

Ideal gas

$$PV = nRT$$

Real gas

Intermolecular force (attraction vs Repulsion) modifies the collision rate.

► Van der Waals equation:

$$\left(P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

attraction repulsion

► Lennard-Jones Potential:

$$V_{LJ}(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

repulsive attractive

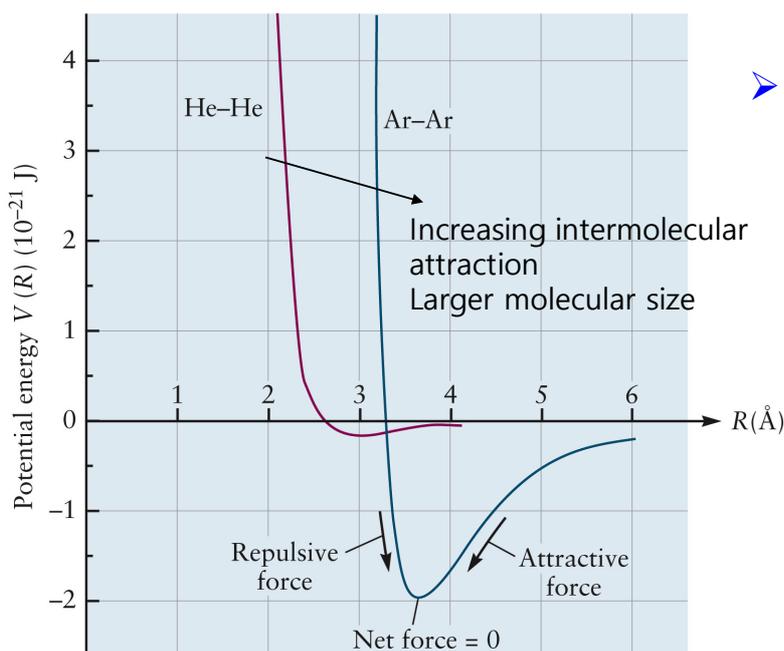
► **Compression (or Compressibility) factor, Z**

$$Z = \frac{V_m}{V_m^{\text{ideal}}} = \frac{V_m}{RT/P} = \frac{PV_m}{RT}$$

- For an ideal gas, $Z = 1$.
- Real gases, deviation from $Z = 1$ as $P \uparrow$.
 $Z < 1$ for attractive force
 $Z > 1$ for repulsion

◆ Intermolecular Forces → potential energy curve

Where are the **depth** and **location** of the potential minimum?



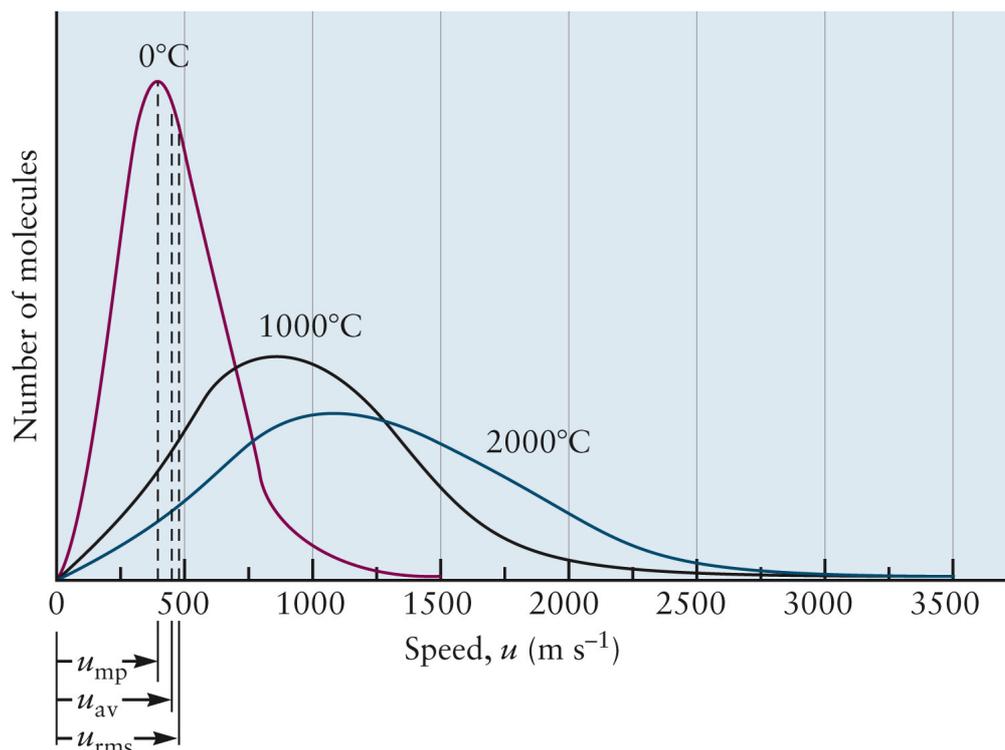
► Lennard-Jones Potential:

$$V_{LJ}(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

repulsive attractive

ϵ : depth (→ potential energy)
 σ : the distance at which $V(R)$ passes through zero.

Maxwell-Boltzmann distribution of speed



General Chemistry I



Intermolecular forces for gas, liquid and solid
 → determination of physical property
 (e.g. boiling point)

General Chemistry I



- 10.1 Bulk Properties of Gases, Liquids, and Solids: Molecular Interpretation
- 10.2 Intermolecular Forces: Origins in Molecular Structure
- 10.3 Intermolecular Forces in Liquids
- 10.4 Phase Equilibrium
- 10.5 Phase Transitions
- 10.6 Phase Diagrams

10.1 BULK PROPERTIES OF GASES, LIQUIDS, AND SOLIDS: MOLECULAR INTERPRETATION ⁴⁴⁴

➤ Molar Volume (V_m , inversely related to the number density)

Solids, liquids: $10\text{--}100\text{ cm}^3/\text{mol}$, $3\text{--}5\text{ \AA}$ between molecules
(cf. bond lengths; $0.5\text{--}2.5\text{ \AA}$)

Gases: $24000\text{ cm}^3/\text{mol}$, $\sim 30\text{ \AA}$ between molecules

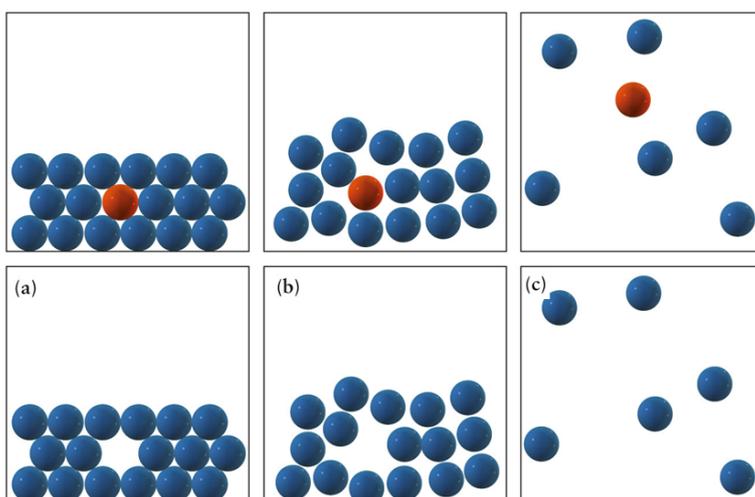


Fig. 10.1 Intermolecular forces create structure in liquids and solids. (a) Solid (b) Liquid (c) Gas

