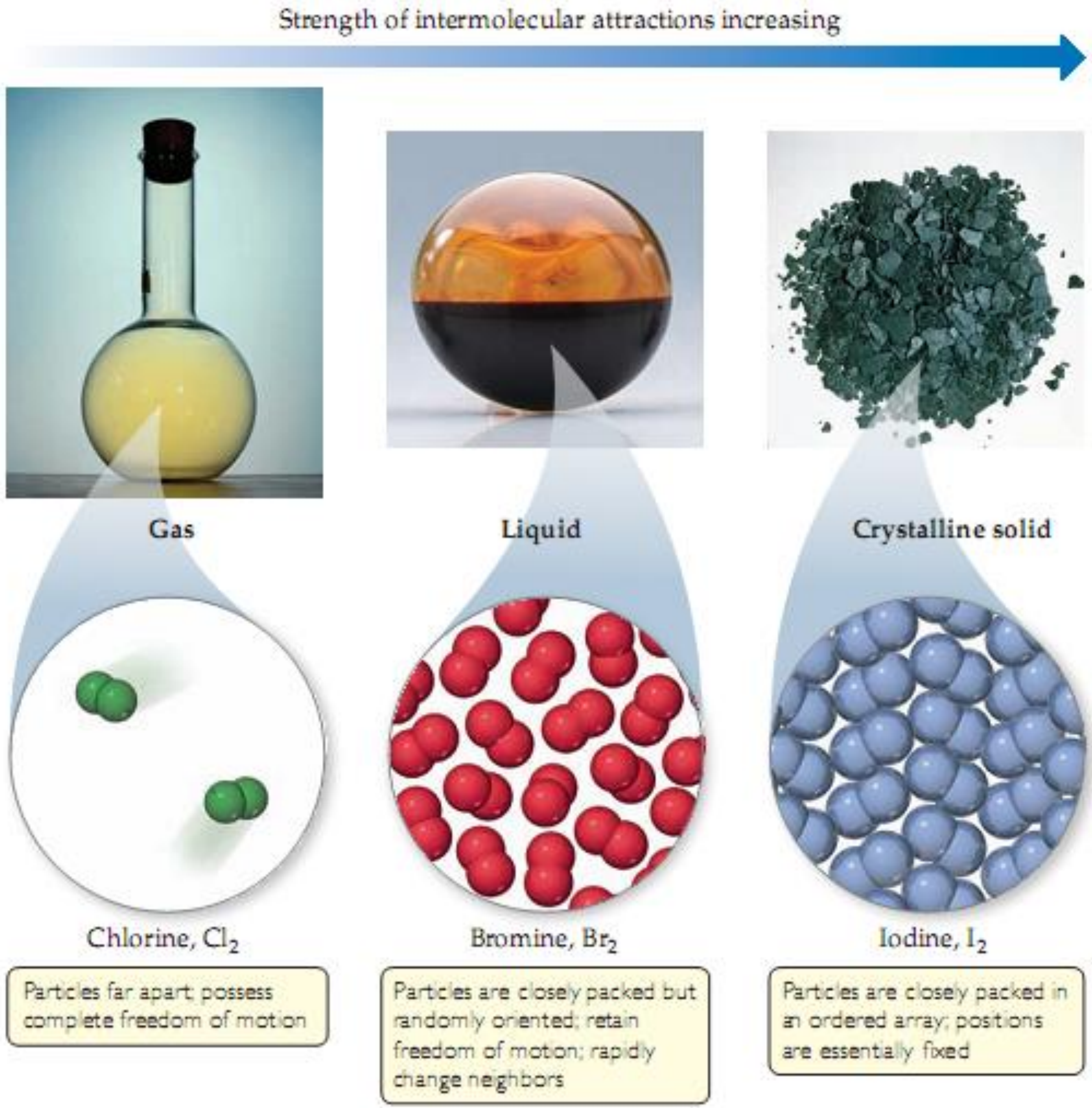
GENERAL CHEMISTRY

Chapter 11
Liquids and Intermolecular Forces

Contents

10-1 A Molecular Comparison of Gases, Liquids, and Solids

Gas	**Liquid**	**Solid**
Assumes the **shape** and **volume** of its container	Assumes the **shape** of the portion of its container it occupies, but not the **volume**	Maintains a fixed **shape** and **volume**
Highly compressible	**Not really** compressible	**Not** compressible
Viscosity **Low** viscous	Viscosity **Moderate** viscous	Viscosity **High** viscous



Strength of intermolecular attractions increasing
Gas
Liquid
Crystalline solid
Chlorine, Cl_2
Bromine, Br_2
Iodine, I_2
Particles far apart; possess complete freedom of motion
Particles are closely packed but randomly oriented; retain freedom of motion; rapidly change neighbors
Particles are closely packed in an ordered array; positions are essentially fixed

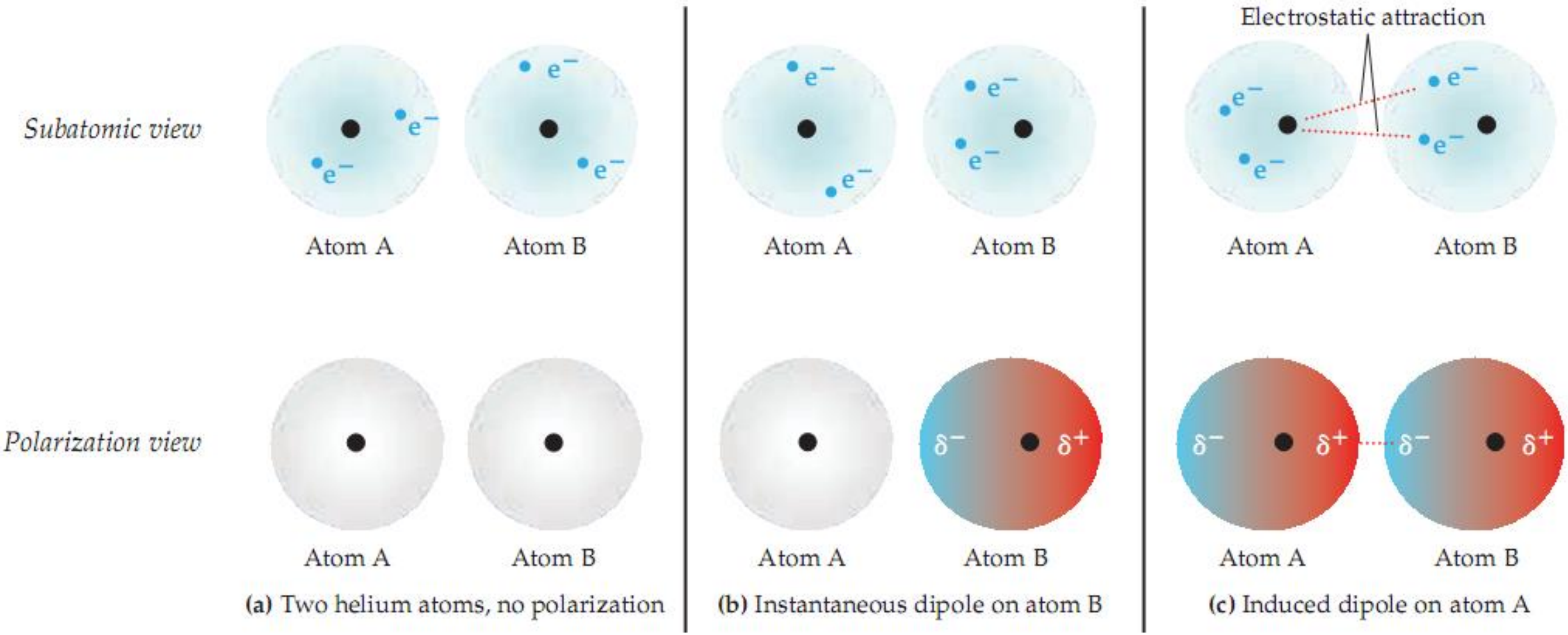
11-2 Intermolecular Forces

TABLE 11.2 Melting and Boiling Points of Representative Substances

Force Holding Particles Together	Substance	Melting Point (K)	Boiling Point (K)
Chemical bonds			
Ionic bonds	Lithium fluoride (LiF)	1118	1949
Metallic bonds	Beryllium (Be)	1560	2742
Covalent bonds	Diamond (C)	3800	4300
Intermolecular forces			
Dispersion forces	Nitrogen (N_2)	63	77
Dipole–dipole interactions	Hydrogen chloride (HCl)	158	188
Hydrogen bonding	Hydrogen fluoride (HF)	190	293

