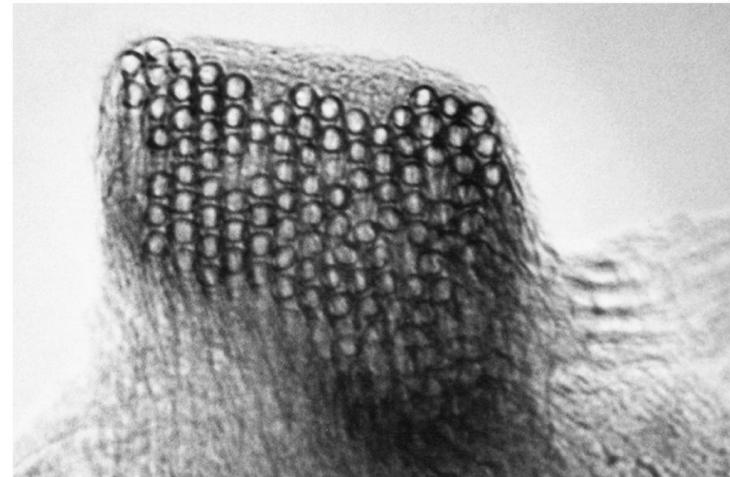


Petrucci • Harwood • Herring • Madura

Ninth
Edition

GENERAL CHEMISTRY

Principles and Modern Applications



Chapter 12: Liquids, Solids, and Intermolecular Forces

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University of Windsor, Canada
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- 12-7 Network Covalent Solids and Ionic Solids
- 12-8 Crystal structures
- 12-8 Energy Changes in the Formation of Ionic Crystals

➤ *Focus On Liquid Crystals*

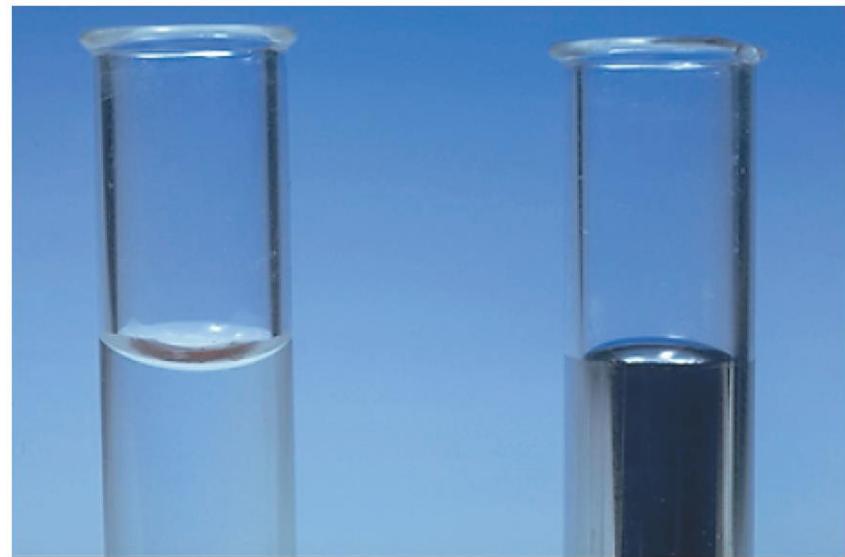
12-1 Intermolecular Forces and Some Properties of Liquids

- ◆ Cohesive Forces
 - Intermolecular forces between like molecules.
- ◆ Adhesive Forces
 - Intermolecular forces between unlike molecules.
- ◆ Surface Tension γ
 - Energy or work required to increase the surface area of a liquid.
- ◆ Viscosity η
 - A liquids resistance to flow

Intermolecular Forces



Intermolecular Forces



12-2 Vaporization of Liquids: Vapor Pressure

- Molecules in vapor state
- → Molecules undergoing vaporization
- ← Molecules undergoing condensation

