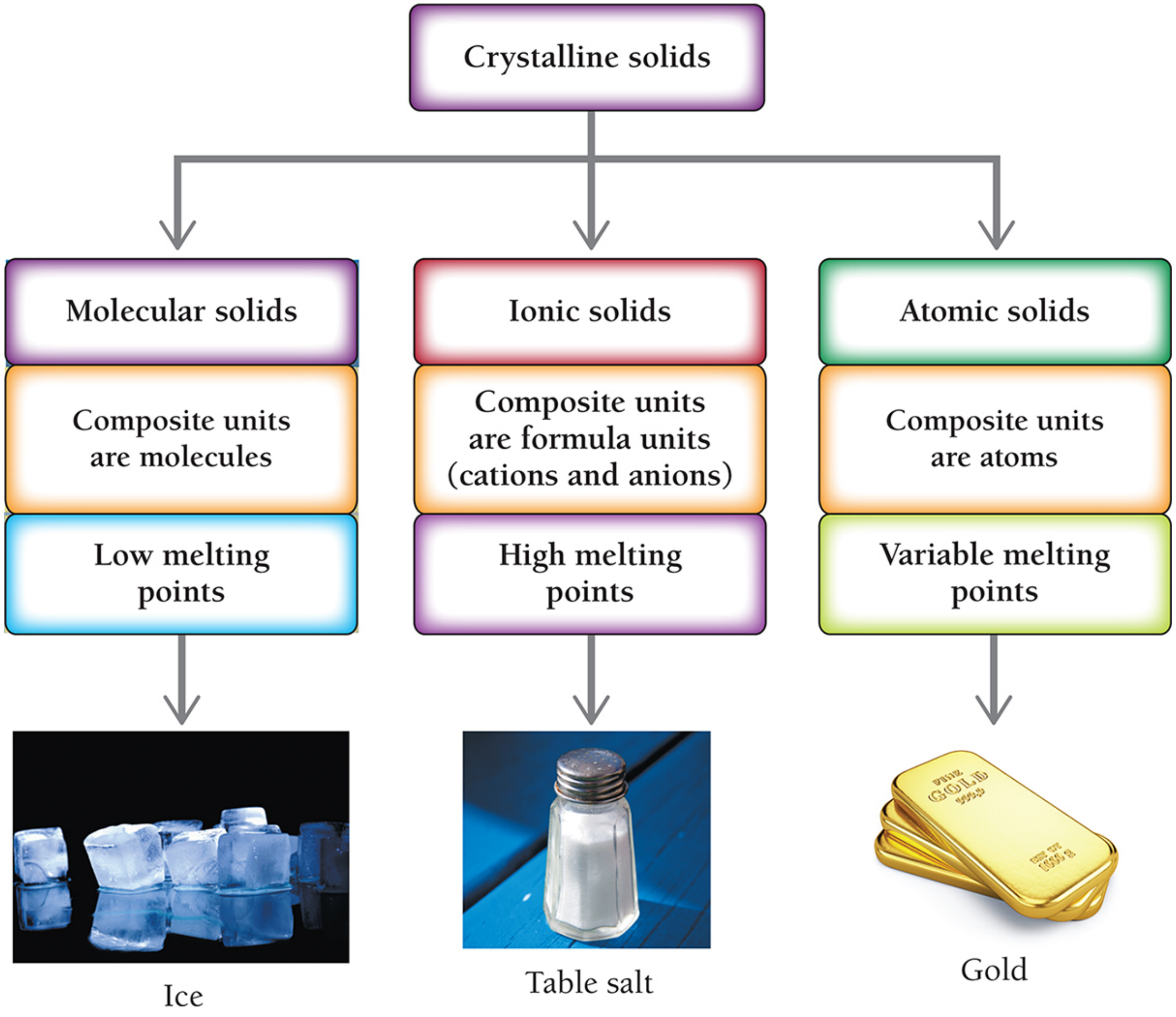


Amorphous
(glass)