van der Waals forces

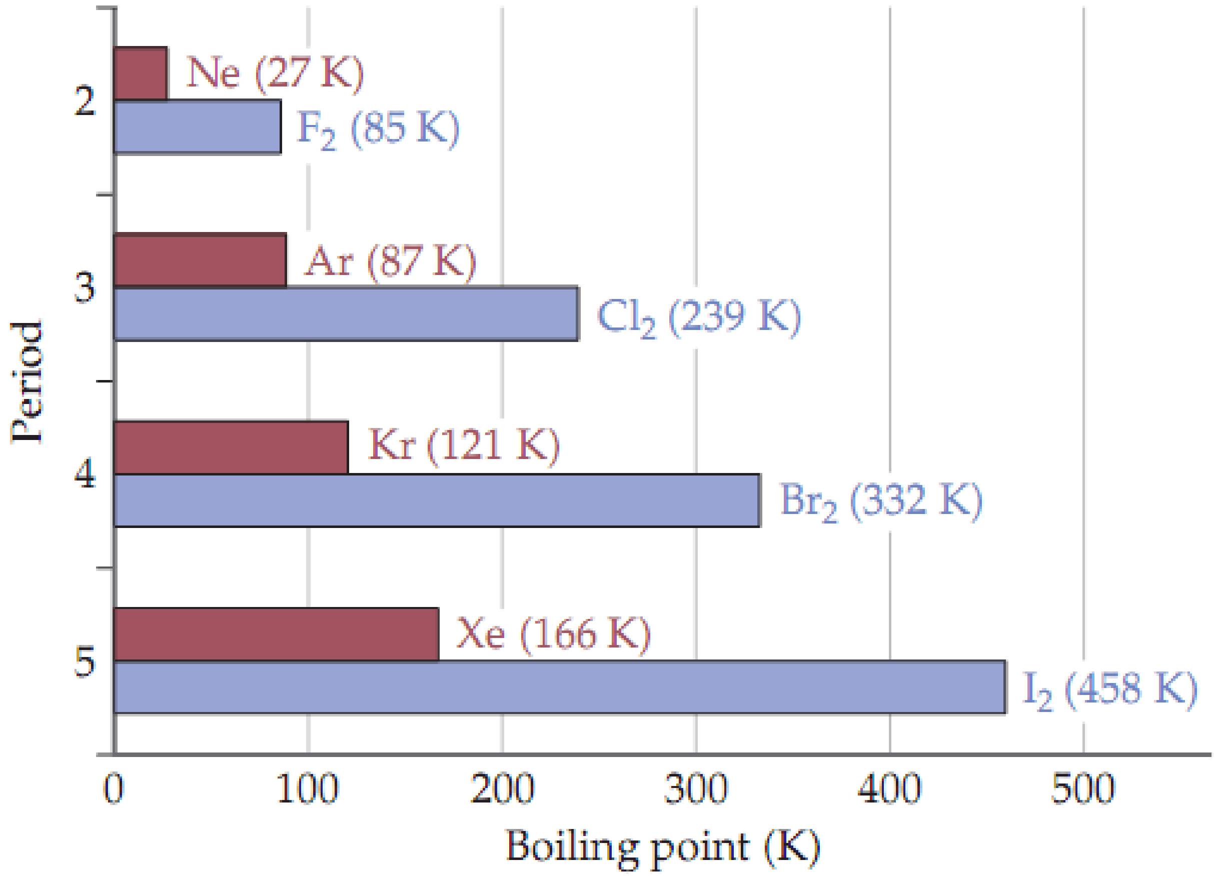
Dispersion Forces



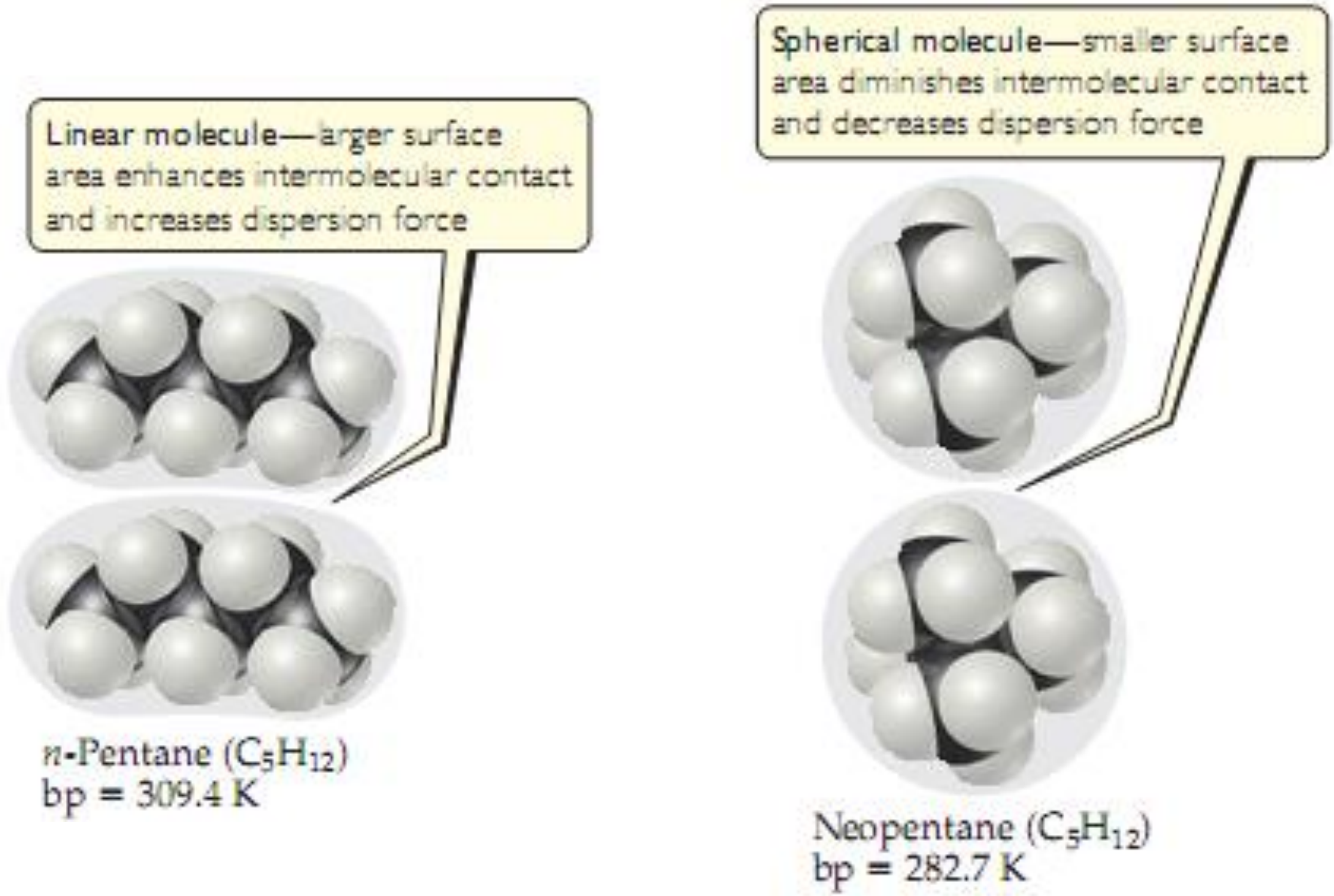
(a) Two helium atoms, no polarization (b) Instantaneous dipole on atom B (c) Induced dipole on atom A

London dispersion forces or induced dipole–induced dipole interactions

Dispersion forces tend to increase in strength with increasing molecular weight.

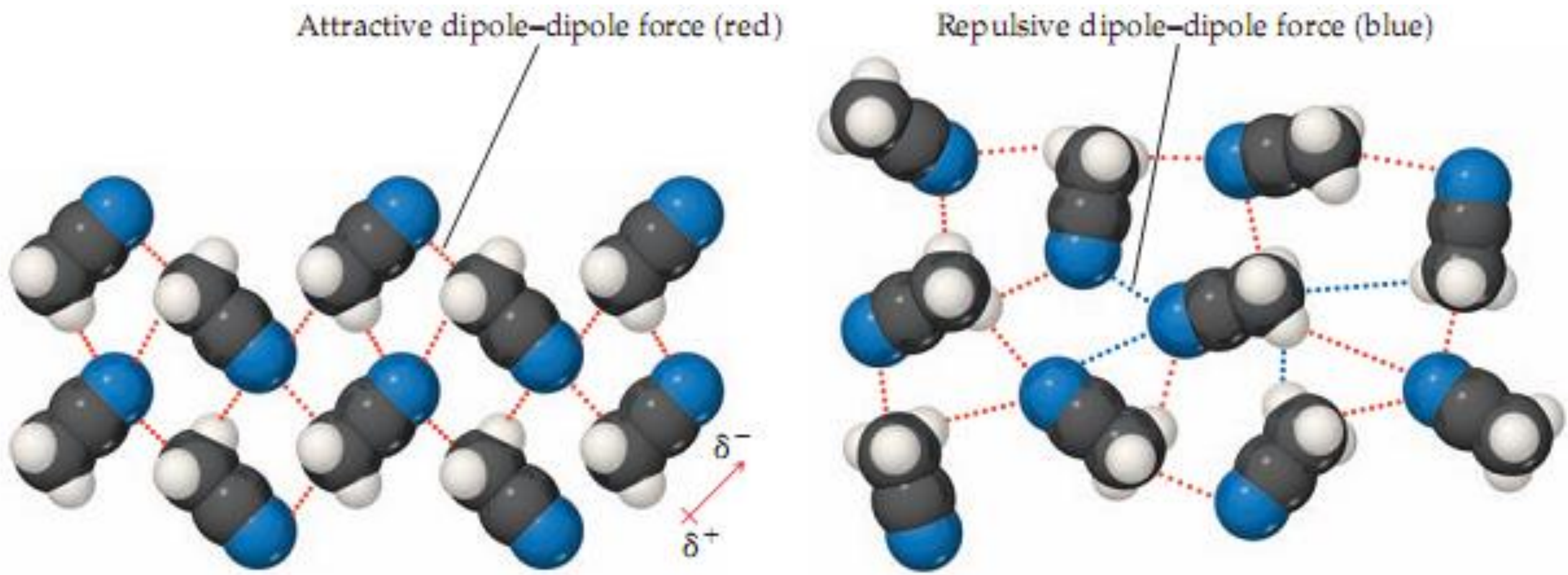


Molecular shape affects intermolecular attraction



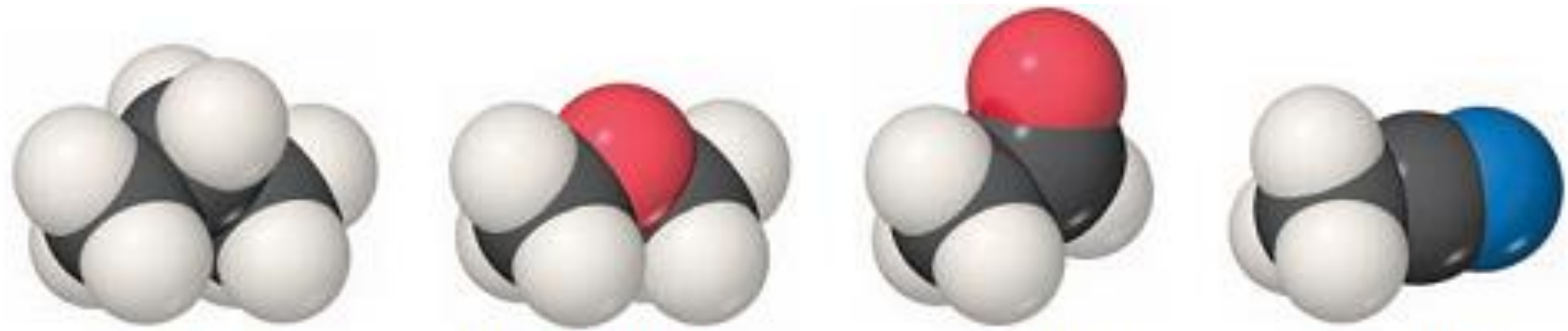
Dipole–Dipole Interactions

- dipole–dipole interactions originate from electrostatic attractions between the partially positive end of one molecule and the partially negative end of a neighboring molecule.