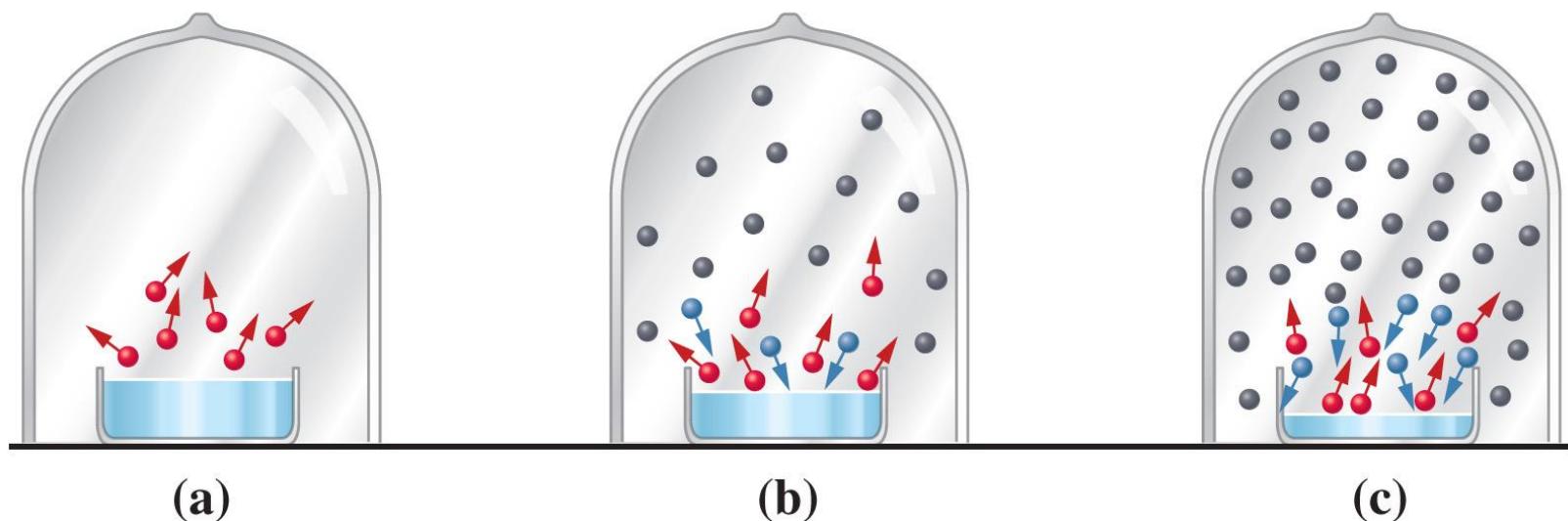


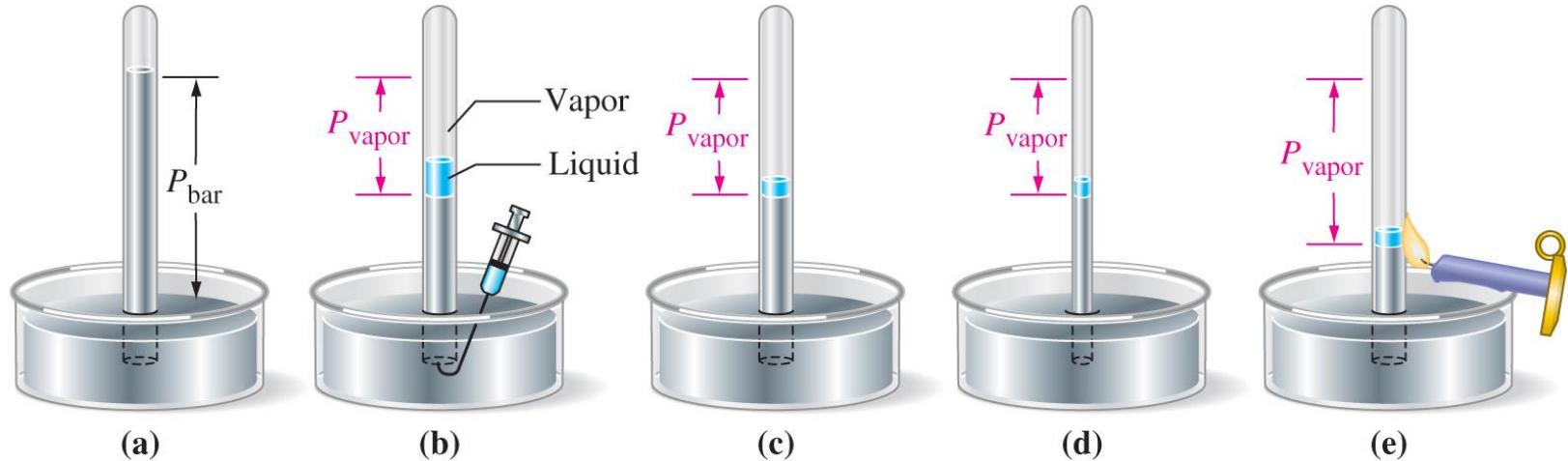
TABLE 12.1 Some Enthalpies of Vaporization at 298 K^a

Liquid	ΔH_{vap} , kJ mol ⁻¹
Diethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$	29.1
Methyl alcohol, CH_3OH	38.0
Ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$	42.6
Water, H_2O	44.0

^a ΔH_{vap} values are somewhat temperature-dependent (see Exercise 82).

$$\Delta H_{\text{vap}} = H_{\text{vapor}} - H_{\text{liquid}} = -\Delta H_{\text{condensation}}$$

Boiling Point



Mercury
manometer

Vapor
pressure
of liquid

P_{vap}
independent
of V_{liq}

P_{vap}
independent
of V_{gas}

P_{vap}
dependent on
 T

Vapor Pressure and Boiling Point

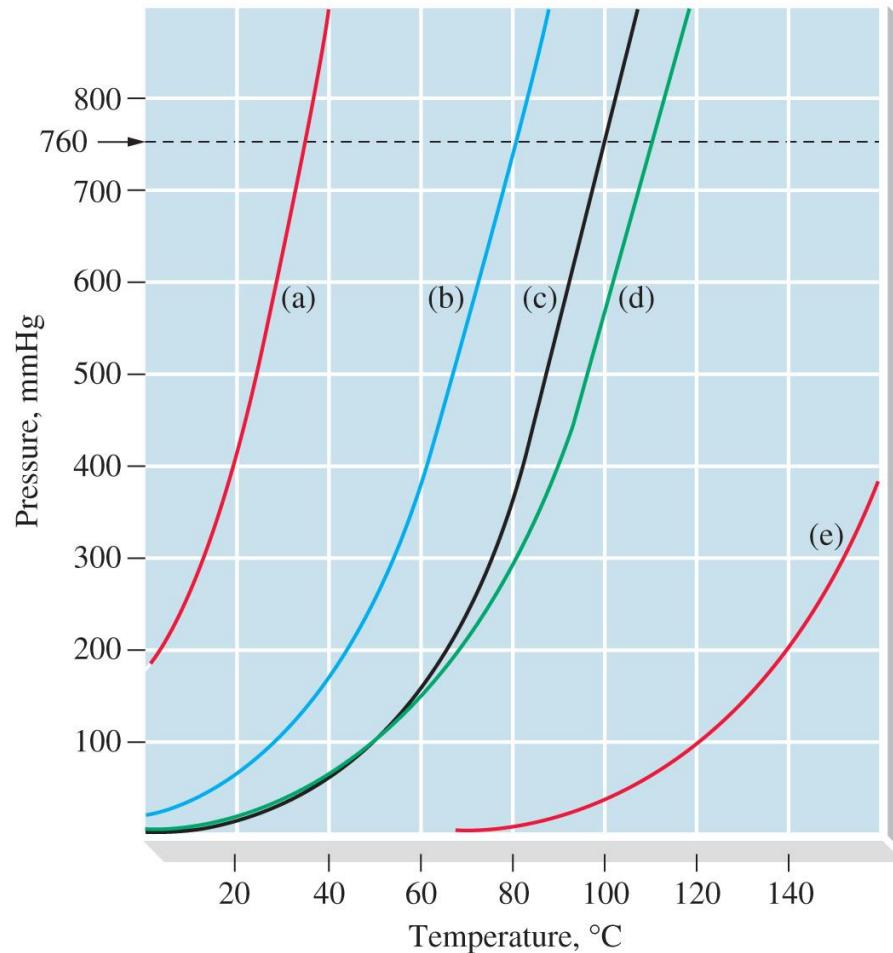


TABLE 12.2 Vapor Pressure of Water at Various Temperatures

Temperature, °C	Pressure, mmHg	Temperature, °C	Pressure, mmHg	Temperature, °C	Pressure, mmHg
0.0	4.6	29.0	30.0	93.0	588.6
10.0	9.2	30.0	31.8	94.0	610.9
20.0	17.5	40.0	55.3	95.0	633.9
21.0	18.7	50.0	92.5	96.0	657.6
22.0	19.8	60.0	149.4	97.0	682.1
23.0	21.1	70.0	233.7	98.0	707.3
24.0	22.4	80.0	355.1	99.0	733.2
25.0	23.8	90.0	525.8	100.0	760.0
26.0	25.2	91.0	546.0	110.0	1074.6
27.0	26.7	92.0	567.0	120.0	1489.1
28.0	28.3				