Types of Crystalline Solids

1. Molecular solids
2. Ionic solids
3. Atomic solids
   a) Covalent
   b) Nonbonding
   c) Metallic

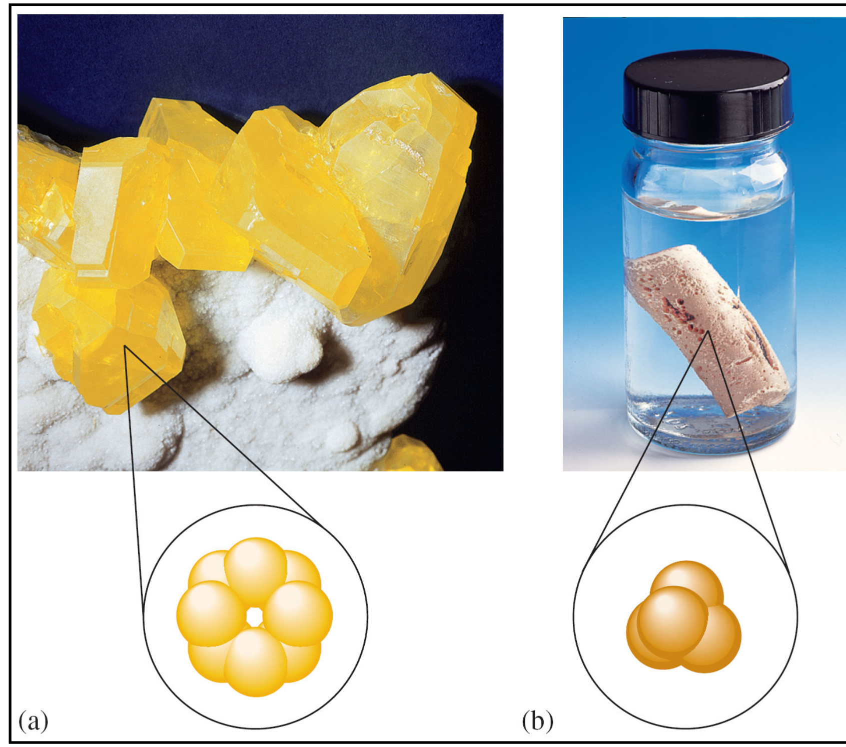
Types of Crystalline Solids