➤ Compressibility

❖ **Isothermal compressibility,** $\kappa_T = -\frac{1}{V} \left(\frac{dV}{dP} \right)_T$

~ Fractional volume decrease against the pressure increase

Solids, liquids: nearly incompressible, (nearly) in contact,
strong intermolecular forces

Gases: highly compressible, space between molecules

➤ Thermal Expansion

❖ **Thermal Expansion Coefficient,**

~ Fractional volume increase against the temperature increase

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

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➤ Ideal gas

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left(\frac{\partial (nRT/P)}{\partial T} \right)_P = \frac{1}{V} \frac{nR}{P} \frac{dT}{dT} = \frac{nR}{nRT} = \frac{1}{T}$$

At 0°C, $\alpha = \frac{1}{T} = \frac{1}{273.15} = 0.00366 \rightarrow 0.366\%$ volume increase by 1 °C

T A B L E 10.1

Isothermal Compressibility[†] and Thermal Expansion Coefficients

Compound	$\kappa/(10^{-6} \text{ atm}^{-1})$	$\alpha/(10^{-4} \text{ K}^{-1})$
Liquids		
Benzene	92.1	12.4
Ethanol	76.8	11.2
Mercury	38.7	1.82
Water	49.7	2.1
Solids		
Copper	0.735	0.501
Diamond	0.187	0.030
Iron	0.597	0.354
Lead	2.21	0.861

General [†]Values at 20°C.



➤ Fluidity and Rigidity

- Fluidity of gases and liquids vs. rigidity of solids
- **shear viscosity**: the resistance of a material to macroscopic flow
most liquids 16 orders of magnitude smaller than those of solids

➤ Diffusion

- Molecules of one type migrate into regions initially occupied only by the other type.
- **diffusion constant**: measuring the rate of diffusive mixing
- In liquids, quickly changing the neighbors and finding new interactions due to low shear viscosity
In solids, a durable arrangement of neighbors

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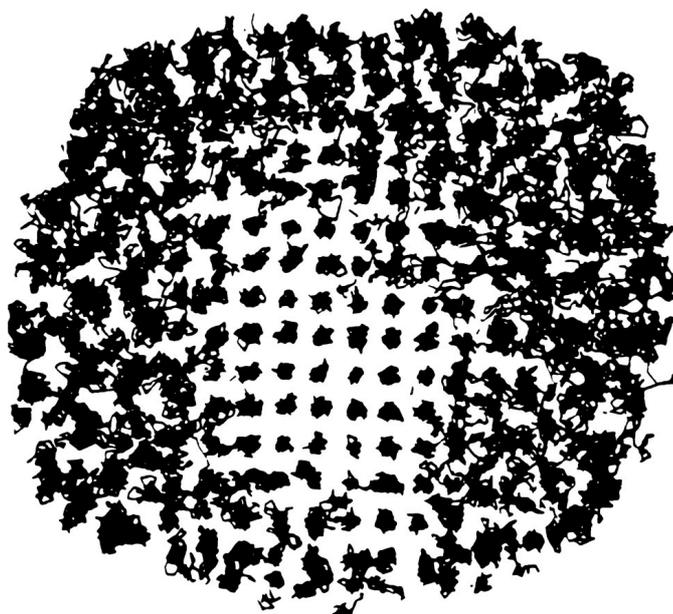


Fig. 10.2 Computer simulated picture of the motion of atoms in a tiny melting crystal, the atoms at the center (in the solid) moves erratically about the particular sites. The atoms at the surface (in the liquid) move much greater distance.

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T A B L E 10.2

The diffusion coefficient in solids at different temperatures is generally found to be well predicted by the [Arrhenius equation](#)

Diffusion Constants

$$D = D_0 e^{-E_A/(kT)}$$

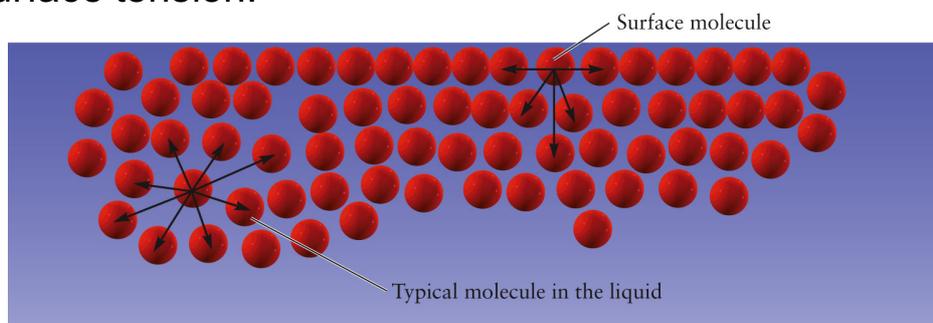
Diffusing Species	Host Material	Diffusion Constant ($\text{m}^2 \text{s}^{-1}$)	Temperature (K)
Ar	Ar	2.3×10^{-6}	100
Ar	Ar	1.86×10^{-5}	300
N ₂	N ₂	2.05×10^{-5}	300
O ₂	O ₂	1.8×10^{-5}	273
CH ₄	CH ₄	2.06×10^{-5}	273
HCl	HCl	1.24×10^{-5}	295
Cu	Cu	4.2×10^{-19}	500
Al	Al	4.2×10^{-14}	500
Cu	Al	4.1×10^{-14}	500
Cu	Ni	1.3×10^{-22}	500
Fe	Fe	3.0×10^{-21}	500
Fe	Fe	1.8×10^{-15}	900
C	Fe	1.7×10^{-10}	900

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◆ Surface tension,

- Intermolecular attractions among the molecules in a liquid.
- Resistance of the surface of a liquid to an increase in its area in unit of $\text{N} \cdot \text{m}^{-1}$ or $\text{J} \cdot \text{m}^{-2}$
- Surface tension is the net inward pull of surface molecules.
- Liquids with strong intermolecular interaction have high surface tension.



Surface has greater potential energy than interior.

→ Energy is required to increase the surface area of a liquid.

~ Tendency of a liquid toward minimal surface area → sphere



Fig. 10.3 (a) Spherical shape of a water droplet after it hits the surface of a pool and bounced up. (b) A water drop and a mercury drop at the dropper tip. The mercury drop is a perfect sphere whereas the water drop sags slightly due to difference in the surface tension.

General Chemistry I



TABLE. Interionic and Intermolecular Interactions

Type of interaction	Typical energy (kJ·mol ⁻¹)	Interacting species
ion-ion	250	ions only
ion-dipole	15	ions and polar molecules
dipole-dipole	2	stationary polar molecules
	0.3	rotating polar molecules
dipole-induced-dipole	2	at least one molecule must be polar
London (dispersion) [†]	2	all types of molecules
hydrogen bonding	20	molecules containing an N-H, O-H, or F-H bond; a shared H atom links the molecules

*The total interaction experienced by a species is the sum of all the interactions in which it can participate.

[†]Also known as the induced-dipole-induced-dipole interaction.