The Critical Point



About 10 °C
below T_c



About 1 °C
below T_c



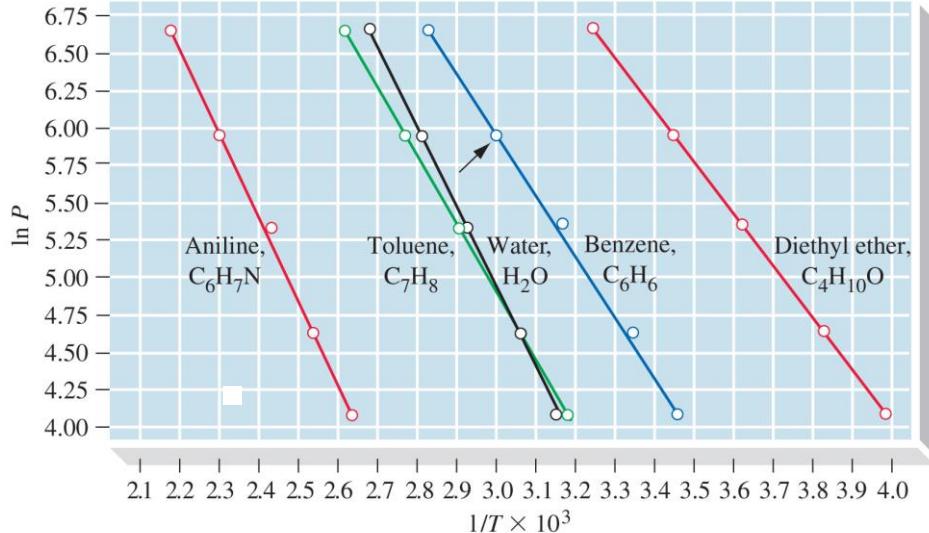
Critical
temp. T_c

**TABLE 12.3 Some Critical Temperatures, T_c ,
and Critical Pressures, P_c**

Substance	T_c , K	P_c , atm
"Permanent" gases^a		
H ₂	33.3	12.8
N ₂	126.2	33.5
O ₂	154.8	50.1
CH ₄	191.1	45.8
"Nonpermanent" gases^b		
CO ₂	304.2	72.9
HCl	324.6	82.1
NH ₃	405.7	112.5
SO ₂	431.0	77.7
H ₂ O	647.3	218.3

^a Permanent gases cannot be liquefied at 25 °C (298 K).
^b Nonpermanent gases can be liquefied at 25 °C.

Clausius-Clapeyron Equation



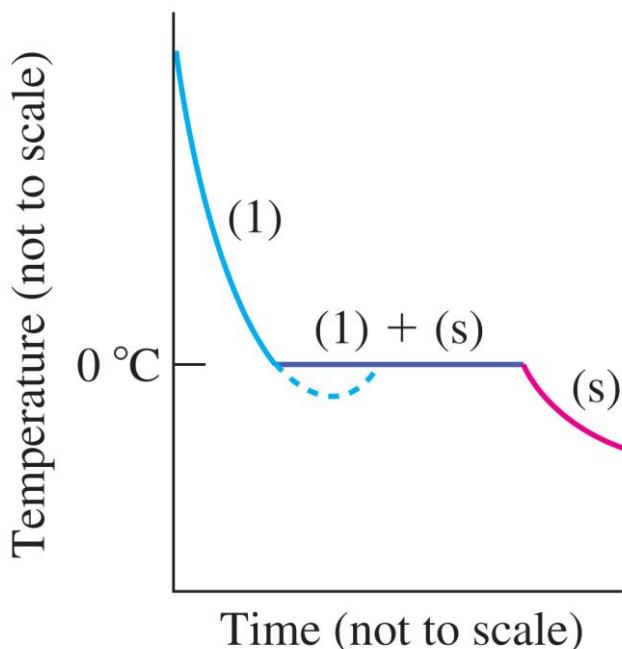
$$\ln P = -A \left(\frac{1}{T} \right) + B$$

$$A = -\frac{\Delta H_{\text{vap}}}{R}$$

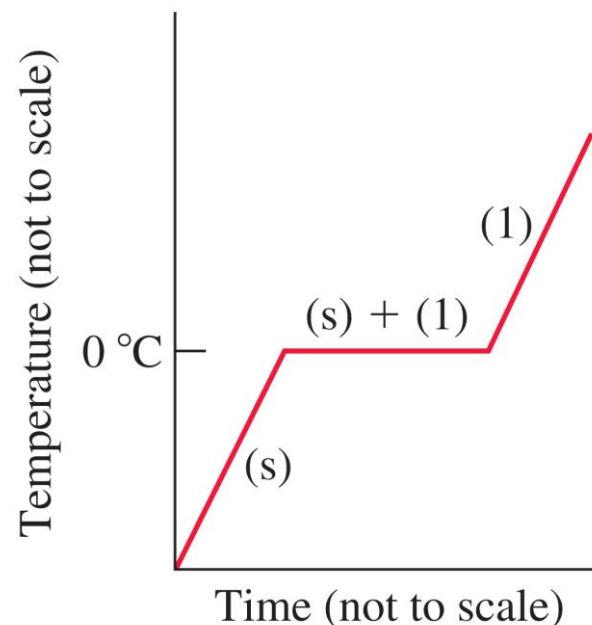
$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

12-3 Some Properties of Solids

Freezing Point



Melting Point



$$\Delta H_{\text{fus}}(\text{H}_2\text{O}) = +6.01 \text{ kJ/mol}$$

TABLE 12.4 Some Enthalpies of Fusion

Substance	Melting Point, °C	ΔH_{fus} , kJ mol ⁻¹
Mercury, Hg	−38.9	2.30
Sodium, Na	97.8	2.60
Methyl alcohol, CH ₃ OH	−97.7	3.21
Ethyl alcohol, CH ₃ CH ₂ OH	−114	5.01
Water, H ₂ O	0.0	6.01
Benzoic acid, C ₆ H ₅ COOH	122.4	18.08
Naphthalene, C ₁₀ H ₈	80.2	18.98