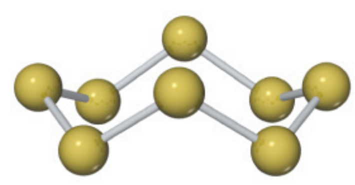
Molecular Solids

CO_2

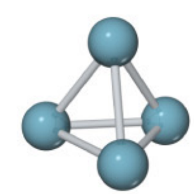
$C_6H_{12}O_6$



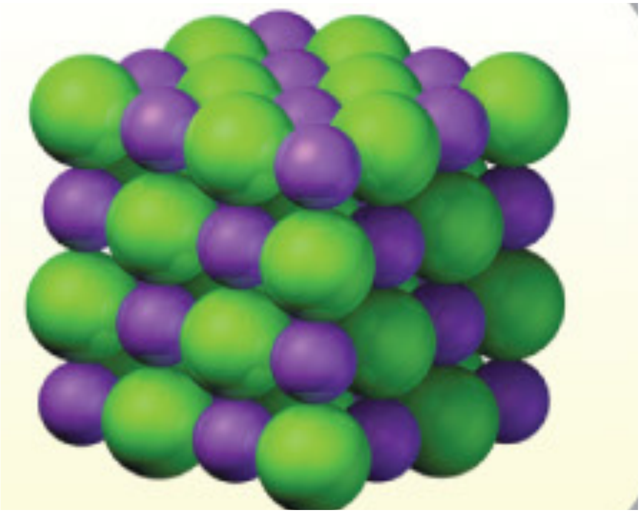
S_8



P_4

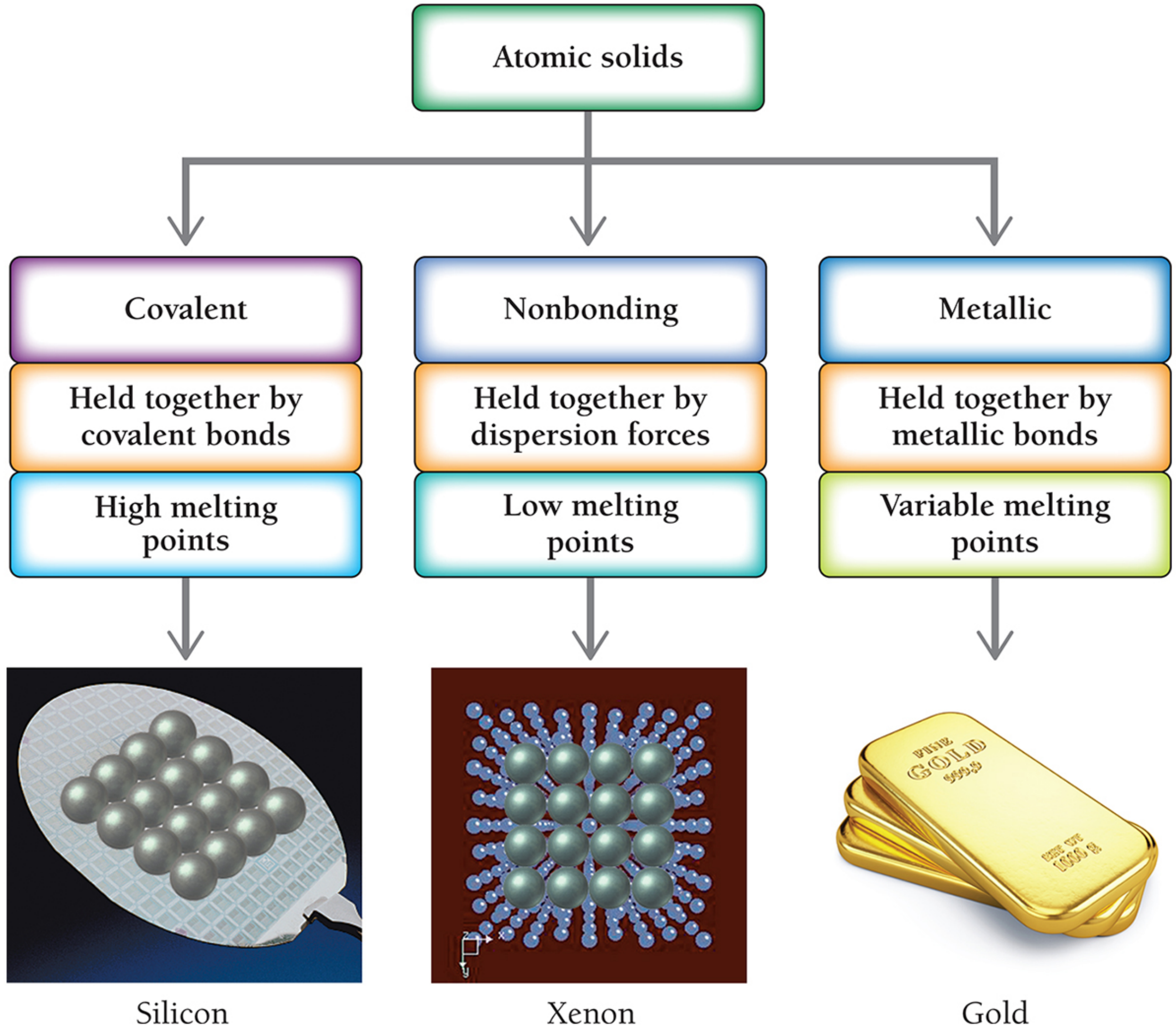