10.2 INTERMOLECULAR FORCES: ORIGINS IN MOLECULAR STRUCTURE

◆ Ion-Ion Forces (as strong as those in the covalent bond)

- Strong, Long-range, Not directional

$$U \propto \frac{1}{R} \quad \text{Coulombic potential}$$

◆ Dipole-Dipole Forces

- Depends on orientations of two **dipolar molecules**.
- Potential energy between two dipoles $\propto \frac{1}{R^3}$
~ shorter range than Coulomb potential

➤ Polar covalent bond

bonds in which there is **a partial transfer of charge**
not fully ionic nor fully covalent, but instead a mixture

EN difference ~ 0 covalent
 0.2 ~ 2 polar covalent
 > 2 ionic



- Weaker than thermal energy:
 - ~ Can not hold a rigid molecular assembly
- Strong enough to influence b.p., m.p., and molecular orientations

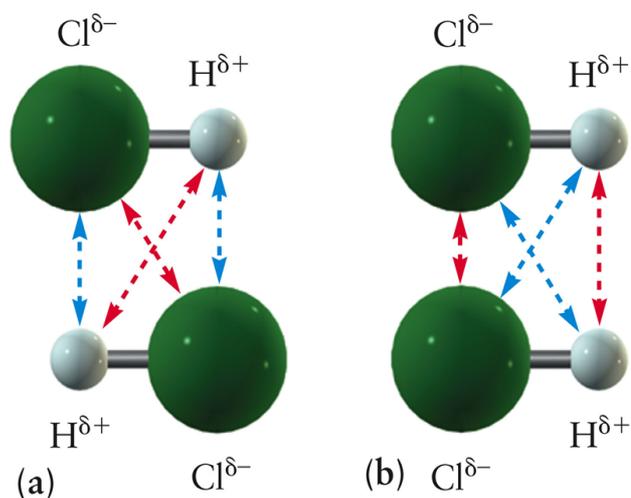


Fig 10.5 The dipole-dipole forces between two HCl molecules depend on their orientations.

◆ Ion-Dipole Forces

- Potential energy between ion and dipole $\propto \frac{1}{R^2}$
- Dissolution of salts in water (polar solvent)

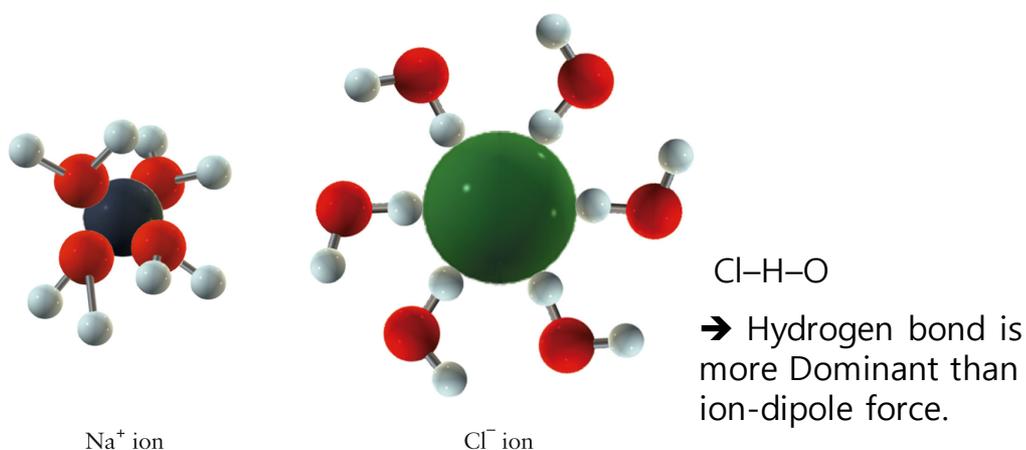


Fig 10.6 Na^+ and Cl^- ions are surrounded by water dipoles. Orientation of water molecules are reversed.

◆ Charge-Induced Dipole Forces

- Ion induces dipole for nonpolar molecule. (Induction force)
- Potential energy between ion and induced dipole $\propto \frac{1}{R^4}$
- Weak and short range
- Electrical **polarizability**
 - ~ Relative tendency of a charge distribution to be distorted from its normal shape by an external electric field
 - ~ Measure by the magnitude of the induced dipole moment



Fig. 10.7 Distortion of electron distribution of Ar as an ion is approached.

◆ Induced Dipole-Induced Dipole Forces

- Nonpolar molecule induces dipole for another nonpolar molecule.
- Potential energy between two induced dipoles $\propto \frac{1}{R^6}$
- Weak (~1 kJ/mol) and short range,
- Attraction between Ar atoms: **London dispersion force**
(= van der Waals force)

Fluctuation of electron distribution in one molecule

Temporary dipole

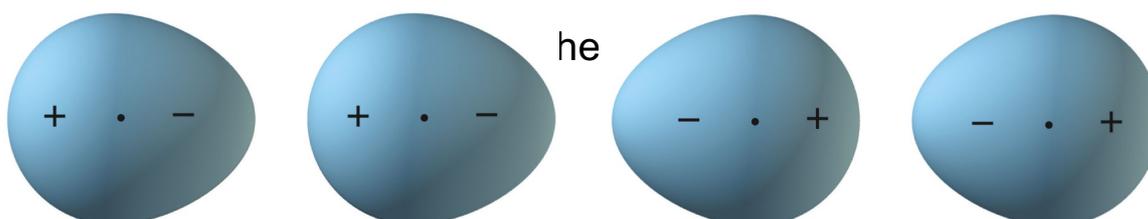
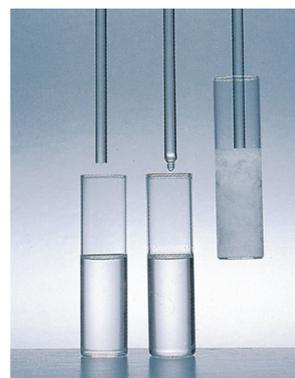


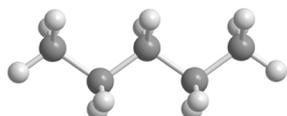
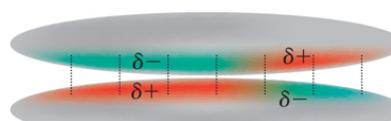
Fig. 10.8 A fluctuation of the electron distribution on one atom induces a corresponding temporary dipole moment on a neighboring atom.

- A large molecule is likely to have a stronger London interactions than a smaller one.

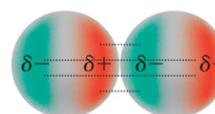
C_5H_{12} ; mobile liquid
 $C_{15}H_{32}$; viscous liquid
 $C_{18}H_{38}$; waxy solid



- Halogens: gases (F_2 , and Cl_2); liquid (Br_2); solid (I_2)
- Rod-shaped (pentane; $T_b = 36\text{ }^\circ\text{C}$) vs. spherical (2,2-dimethylpropane; $T_b = 10\text{ }^\circ\text{C}$)

8 Pentane, C_5H_{12} 9 2,2-Dimethylpropane, $C(CH_3)_4$ 

(a)



(b)

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◆ INTERACTIONS

▶ Ion – Ion (Coulomb): $E_p = \frac{Q_1 Q_2}{4\pi\epsilon_0 r}$

▶ Ion – Dipole: $E_p \propto -\frac{|z|\mu}{r^2}$

▶ Dipole – Dipole: $E_p \propto -\frac{\mu_1 \mu_2}{r^3}$

▷ Rotating polar gas molecules*:

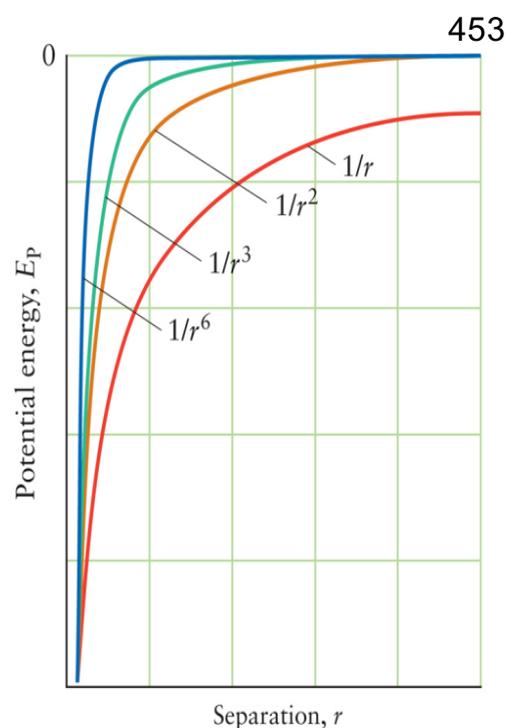
$$E_p \propto -\frac{\mu_1 \mu_2}{r^6}$$

▶ Dipole – Induced dipole*: $E_p \propto -\frac{\mu_1^2 \alpha_2}{r^6}$

▶ London (dispersion)*:
(Induced dipole – Induced dipole) $E_p \propto -\frac{\alpha_1 \alpha_2}{r^6}$

* Van der Waals interactions $E_p \propto -\frac{C}{r^6}$

General Chemistry I



Potential Energies
between ions,
ions and dipoles,
stationary dipoles, and
rotating dipoles.

KCl, Cl₂, 2xHCl, 2xAr

Ar + Ar : dispersion only

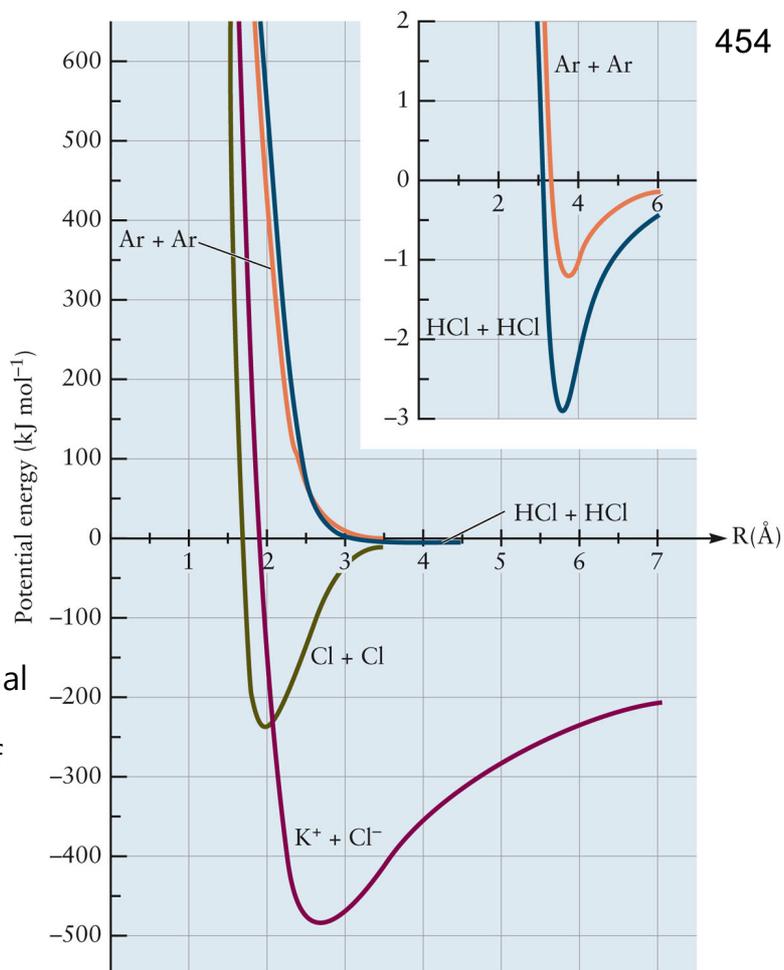
HCl + HCl : dipole-dipole
and dispersion

Cl + Cl : covalent interaction

K⁺ + Cl⁻ : ion-ion interaction

*The kinetic energy of translational motions of molecules is on the order of 2-3 kJ/mol, molecules of KCl and Cl₂ will almost never be dissociated by collision.

General Chemistry I



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◆ Shape of Molecules and Electrostatic Forces

➤ Electrostatic potential energy map

~ Shows the shape and size of the molecule, the sign and magnitude of the electrostatic potential at the “surface” of the molecule.

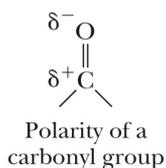
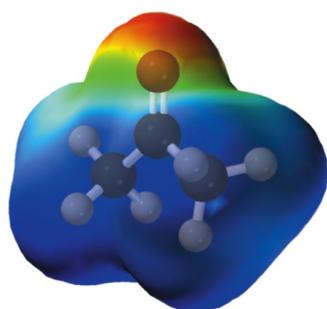


Fig. 10.10 Electrostatic potential energy map of acetone.

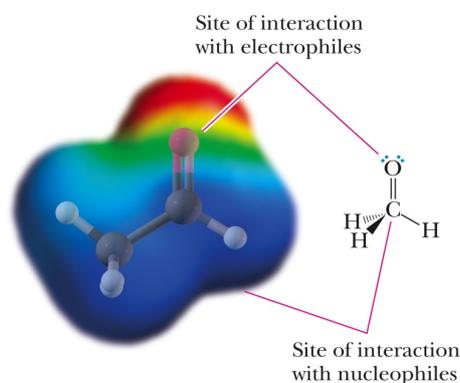


Fig. 10.11 Electrostatic potential energy map of acetaldehyde.

→ The dipole moment and charge separation are shown in both figures.

General Chemistry I

10.3 INTERMOLECULAR FORCES IN LIQUIDS

◆ Hydrogen bonding, $\sim 20 \text{ kJmol}^{-1}$

H bonded to O, N, F (electronegative, lone-pair) interacts with a lone electron pair of another nearby O, N, or F



Strong **electrostatic** interaction; stronger than most intermolecular interactions Ex. H_2O , HF, NH_3

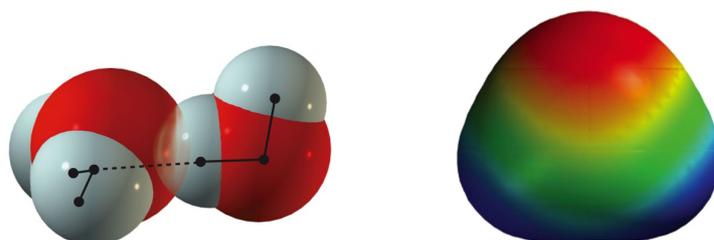


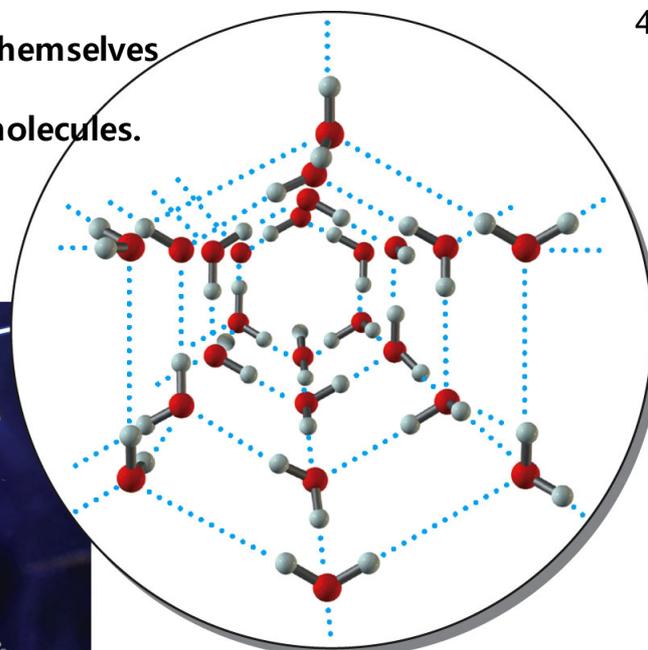
Fig. 10.13 A single hydrogen bond between water molecules forms a dimer and the electrostatic potential energy map for H_2O .