Vapor Boils at Low Pressure



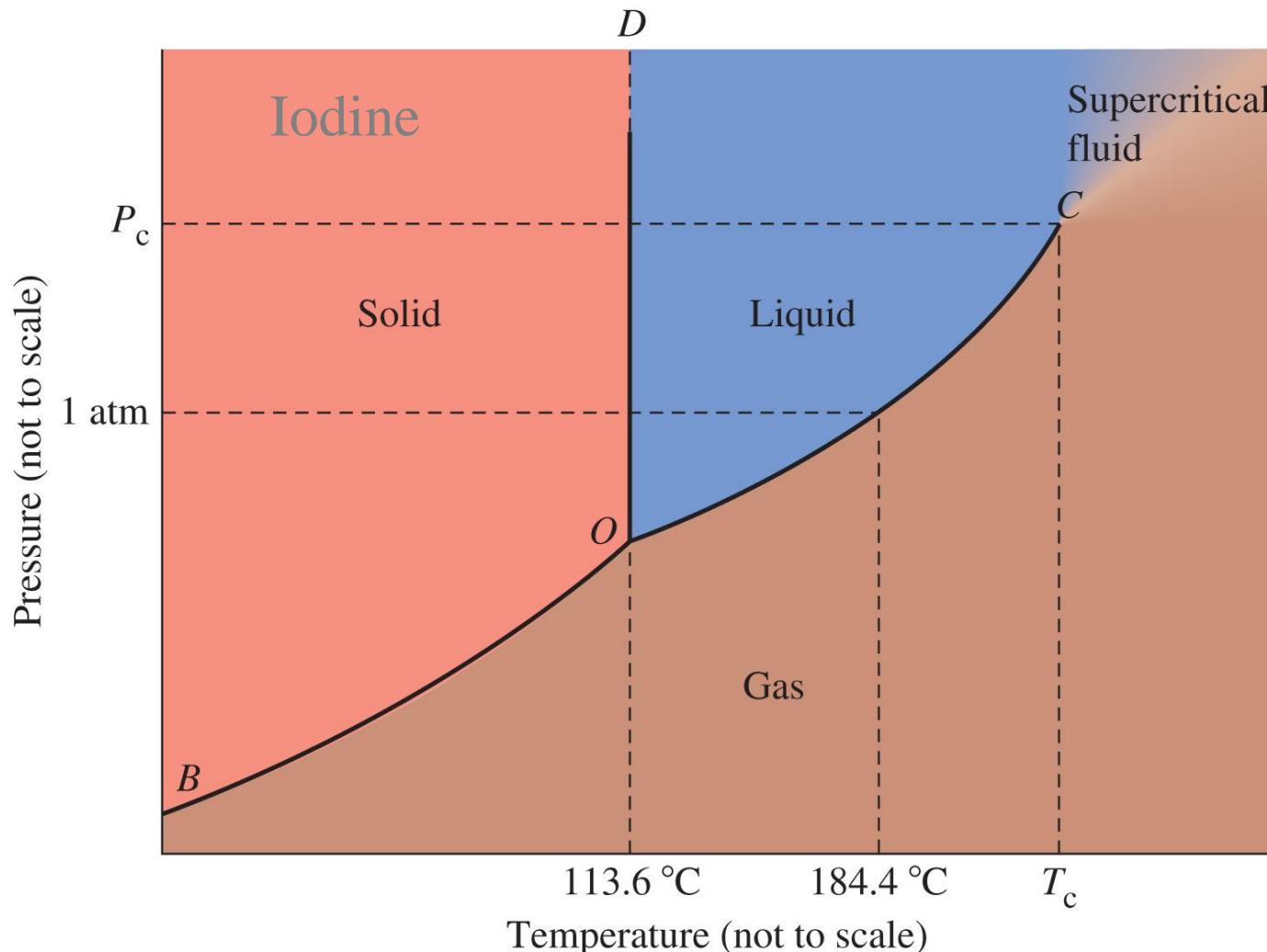
Sublimation



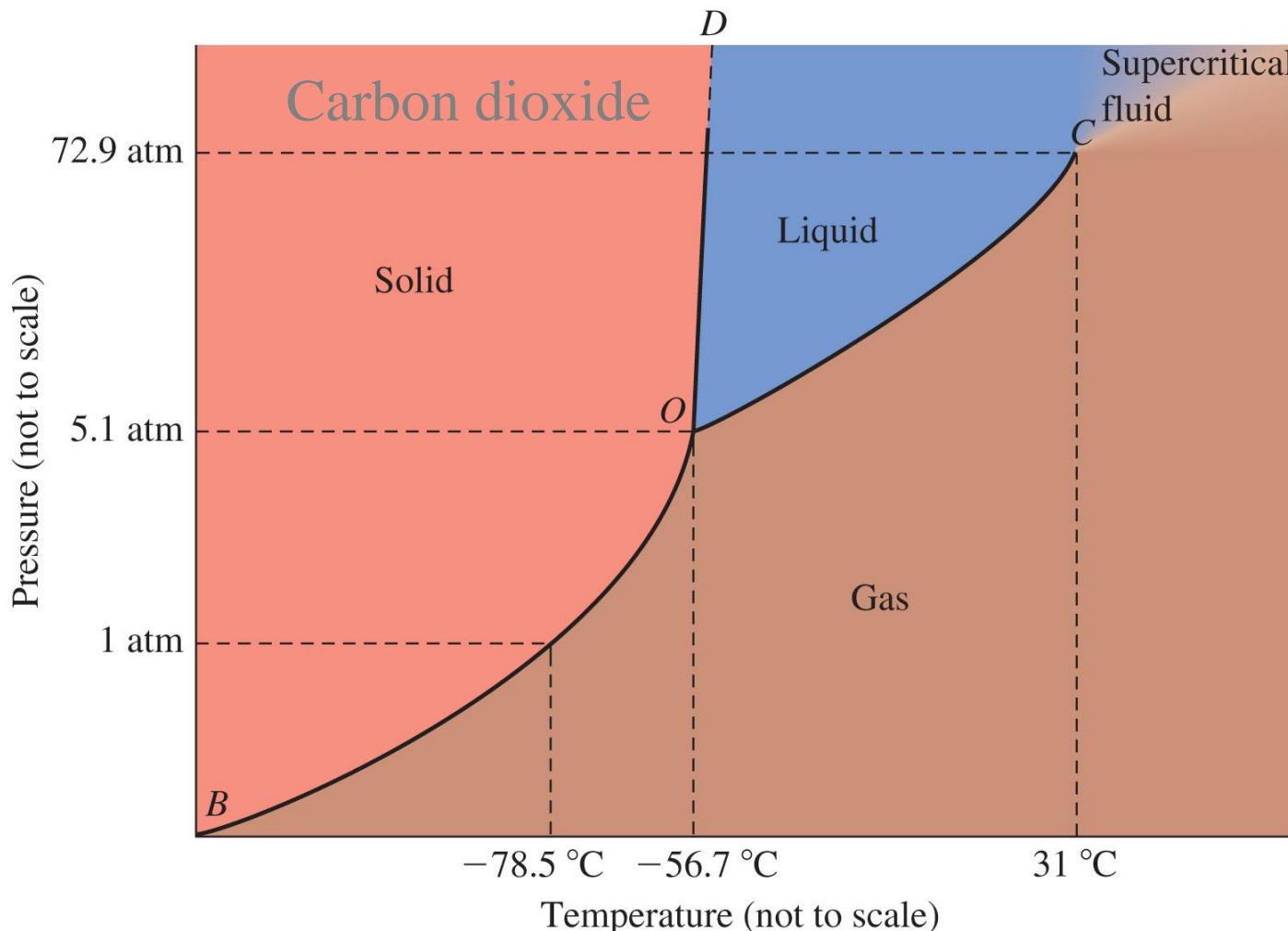
$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