(a) Solid CH_3CN (b) Liquid CH_3CN

Moving from left to right, do the dispersion forces get stronger, get weaker, or stay roughly the same in the molecules shown here?



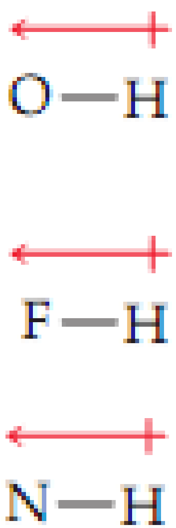
Propane	Dimethyl ether	Acetaldehyde	Acetonitrile
$CH_3CH_2CH_3$	CH_3OCH_3	CH_3CHO	CH_3CN
MW = 44 amu	MW = 46 amu	MW = 44 amu	MW = 41 amu
$\mu = 0.1$ D	$\mu = 1.3$ D	$\mu = 2.7$ D	$\mu = 3.9$ D
bp = 231 K	bp = 248 K	bp = 294 K	bp = 355 K

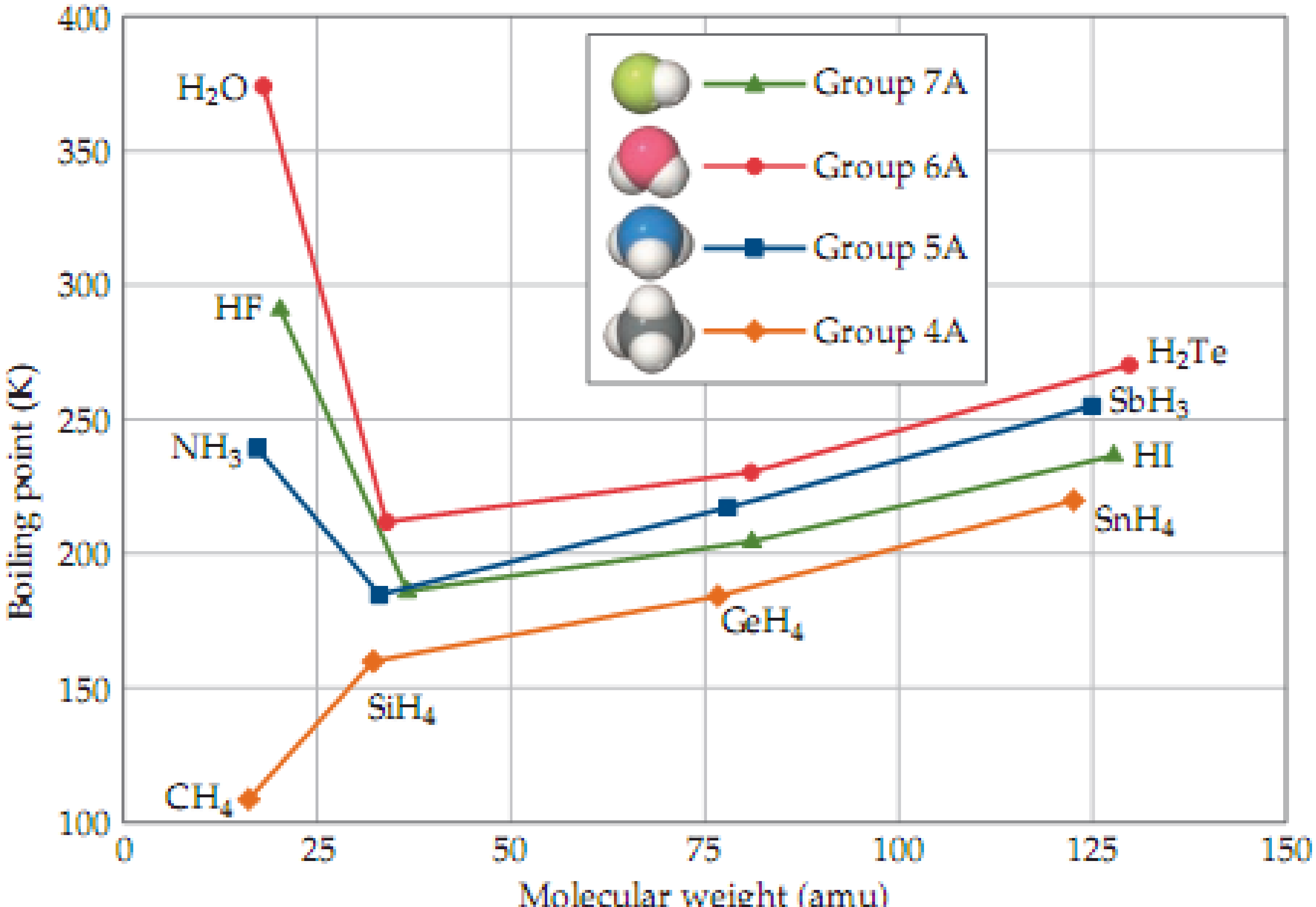
For molecules of approximately equal mass and size, the strength of intermolecular attractions increases with increasing polarity

Increasing polarity
Increasing strength of dipole–dipole forces

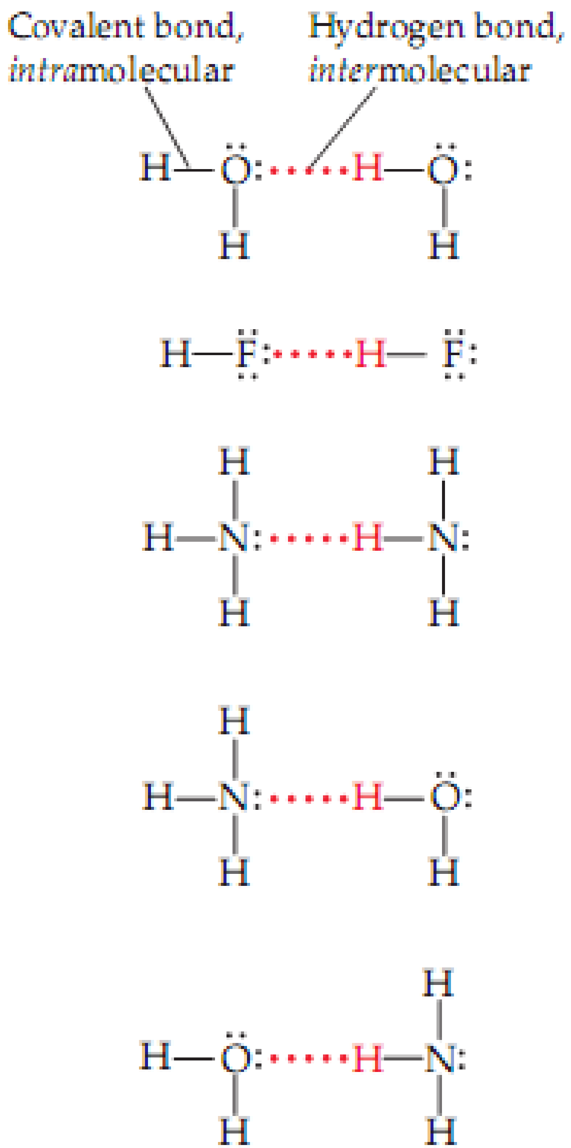
Hydrogen Bonding

A hydrogen bond is an attraction between a hydrogen atom attached to a highly electronegative atom (usually F, O, or N) and a nearby small electronegative atom in another molecule or chemical group





Covalent Bonds vs Hydrogen Bonds



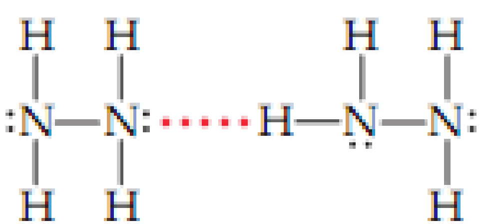
EXAMPLE

In which of these substances is hydrogen bonding likely to play an important role in determining physical properties: methane ($\cancel{CH_4}$), hydrazine (H_2NNH_2), methyl fluoride ($\cancel{CH_3F}$), hydrogen sulfide ($\cancel{H_2S}$)

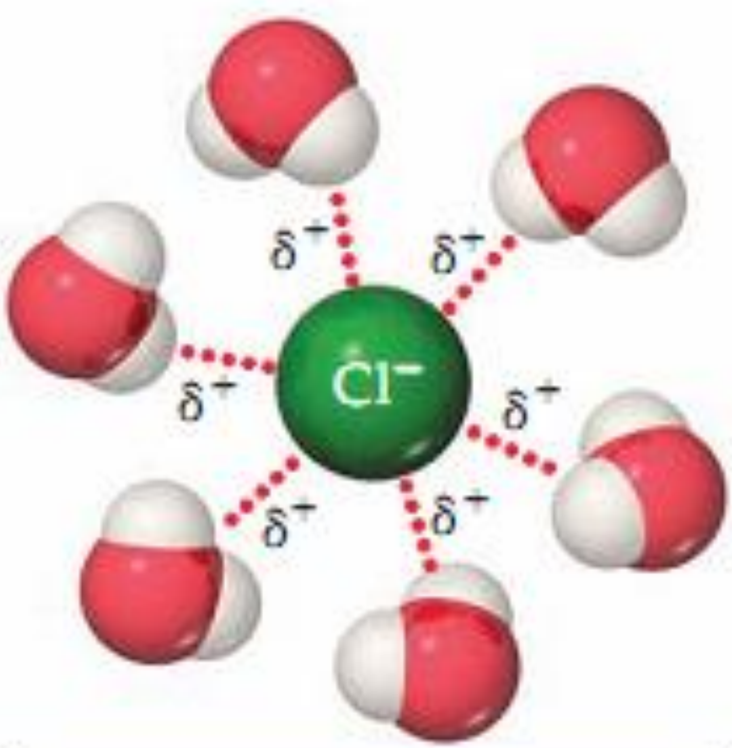
CH_4 and H_2S do not contain H bonded to N, O, or F
➔ Eliminate CH_4 and H_2S