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In the liquid, the molecules orient themselves in directions that minimize the potential energy between the molecules.

The structure of ice

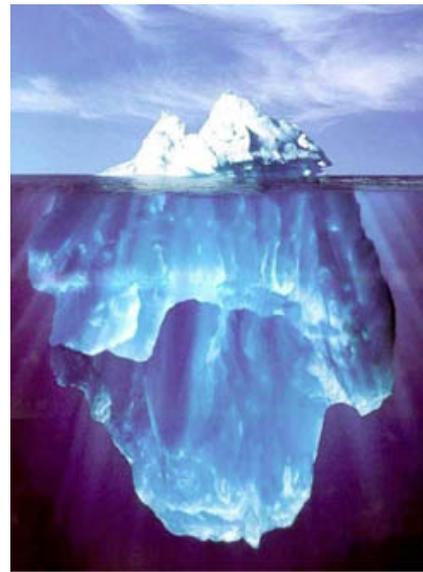
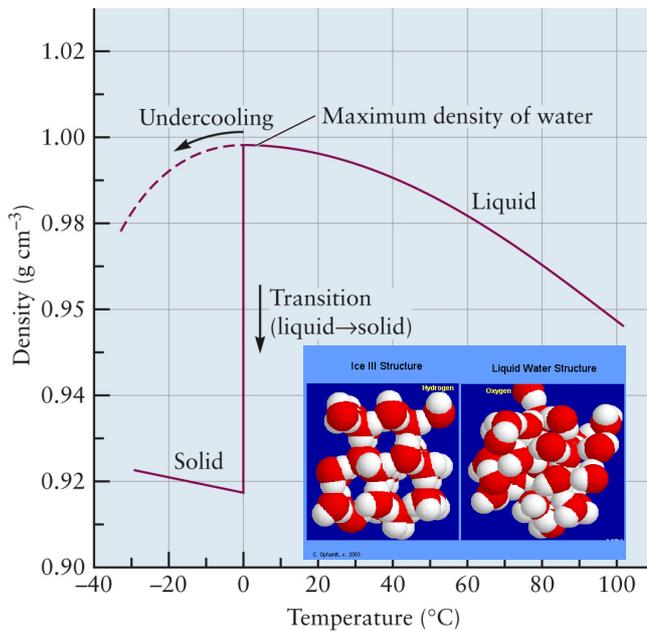


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➤ Special Properties of Water (hydrogen bonding)

Maximum density at 3.98°C, high T_b , high heat capacity



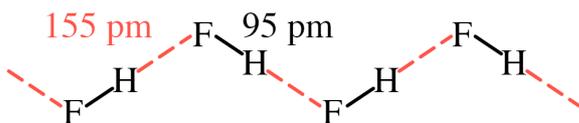
Density of ice is smaller than water!

Ice remains at the surface. Warm water under the ice.

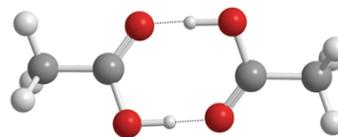
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- Hydrogen fluoride, $(\text{HF})_n$

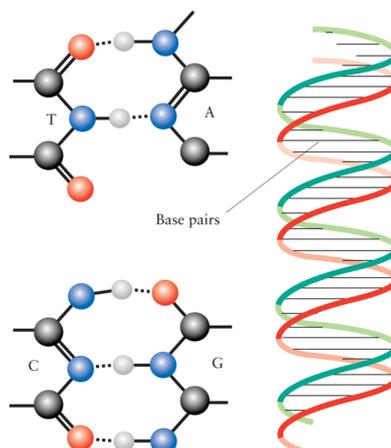


- Acetic acid dimer (vapor)



12 Acetic acid dimer

- DNA double strand



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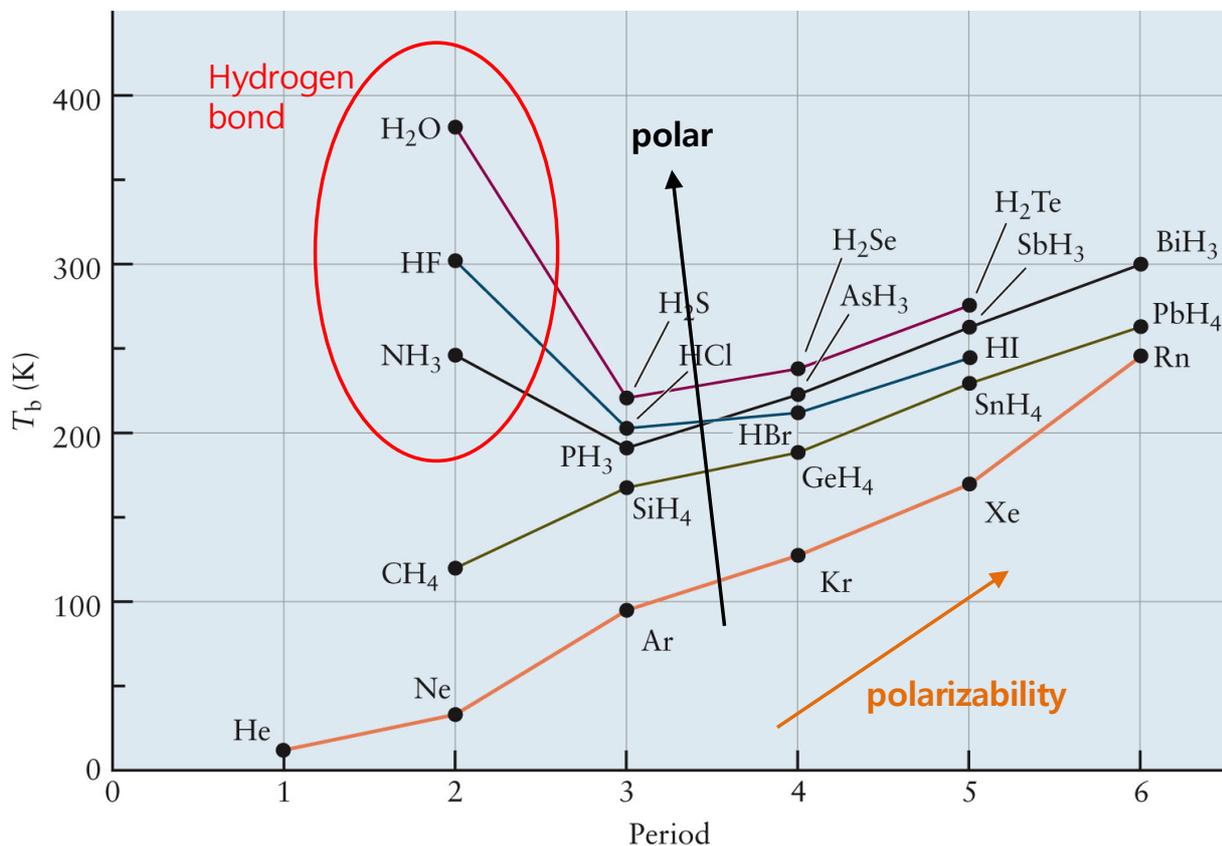


Fig. 10.12 The boiling points of hydrides of some main group elements and the noble gases.