$$= -\Delta H_{\text{deposition}}$$

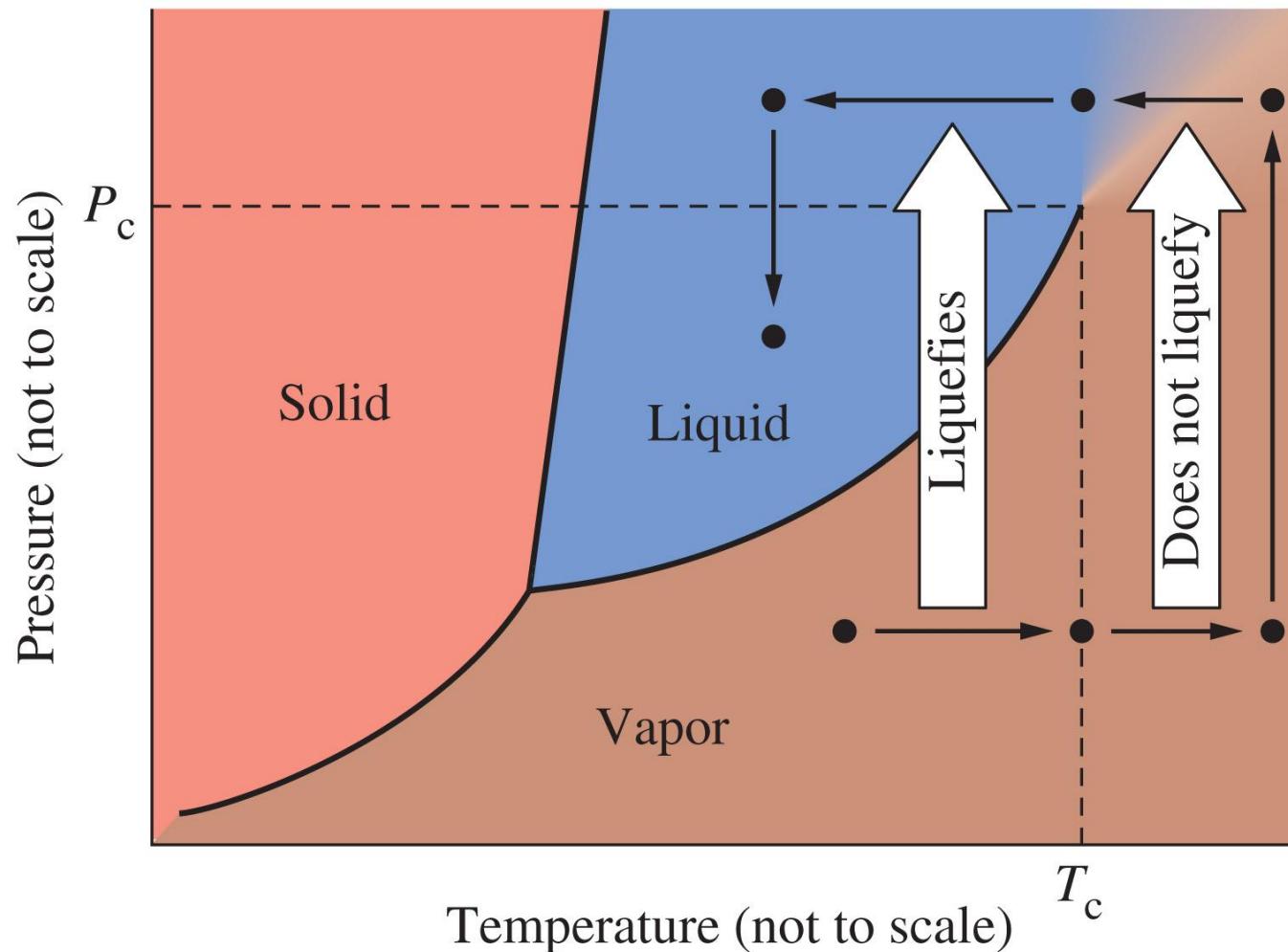
12-4 Phase Diagrams



Phase Diagrams



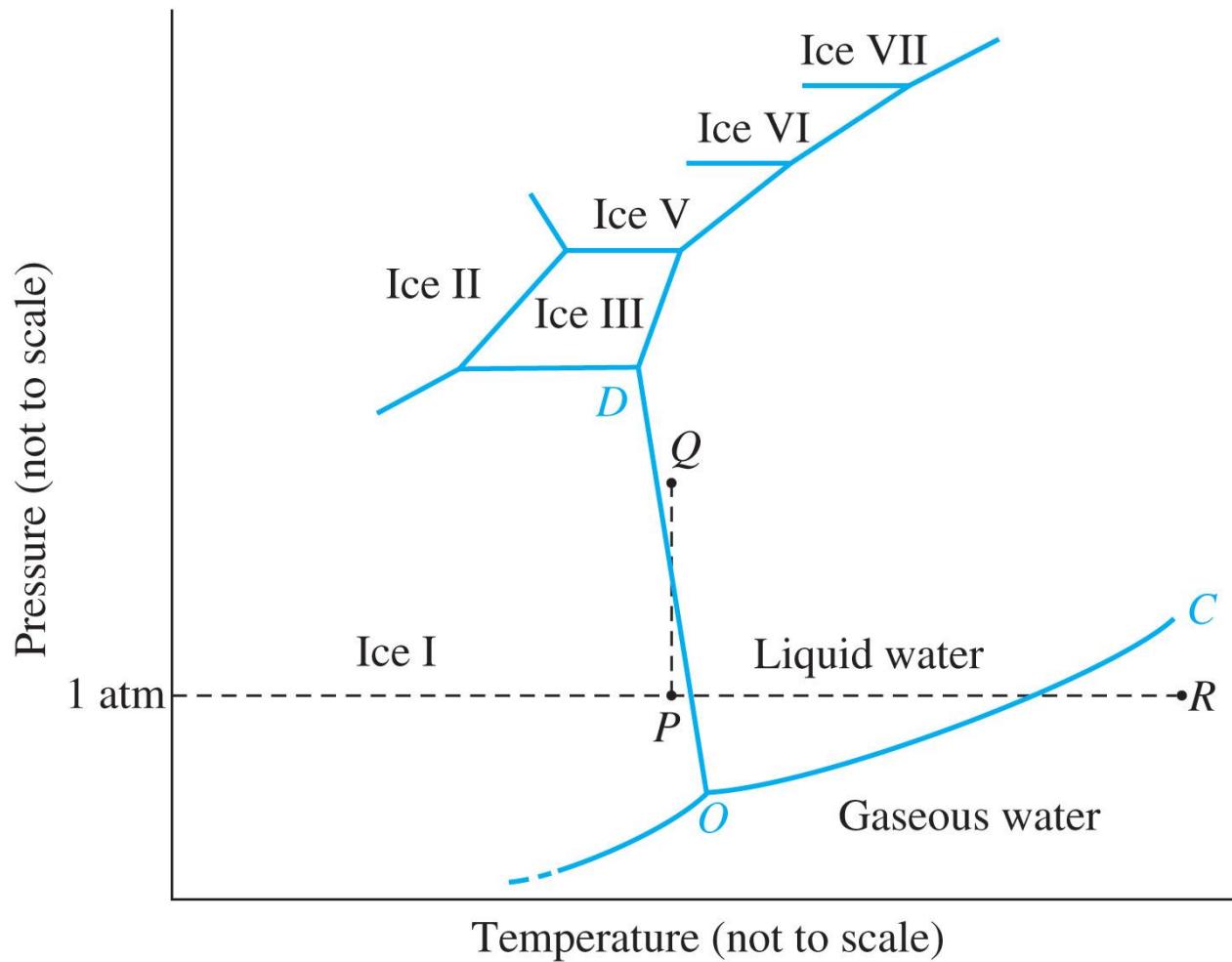
Supercritical Fluids



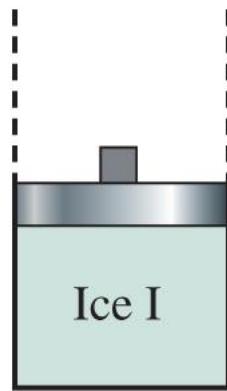
Decaffeination with Supercritical CO₂



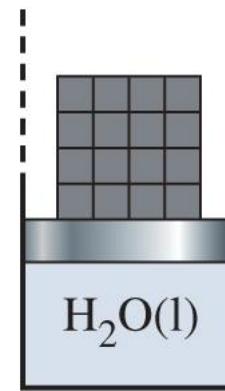
Water



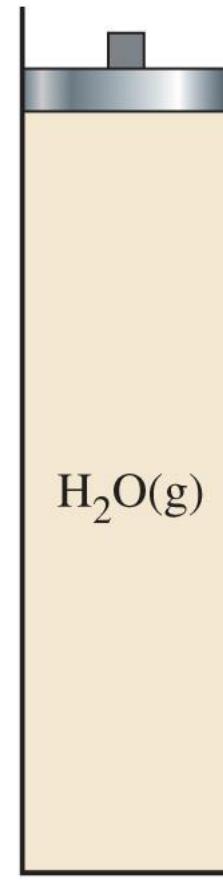
Interpreting a Phase Diagram



At point *P*



At point *Q*



At point *R*

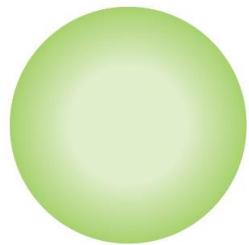
12-5 Van der Waals Forces

- ◆ Instantaneous dipoles.