CH_3F contain C – H and C – F bonds, not H – F bond
➔ Eliminate CH_3F

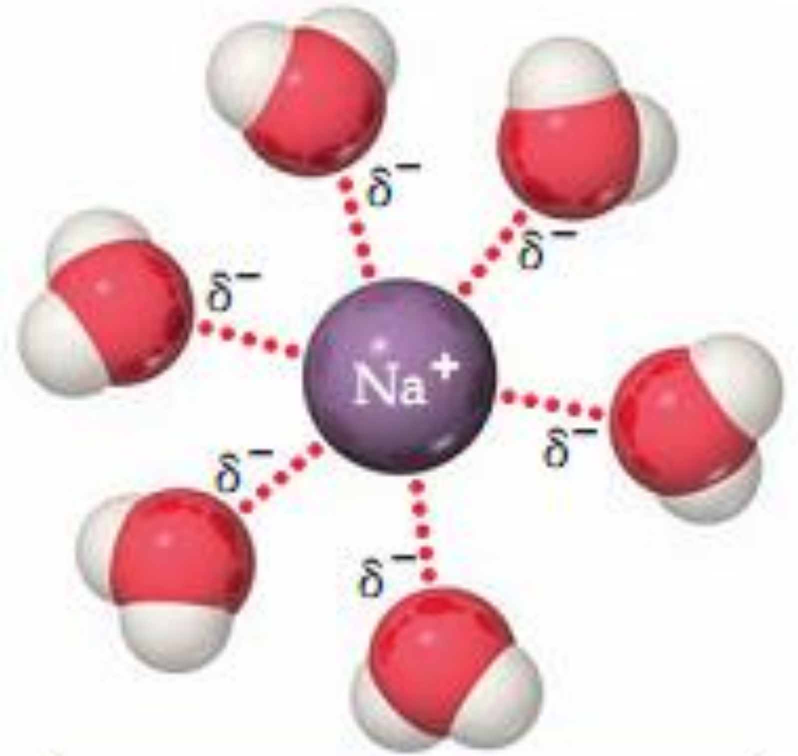
H_2NNH_2 contain N – H bond, and each N has a lone pair



Ion–Dipole Forces



Positive ends of polar molecules are oriented toward negatively charged anion

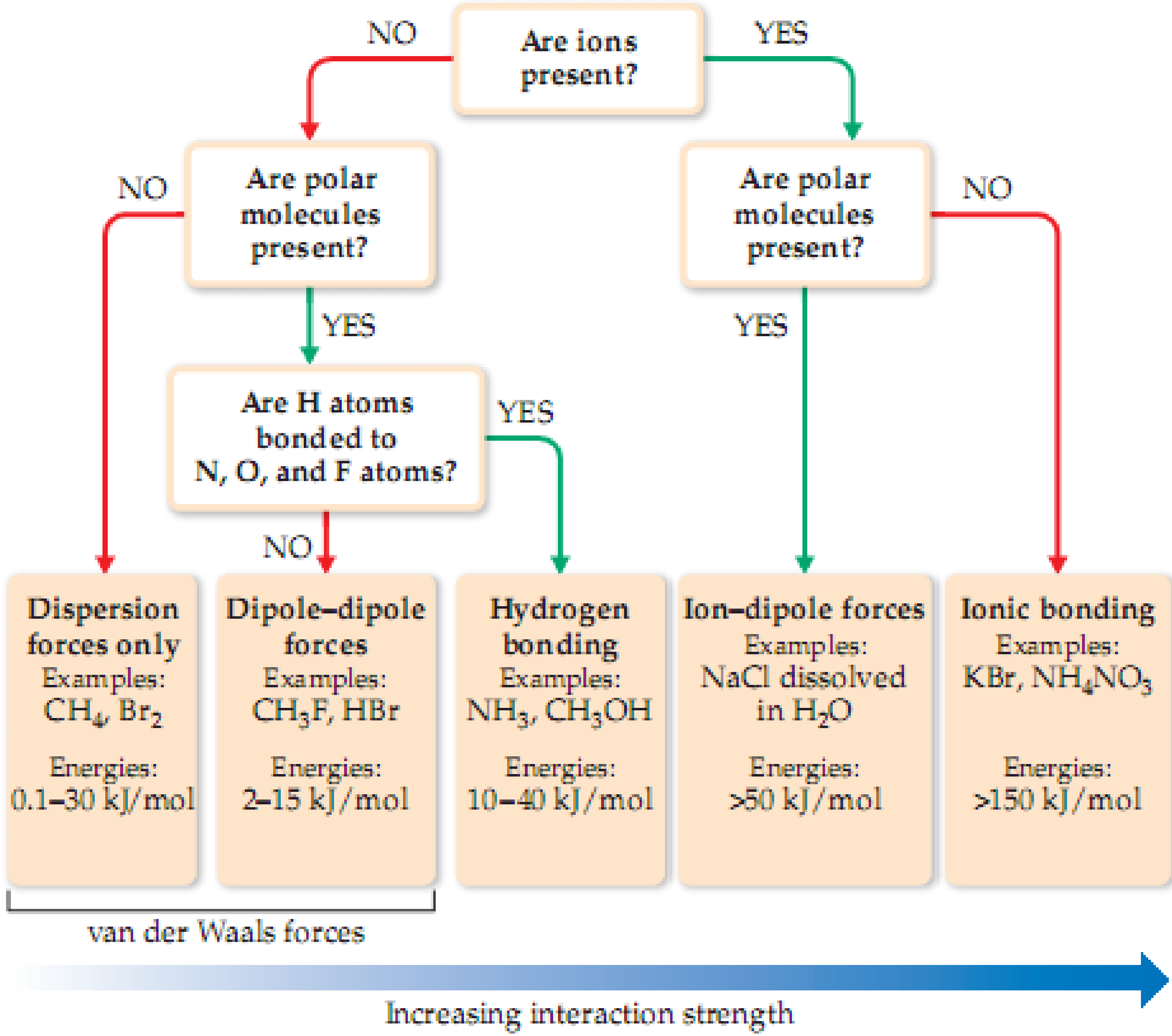


Negative ends of polar molecules are oriented toward positively charged cation

Comparing Intermolecular Forces

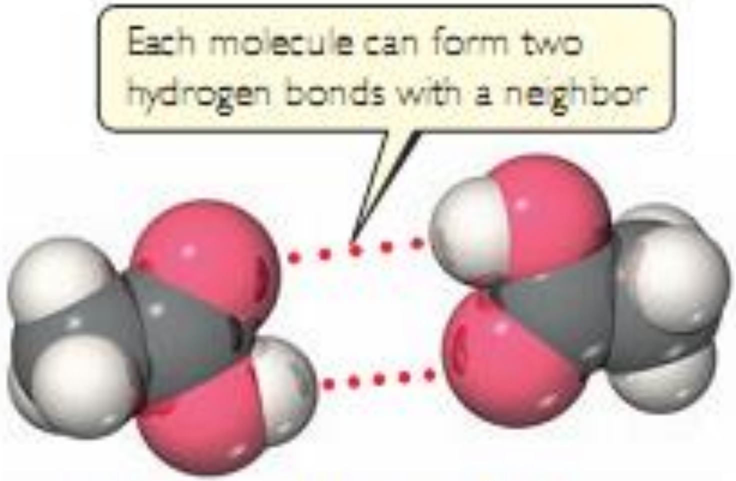
1. When the molecules of two substances have comparable molecular weights and shapes, dispersion forces are approximately equal in the two substances.
2. When the molecules of two substances differ widely inmolecular weights, and there is no hydrogen bonding, dispersion forces tend to determine which substance has the stronger intermolecular attractions.

Flowchart for determining intermolecular forces

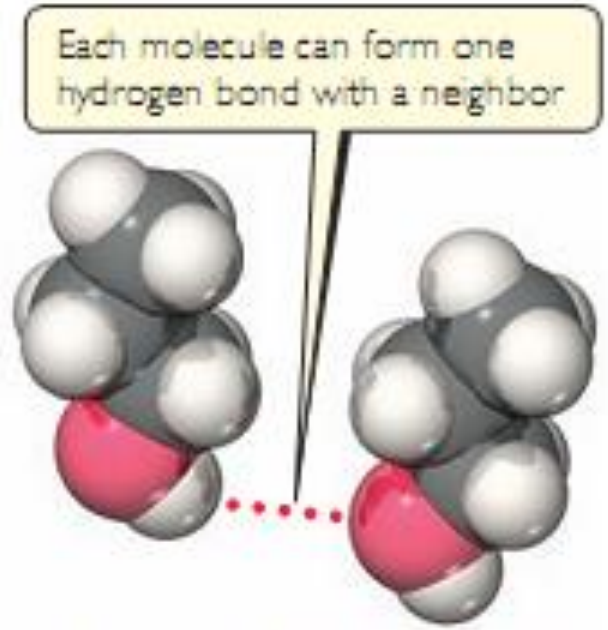


Comparing Intermolecular Forces

The greater the number of hydrogen bonds possible, the more tightly the molecules are held together and, therefore, the higher the boiling point



Acetic acid, CH_3COOH
MW = 60 amu
bp = 391 K



1-Propanol, $CH_3CH_2CH_2OH$
MW = 60 amu
bp = 370 K

EXAMPLE

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

H_2 < Ne < CO < HF < $BaCl_2$

- The attractive forces are stronger for ionic substances than for molecular ones ➔ $BaCl_2$ should have the highest boiling point

- The intermolecular forces of the remaining substances depend on
- molecular weight, H_2: 2; CO: 28; HF: 20; and Ne: 20
- polarity, H_2, Ne: non polar ; CO: slightly polar, HF: polar
- hydrogen bonding HF can hydrogen bond: polar