General



Example

Identify the kinds of intermolecular forces that might arise between molecules of each of the following substances:

(a) NH_2OH ; (b) CBr_4 ; (c) H_2SeO_4 ; (d) SO_2

- (a) London forces, dipole-dipole, hydrogen bonding; (b) London forces;
 (c) London forces, dipole-dipole, hydrogen bonding; (d) London forces, dipole-dipole.

10.4 PHASE EQUILIBRIUM

❖ **Phase** ~ a sample of matter uniform throughout in both chemical and physical states

➤ **Phase Equilibrium**

dynamic process; no net flow of matter between phases

rate of evaporation = rate of condensation

independent of the direction (with enough material)

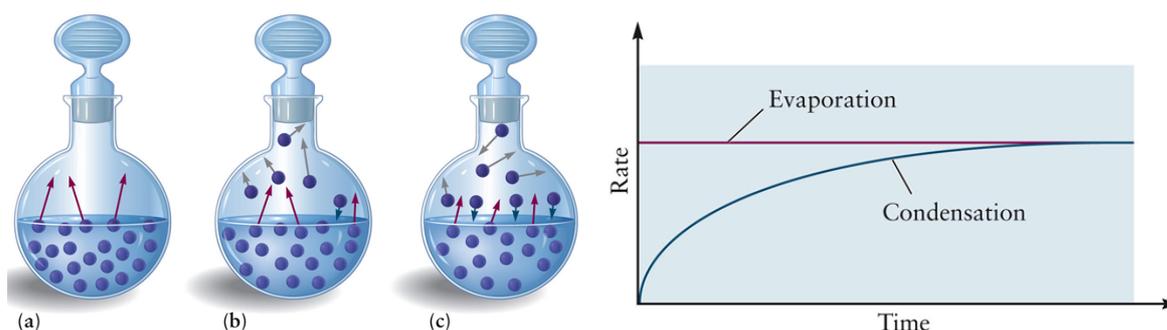


Fig. 10.16 Approach to equilibrium in evaporation and condensation.

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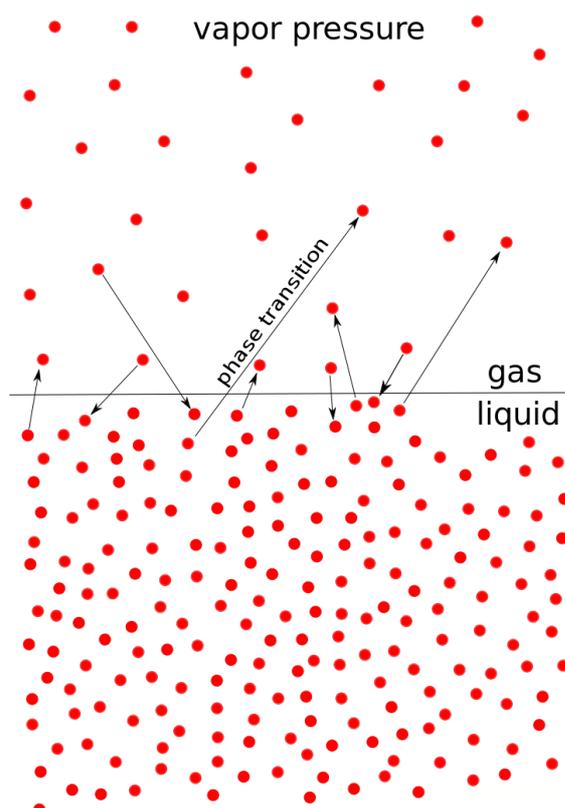
(equilibrium) vapor pressure:

The pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system.

= a liquid's evaporation rate

➔ liquid-vapor system

Volatile: a substance with a high vapor pressure at normal temperature.



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https://en.wikipedia.org/wiki/Vapor_pressure



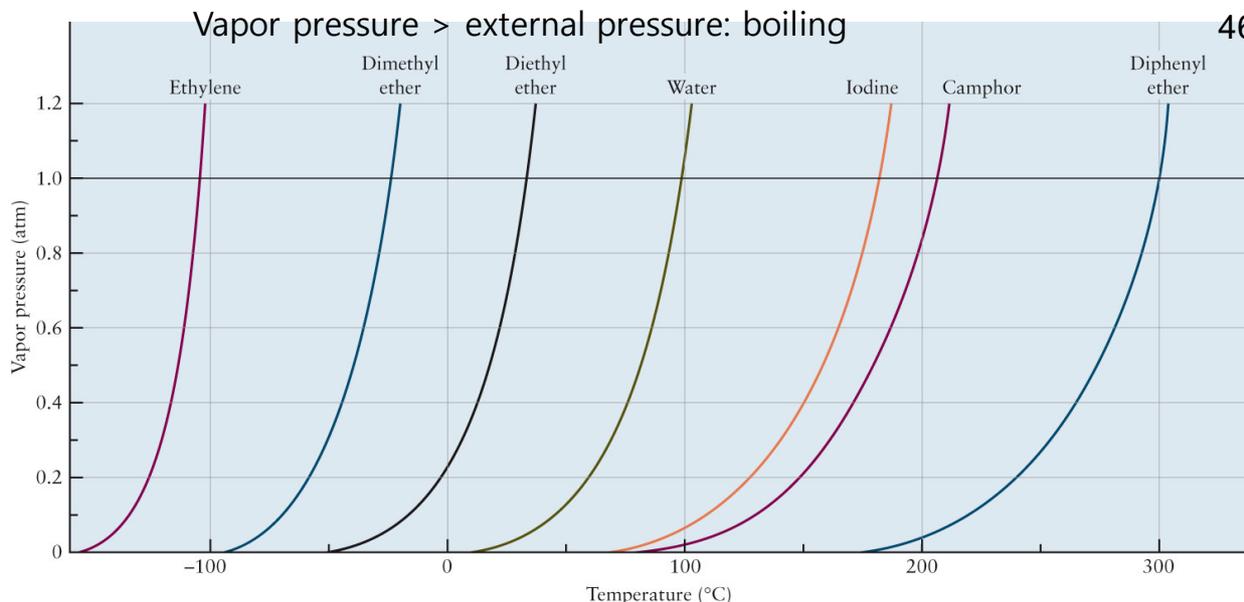


Fig. 10.17 Vapor pressure vs. temperature. The temperature at which the vapor pressure becomes 1 atm defines the **normal boiling point** of liquid and the **normal sublimation point** of a solid.