 - Electrons move in an orbital to cause a polarization.
- ◆ Induced dipoles.
 - Electrons move in response to an outside force.
- ◆ Dispersion or London forces.
 - Instantaneous dipole – induced dipole attraction.
 - Related to polarizability.

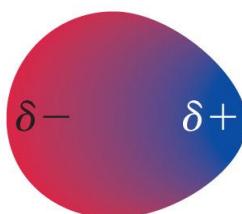
Phenomenon of Induction



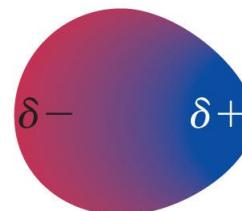
Instantaneous and Induced Dipoles



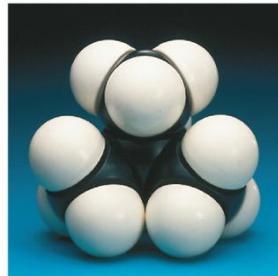
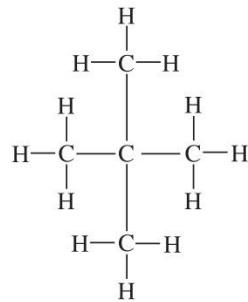
(a)



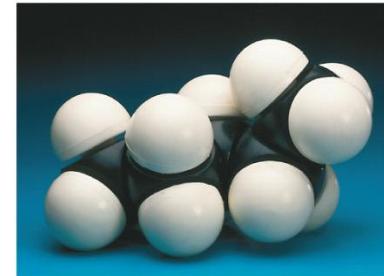
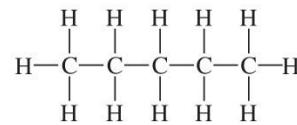
(b)



(c)