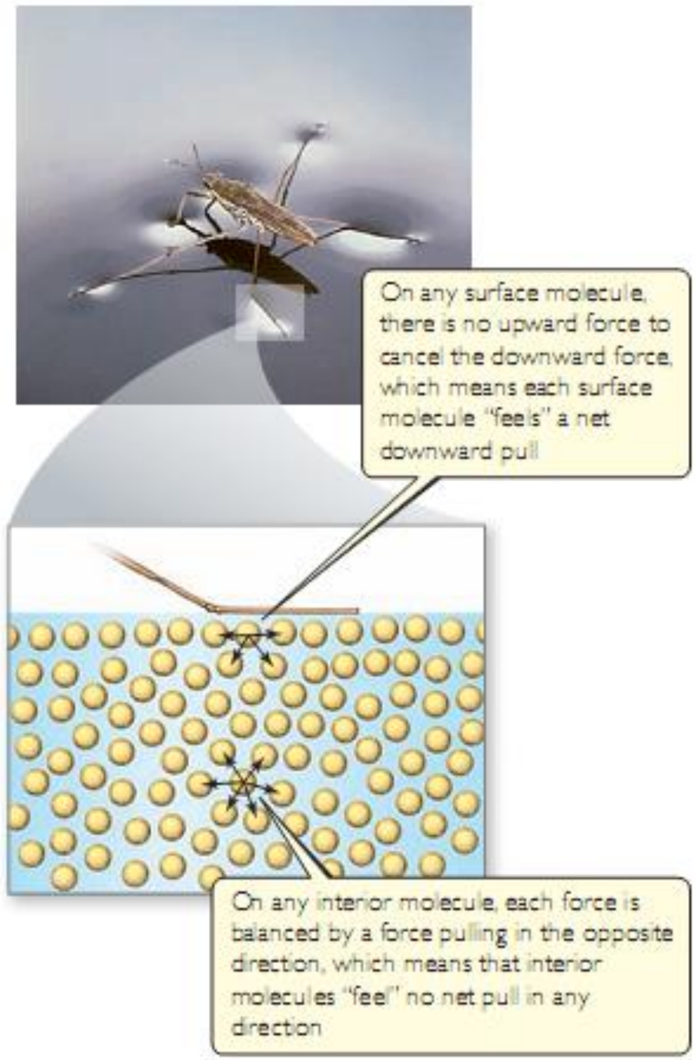
11-3 Select Properties of Liquids

Viscosity

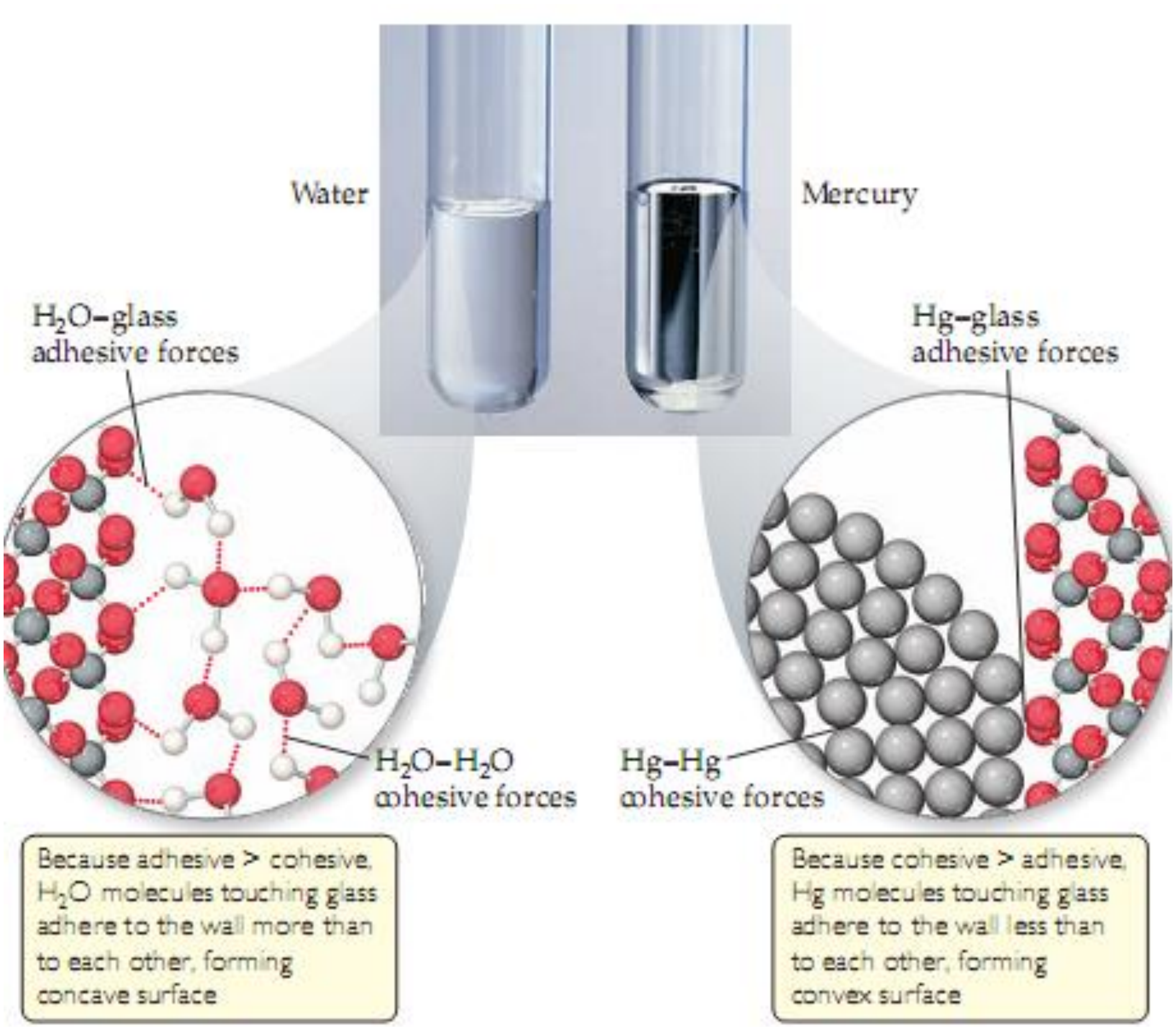
SAE 40
higher number
higher viscosity
slower pouring