$$P_{\text{vapor}}(\text{water}) = 0.03126 \text{ atm (at } 25^\circ\text{C)}$$

$$= 1 \text{ atm (at } 100^\circ\text{C)}$$

← normal boiling point

$$P_{\text{vapor}}(\text{CO}_2) = 1 \text{ atm (at } -78.5^\circ\text{C)}$$

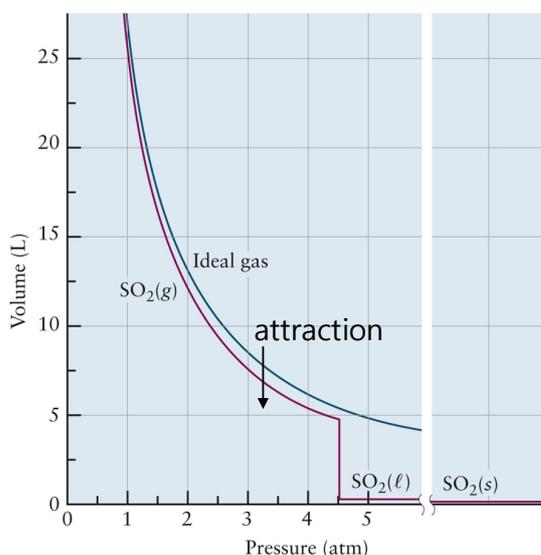
← normal sublimation point

General Chemistry I



10.5 PHASE TRANSITIONS

~ Transformation of a thermodynamic system from one phase or state of matter to another



$$P = 4.52 \text{ atm}$$

$$V = 5.50 \text{ L (Ideal gas: } PV = nRT)$$

$$= 4.74 \text{ L (van der Waals Eq.)}$$

$$P > 4.52 \text{ atm}$$

liquefying (*l*), freezing (*s*)

❖ Liquefying:

intermolecular attractions

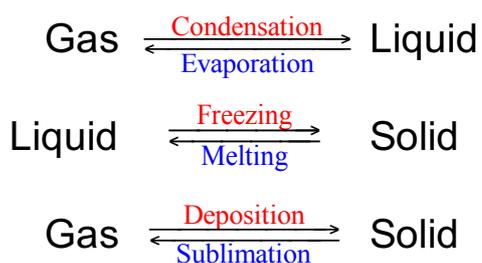
> kinetic energy ($3/2 RT$)

Fig. 10.18. Compression of 1 mol SO_2 at 30°C .

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➤ Phase transitions between three states



Boiling point, T_b
(The vapor pressure = the external pressure)
Melting (Freezing) point, T_f
(solid and liquid coexist.)
Sublimation point, T_s

→ Equilibrium

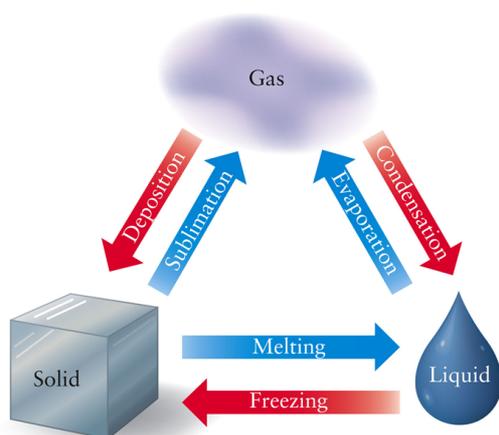


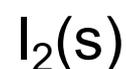
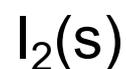
Fig. 10.19 Six phase transitions.
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❖ Superheating

~ Raising the temperature of a liquid above its f.p. without it becoming a gas

❖ Supercooling (undercooling)

~ Lowering the temperature of a liquid or a gas below its f.p. without it becoming a solid



10.6 PHASE DIAGRAMS

➤ Phase Diagram

A plot of P vs. T showing the stable state of a substance

Phase boundaries, Triple point, Critical point

➤ Triple point

Three phases coexist in equilibrium

$T = 0.01^\circ\text{C}$, $P = 0.006 \text{ atm}$ for water

➤ Critical point

Terminal point of liquid-gas boundary

Supercritical fluid

~ no phase boundary (no meniscus)

~ critical opalescence

$T_c = 374.2^\circ\text{C}$, $P_c = 218 \text{ atm}$ for water

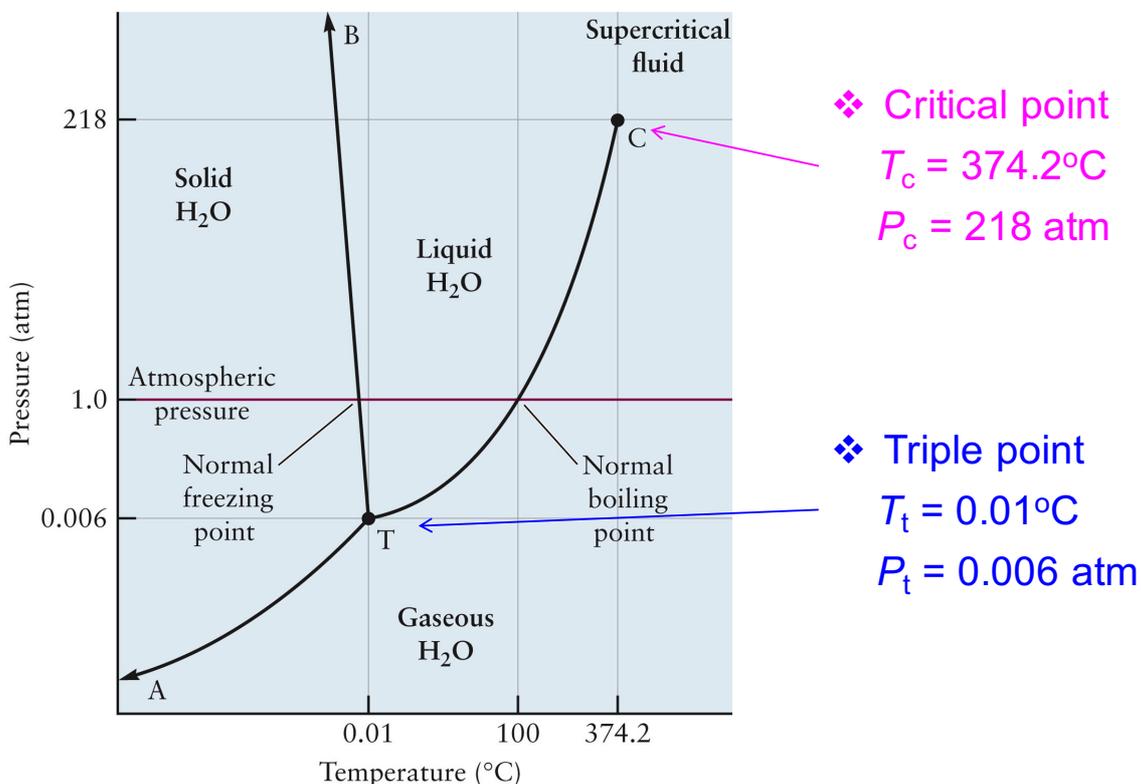
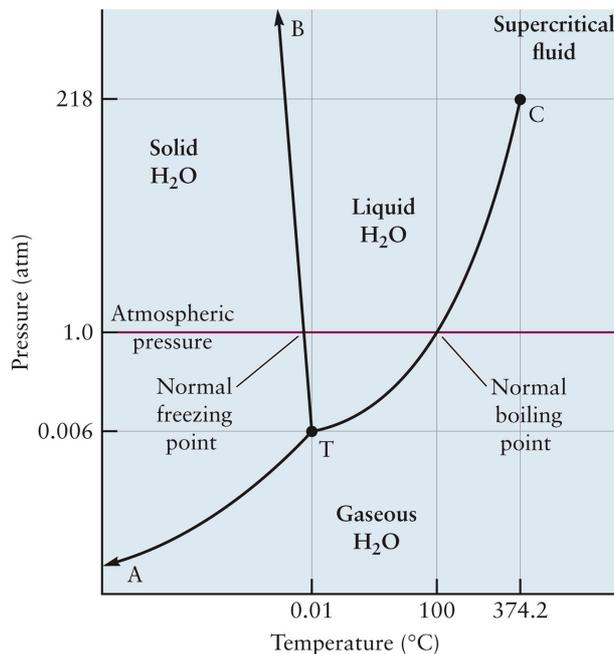
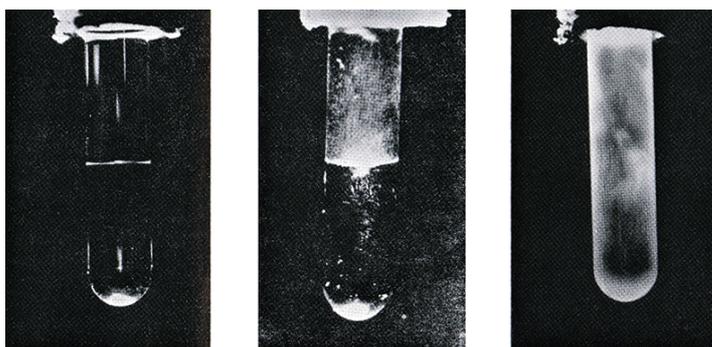
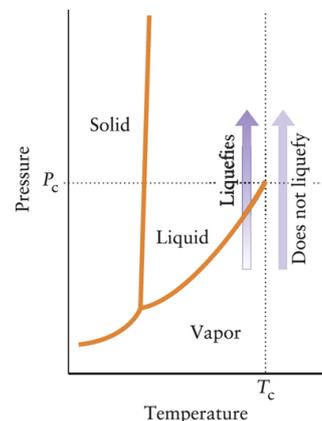