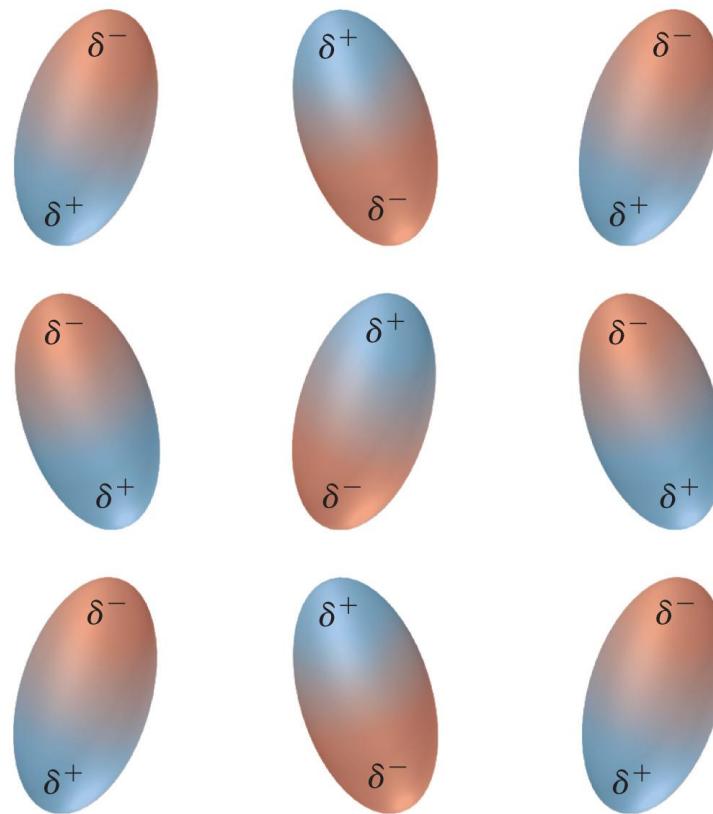
(a) Neopentane
bp = 9.5 °C



(b) Pentane
bp = 36.1 °C

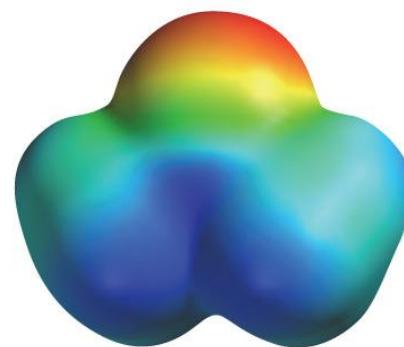
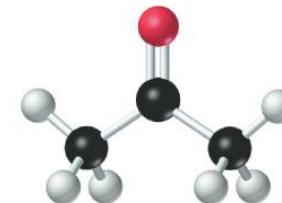
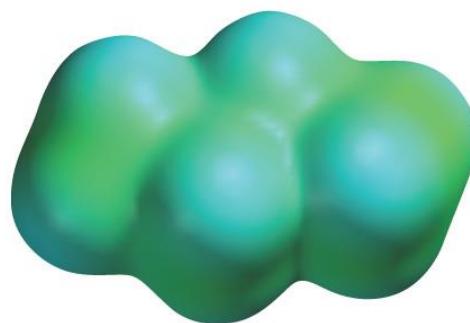
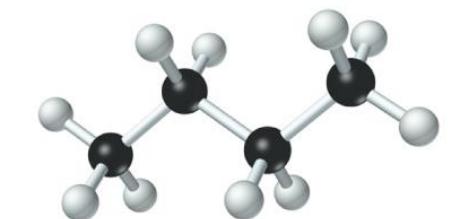
< 10 kJ/mol