SAE 10
lower number
lower viscosity
faster pouring

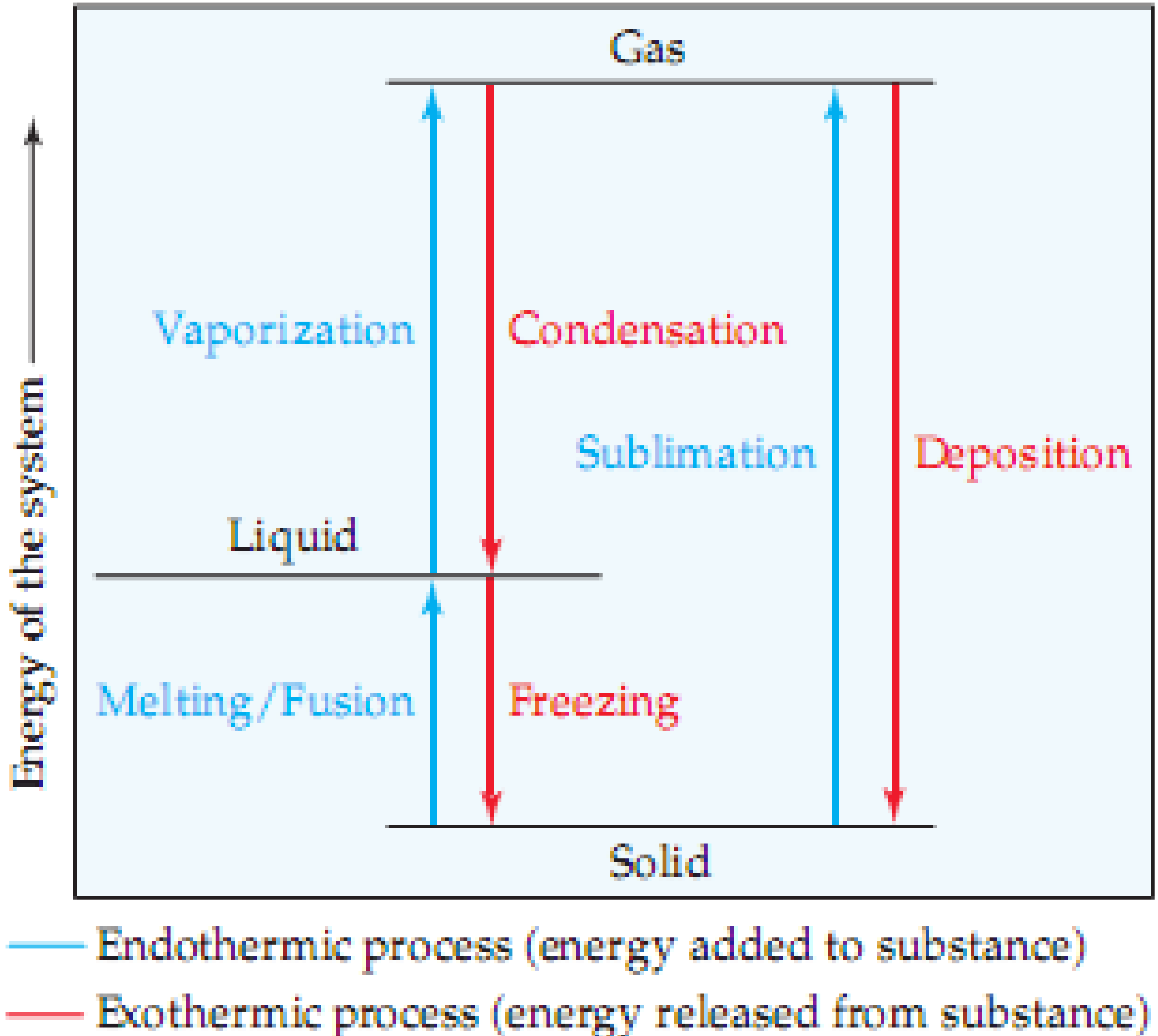
Surface Tension



Capillary Action



11-4 Phase Changes



Energy Changes Accompanying Phase Changes

- Melting
  - **heat of fusion** or *enthalpy of fusion*, ΔH_{fus}

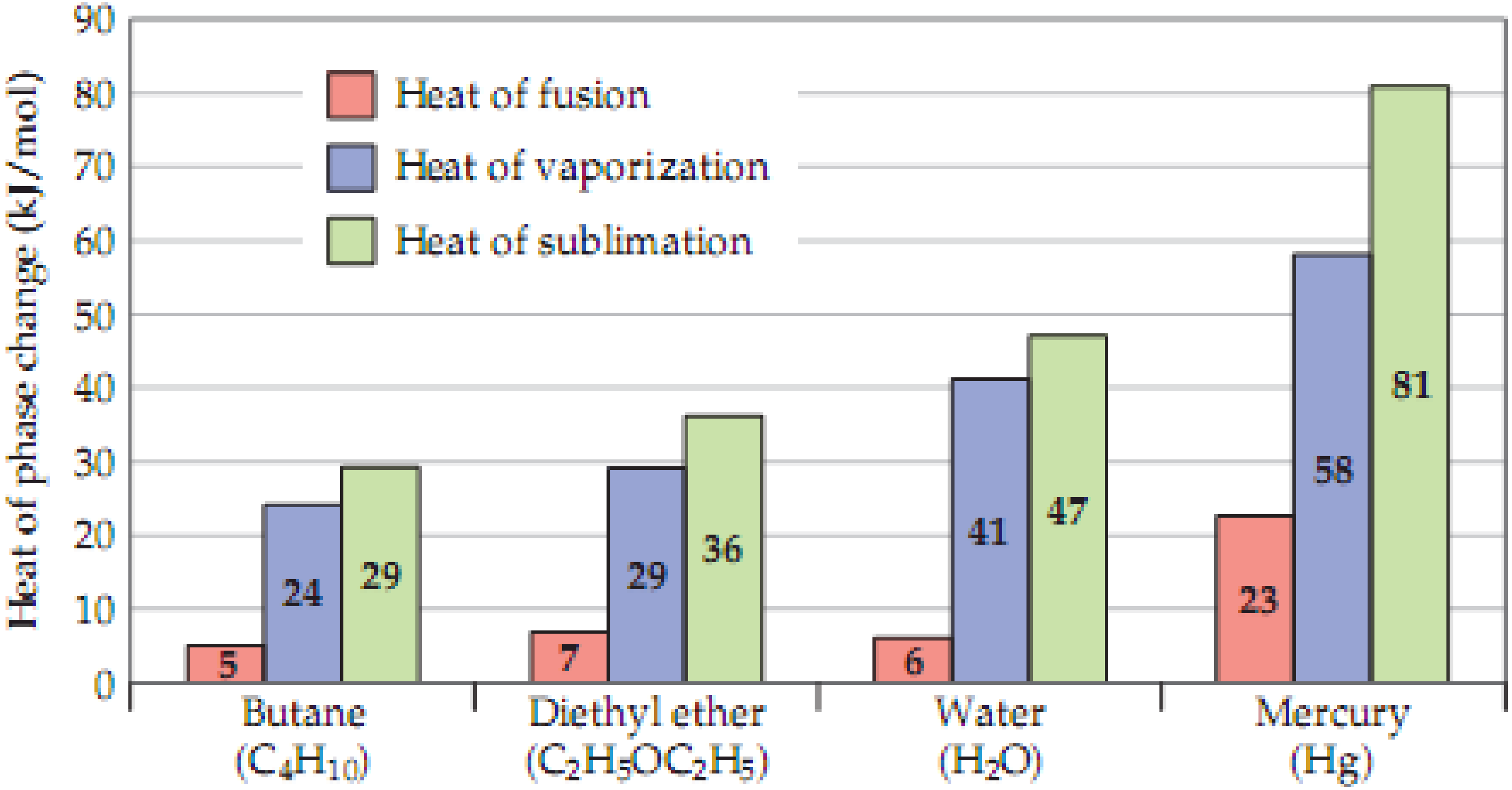
$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = 6.01 \text{ kJ}$$

- Vaporization
  - **heat of vaporization or** *enthalpy of vaporization*, ΔH_{vap}

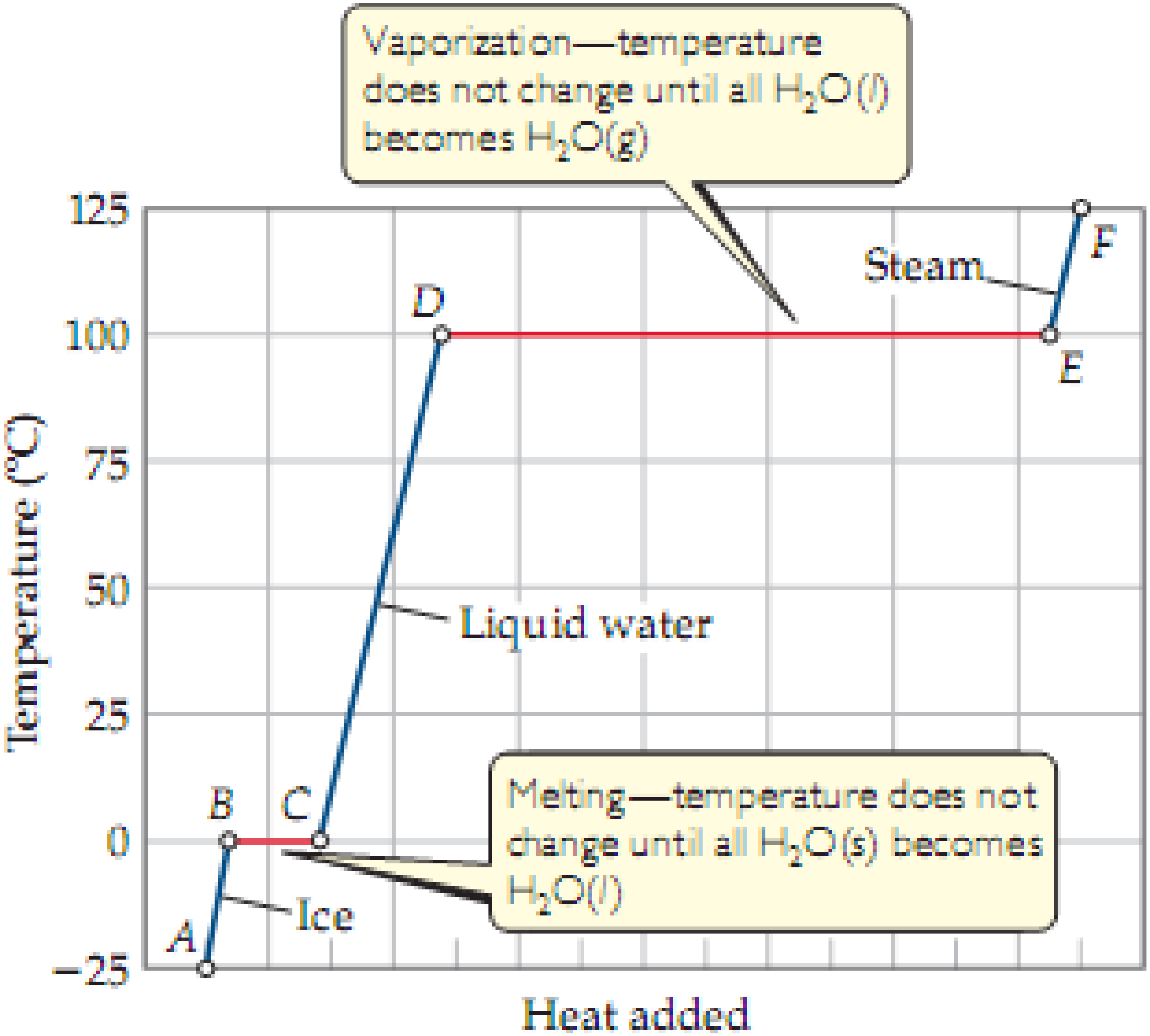
$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H = 40.7 \text{ kJ}$$

- Sublimation
  - **heat of sublimation**, ΔH_{sub}

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$


Heat of phase change (kJ/mol)
90
80
70
60
50
40
30
20
10
0
Heat of fusion
Heat of vaporization
Heat of sublimation
5
24
29
7
29
36
6
41
47
23
58
81
Butane
(C_4H_{10})
Diethyl ether
($C_2H_5OC_2H_5$)
Water
(H_2O)
Mercury
(Hg)