Fig. 10.21 Phase diagram for water.



above T_c



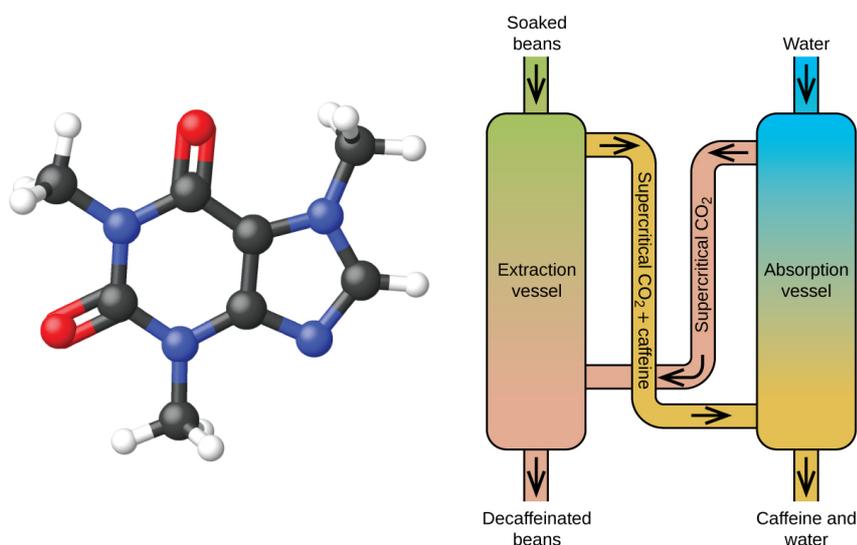
- **Supercritical fluid** – formally a gas, but is dense as a liquid phase and can act as a solvent for liquids and solids.

➔ **supercritical CO₂**: solvents for green chemical reactions; no use of harmful solvents and rapid extraction due to high mobility

Substance	Critical temperature (°C)	Critical pressure (atm)
He	-268 (5.2 K)	2.3
Ne	-229	27
Ar	-123	48
Kr	-64	54
Xe	17	58
H ₂	-240	13
O ₂	-118	50
H ₂ O	374	218
N ₂	-147	34
NH ₃	132	111
CO ₂	31	73
CH ₄	-83	46
C ₆ H ₆	289	49

General Chemistry I

Decaffeinating coffee using supercritical CO₂



Supercritical fluid extraction (SFE) using carbon dioxide is now being widely used as a more effective and environmentally friendly decaffeination method. At temperatures above 304.2 K and pressures above 7376 kPa, CO₂ is a supercritical fluid, with properties of both gas and liquid. Like a gas, it penetrates deep into the coffee beans; like a liquid, it effectively dissolves certain substances. Supercritical carbon dioxide extraction of steamed coffee beans removes 97–99% of the caffeine, leaving coffee's flavor and aroma compounds intact. Because CO₂ is a gas under standard conditions, its removal from the extracted coffee beans is easily accomplished, as is the recovery of the caffeine from the extract.

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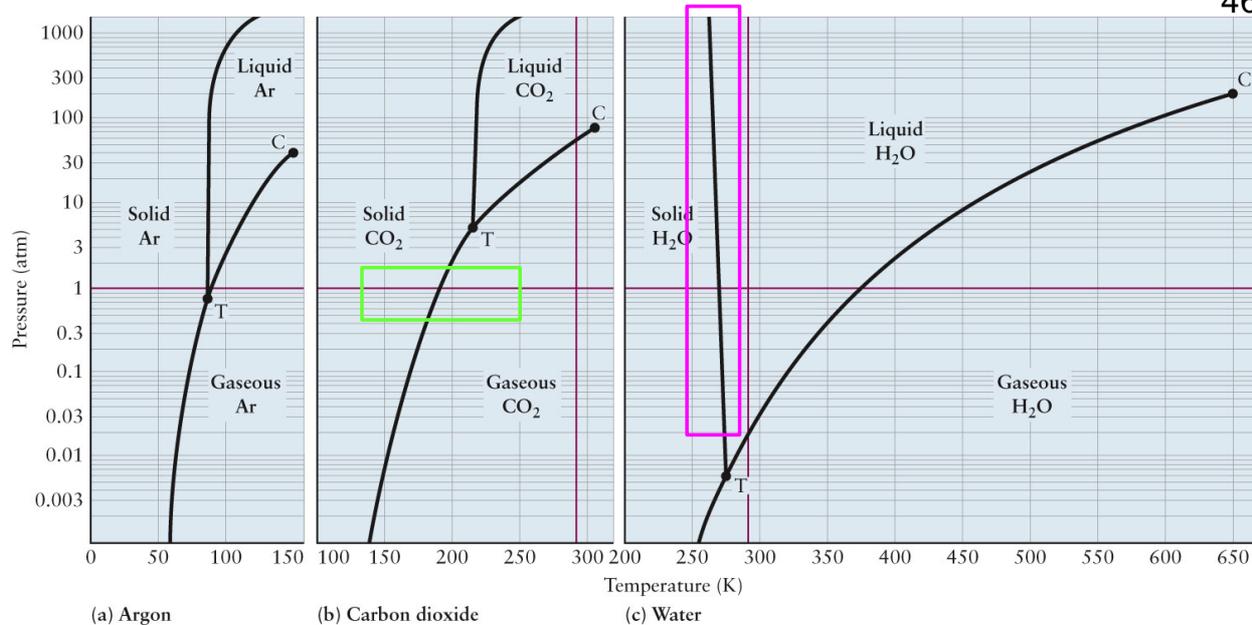


Fig. 10.23 Phase diagrams of Ar, CO₂, and water.

- ❖ Phase boundary between ice (s) and water (l) → **negative slope**
- ❖ **Sublimation** of dry ice to CO₂(g) at 1 atm

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10 Problem Sets

For Chapter 10,

5, 15, 23, 33, 37, 41, 46, 49, 54, 68

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