Ionic Solids

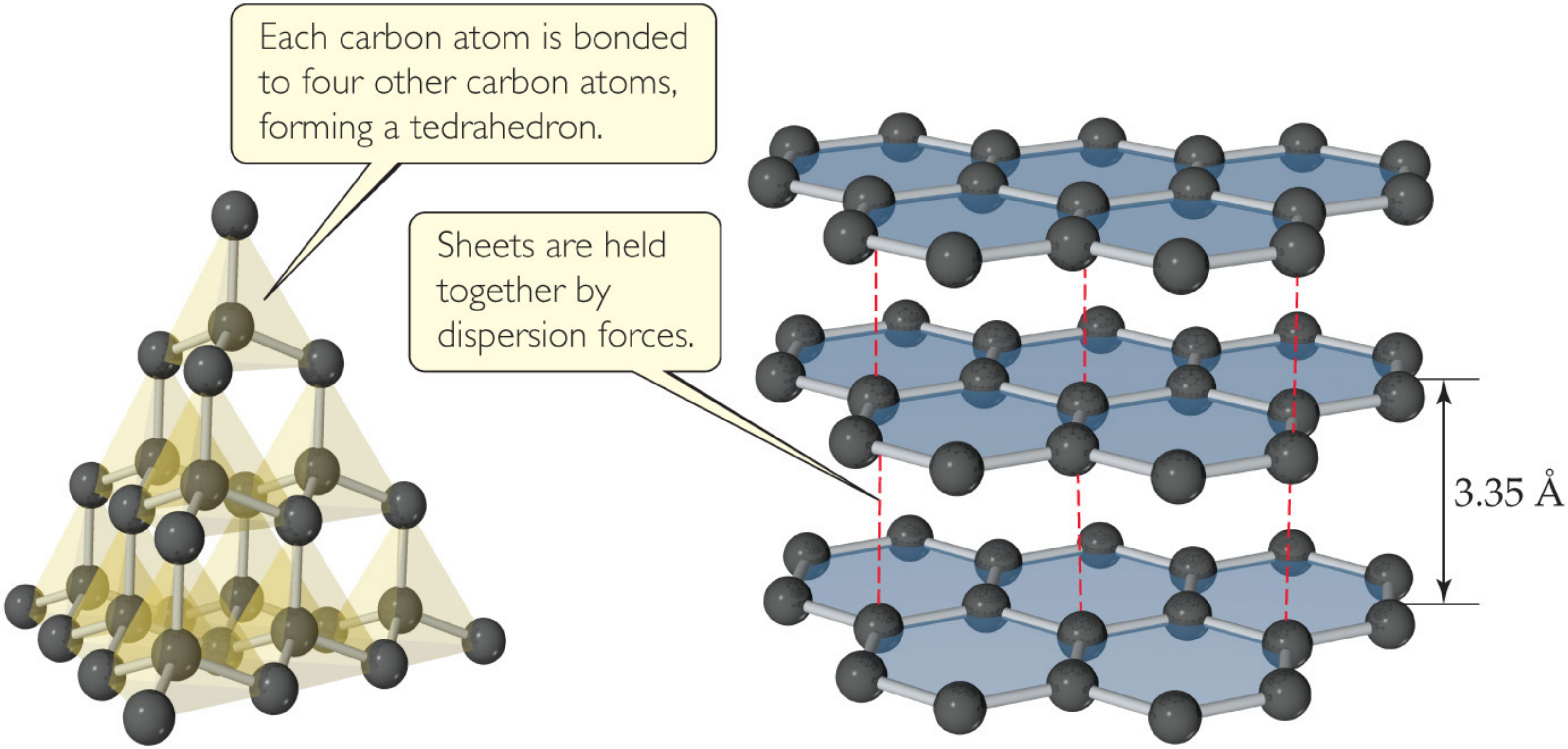


NaCl

Atomic Solids



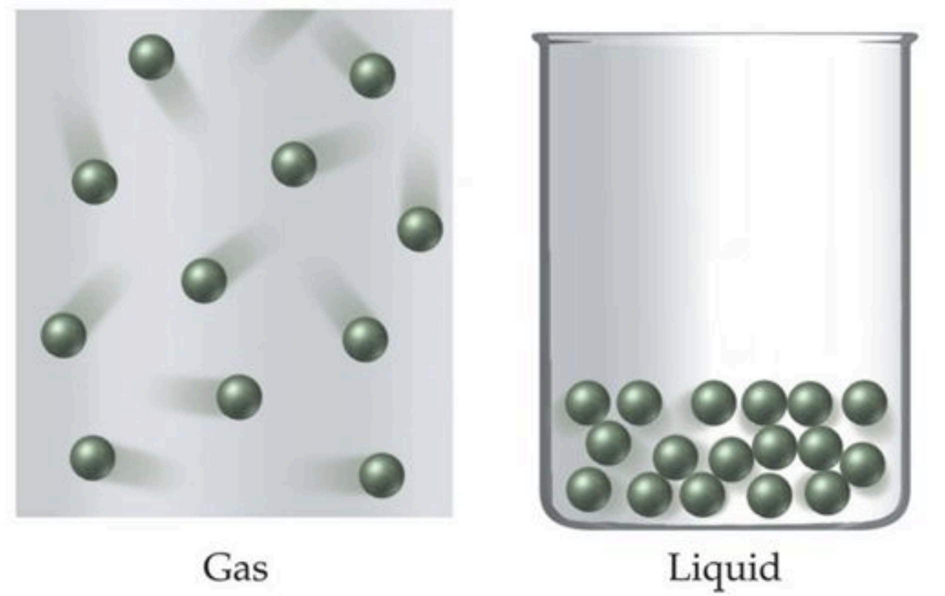
Covalent Atomic Solids



(a) Diamond (b) Graphite

Carbon

Nonbonding Atomic Solids