Heating Curves



Critical Temperature and Pressure

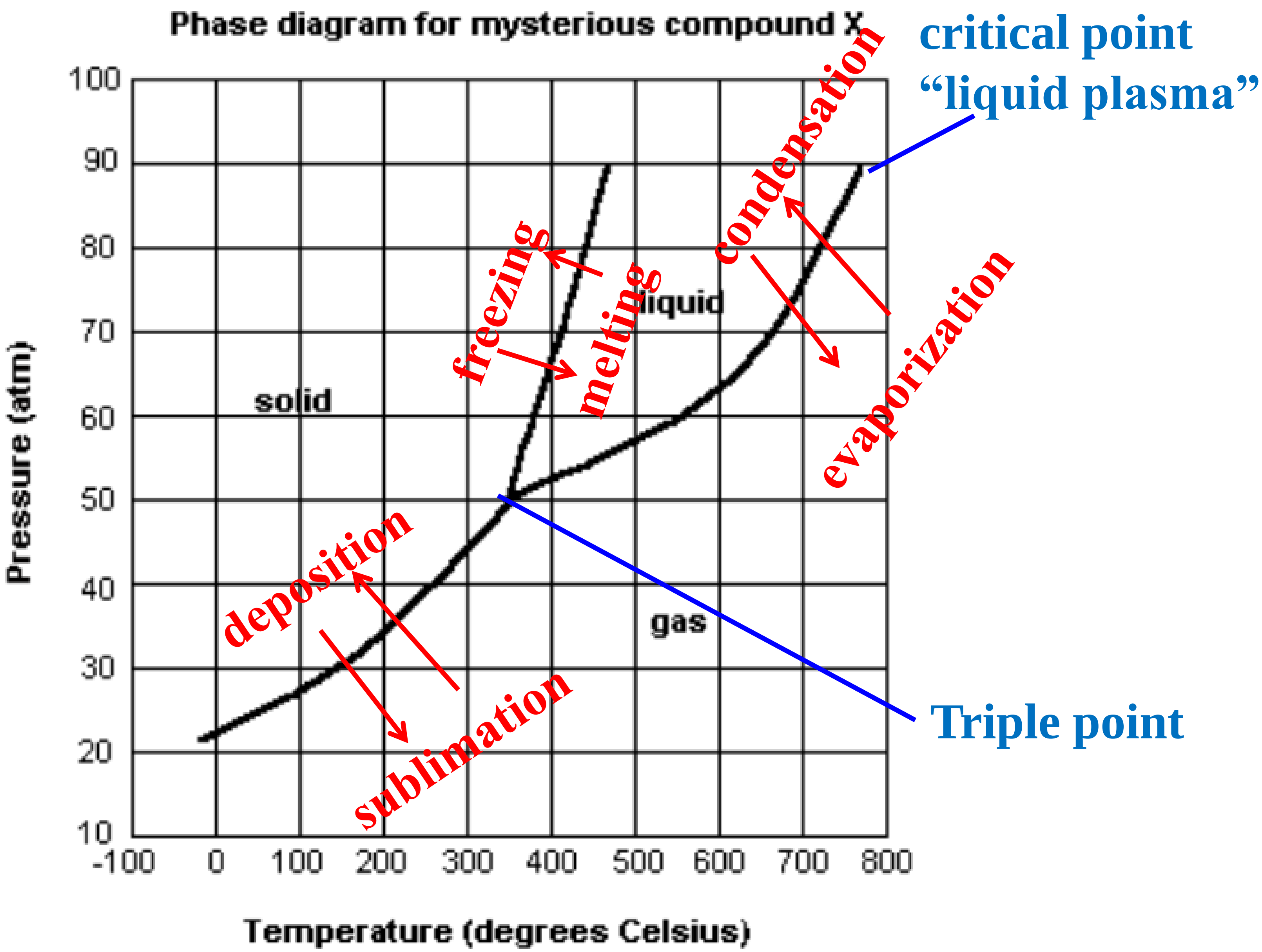
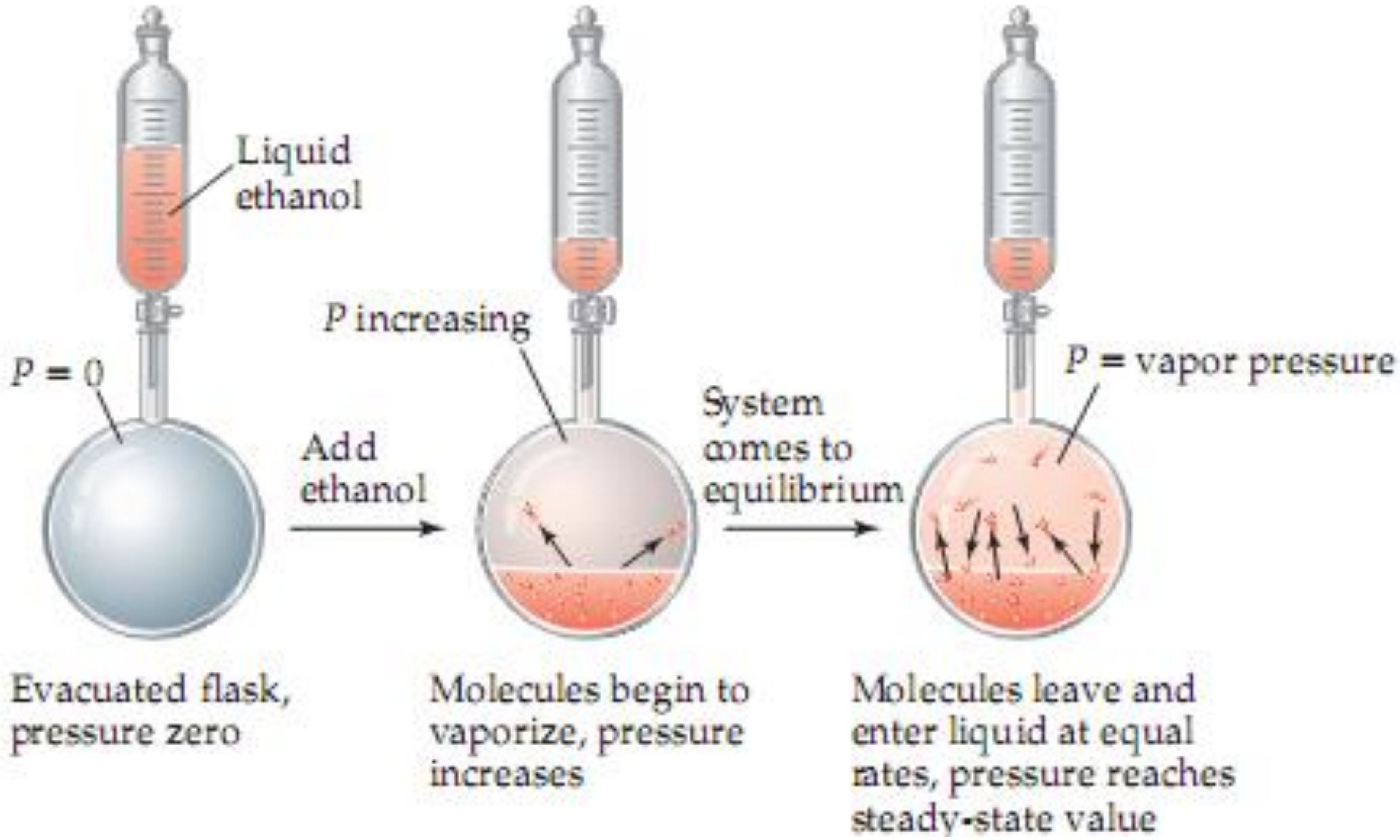


Table 11.6 Critical Temperatures and Pressures of Selected Substances

Substance	Critical Temperature (K)	Critical Pressure (atm)
Nitrogen, N_2	126.1	33.5
Argon, Ar	150.9	48.0
Oxygen, O_2	154.4	49.7
Methane, CH_4	190.0	45.4
Carbon dioxide, CO_2	304.3	73.0
Phosphine, PH_3	324.4	64.5
Propane, $CH_3CH_2CH_3$	370.0	42.0
Hydrogen sulfide, H_2S	373.5	88.9
Ammonia, NH_3	405.6	111.5
Water, H_2O	647.6	217.7

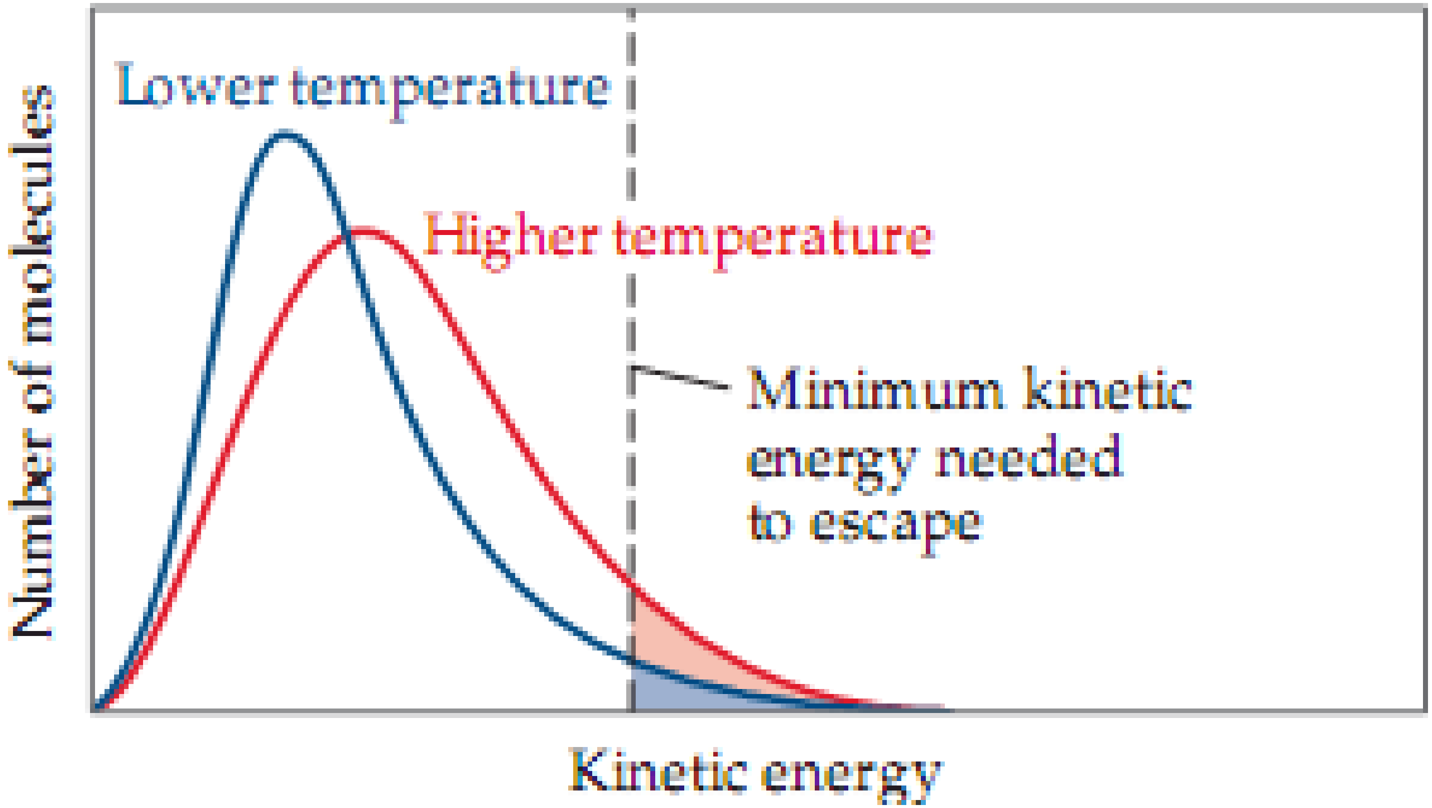
The greater the intermolecular forces, the higher the critical temperature of a substance

11-5 Vapor Pressure



The vapor pressure of a liquid is the pressure exerted by its vapor when the liquid and vapor are in dynamic equilibrium