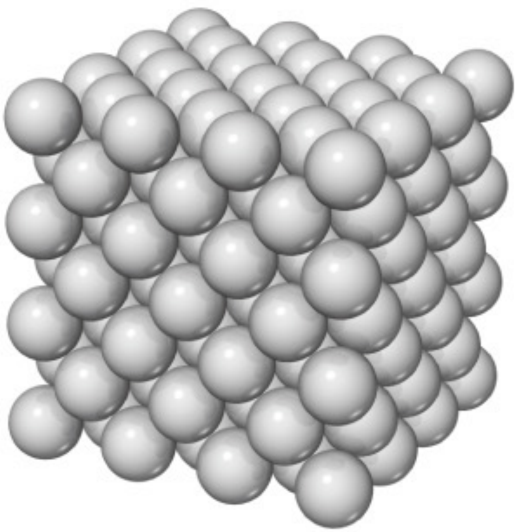


Ne at room temp

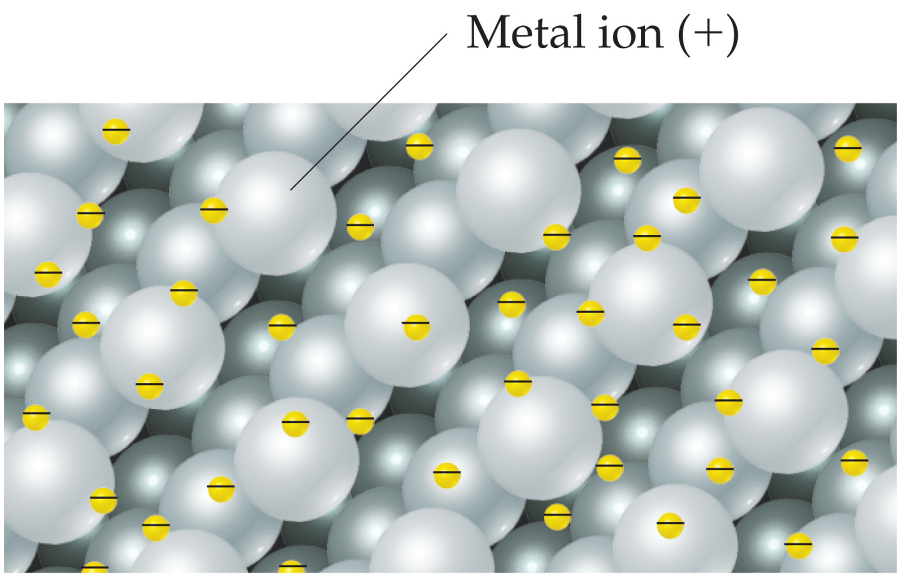
Ne below 27 K

Metallic Atomic Solids

Group 3A



Al
12 nearest neighbors



Electron Sea Model for Al

Ex Probs