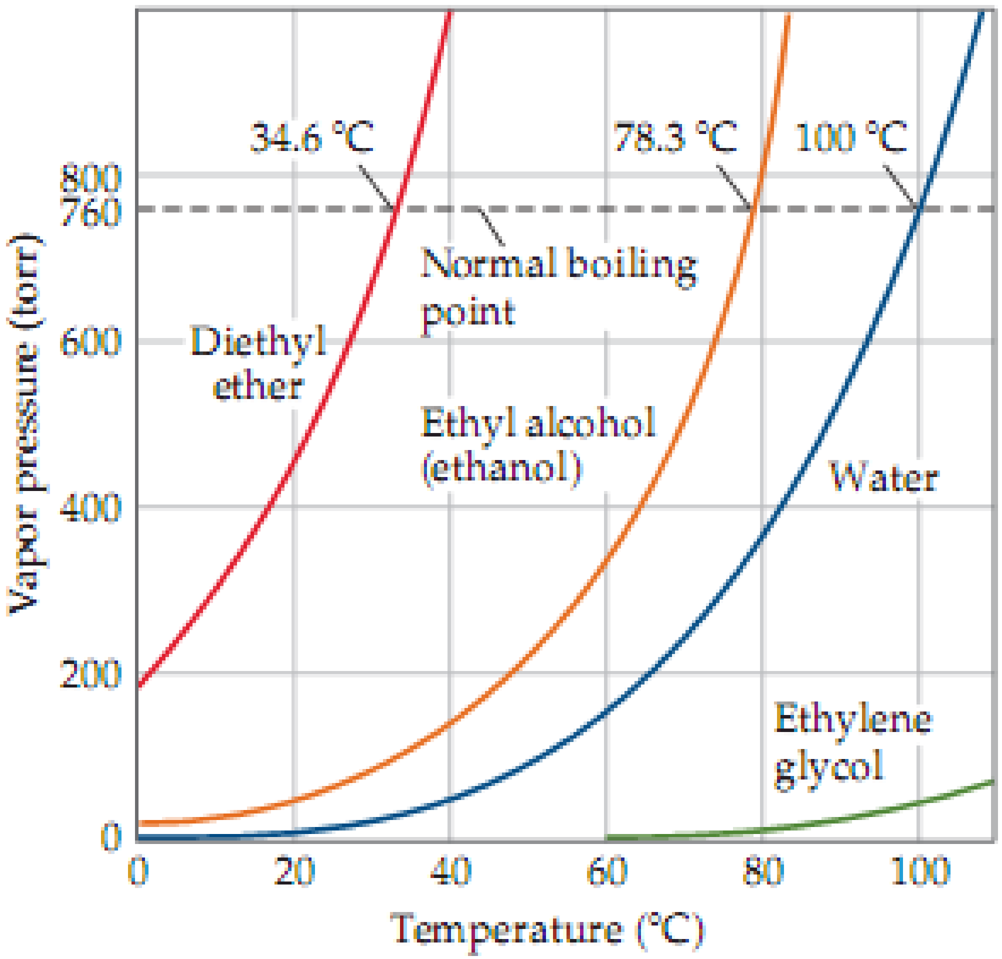
Volatility, Vapor Pressure, and Temperature



Blue area = number of molecules having enough energy to evaporate at lower temperature

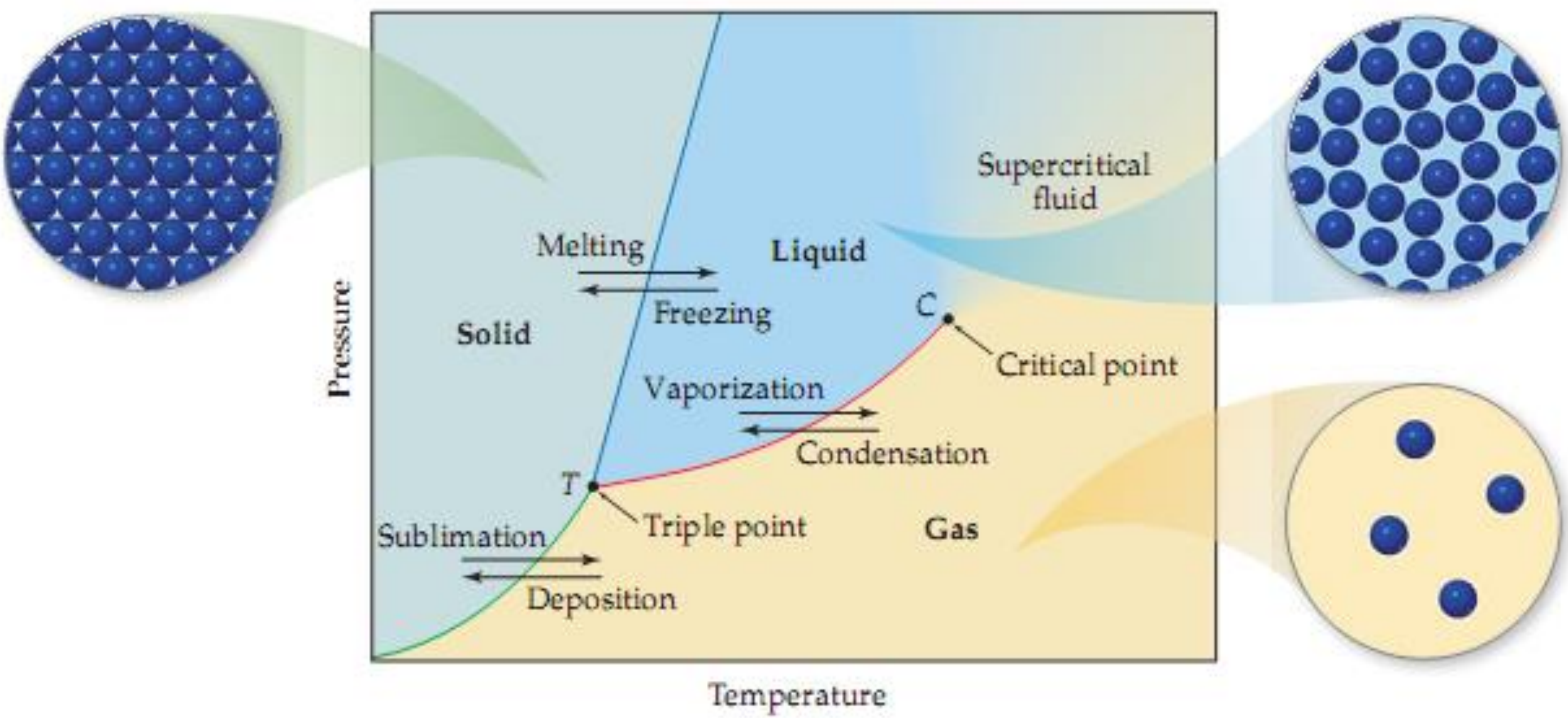
Red + blue areas = number of molecules having enough energy to evaporate at higher temperature

Vapor Pressure and Boiling Point



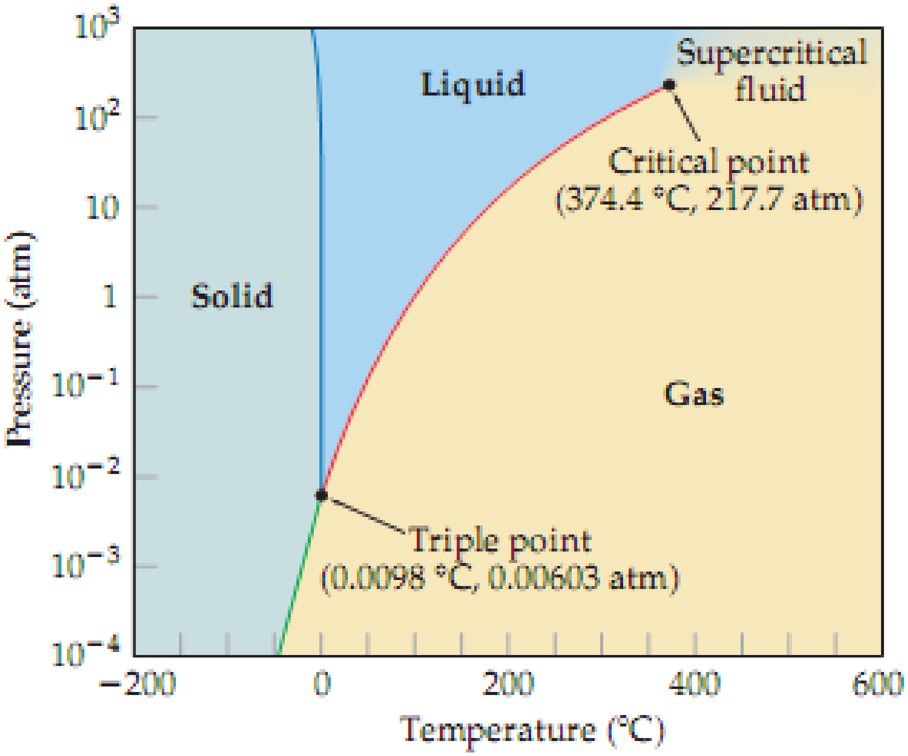
The boiling point of a liquid at 1 atm (760 torr) pressure is called its **normal boiling point**

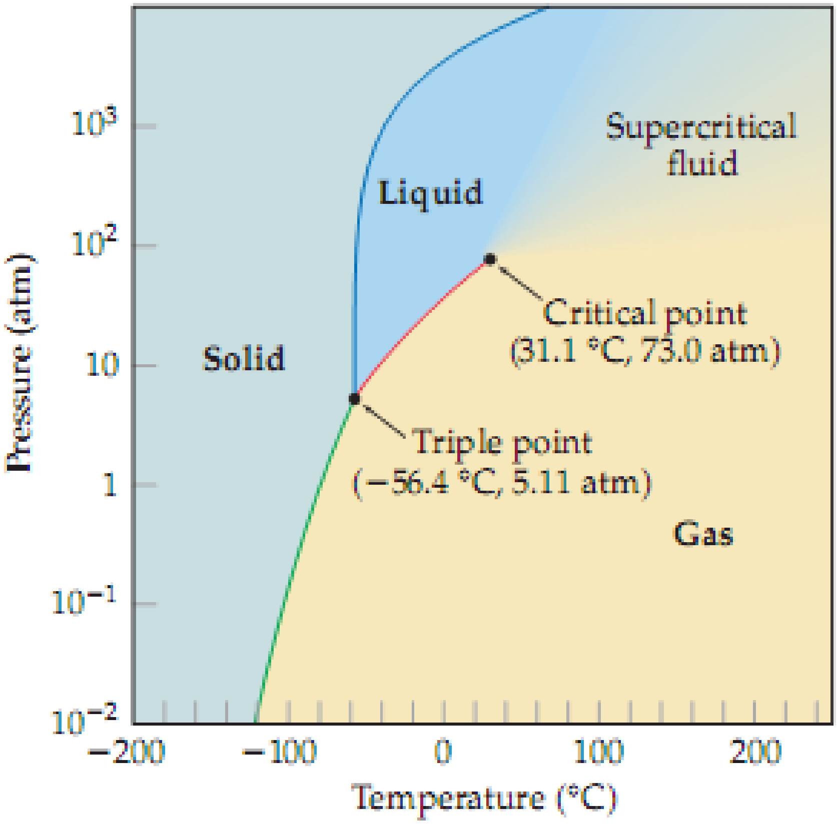
11-6 Phase Diagram



The red curve is the vapor-pressure curve
The green curve is the sublimation curve
The blue curve is the melting curve

The Phase Diagrams of H_2O and CO_2





Phase diagram of H_2O

Phase diagram of CO_2.

Homeworks

11.92

11.96

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