Dipole Dipole Interactions

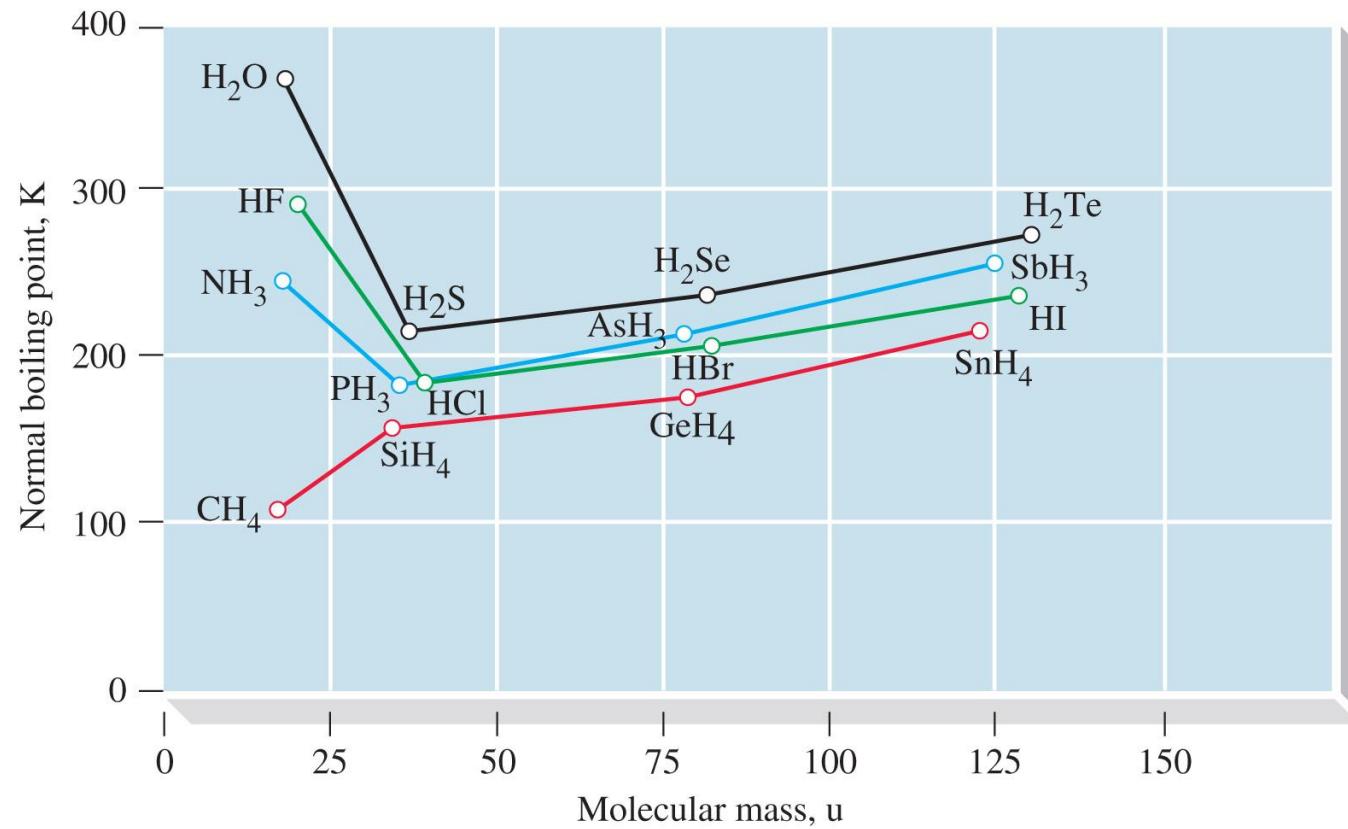


5 to 20 kJ/mol

Electrostatic Potential Maps

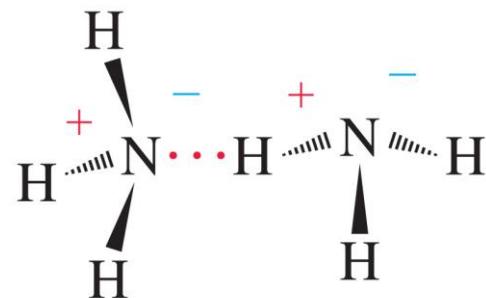
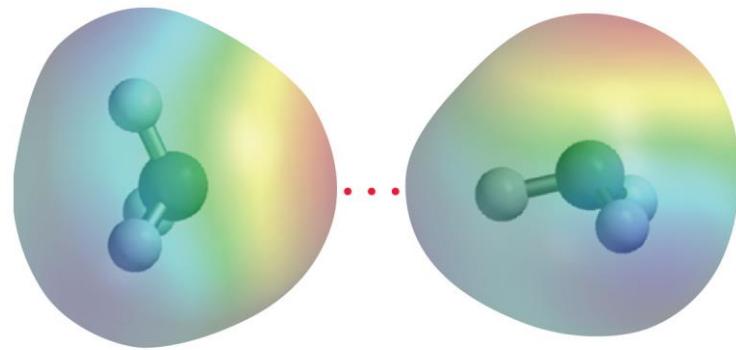
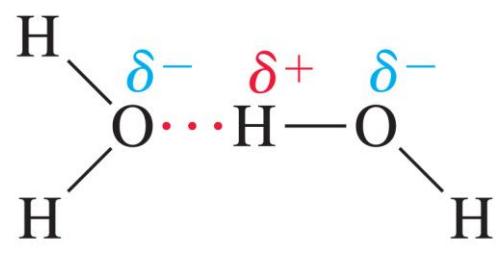
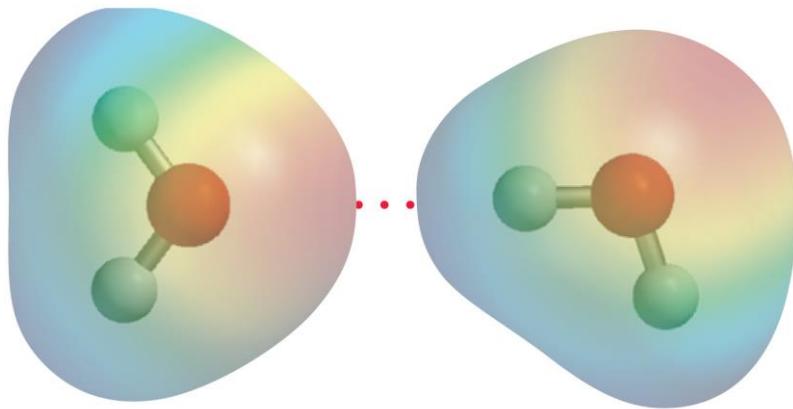


12-6 Hydrogen Bonding

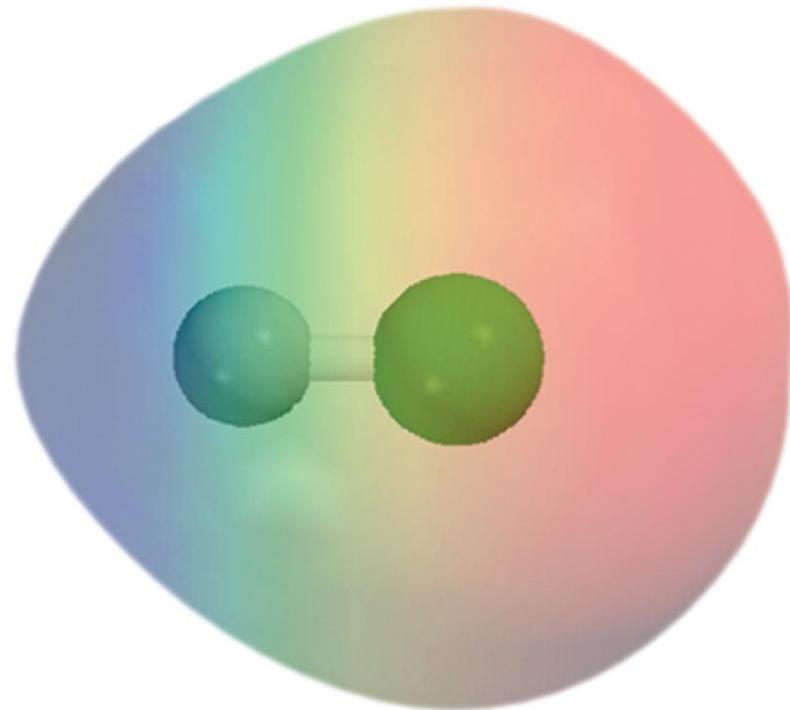
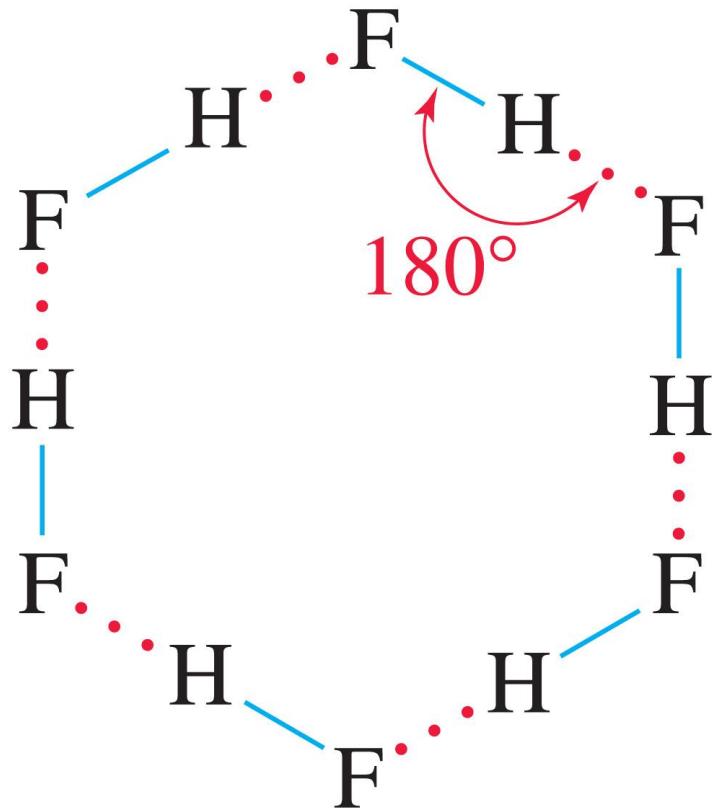


15 to 40 kJ/mol

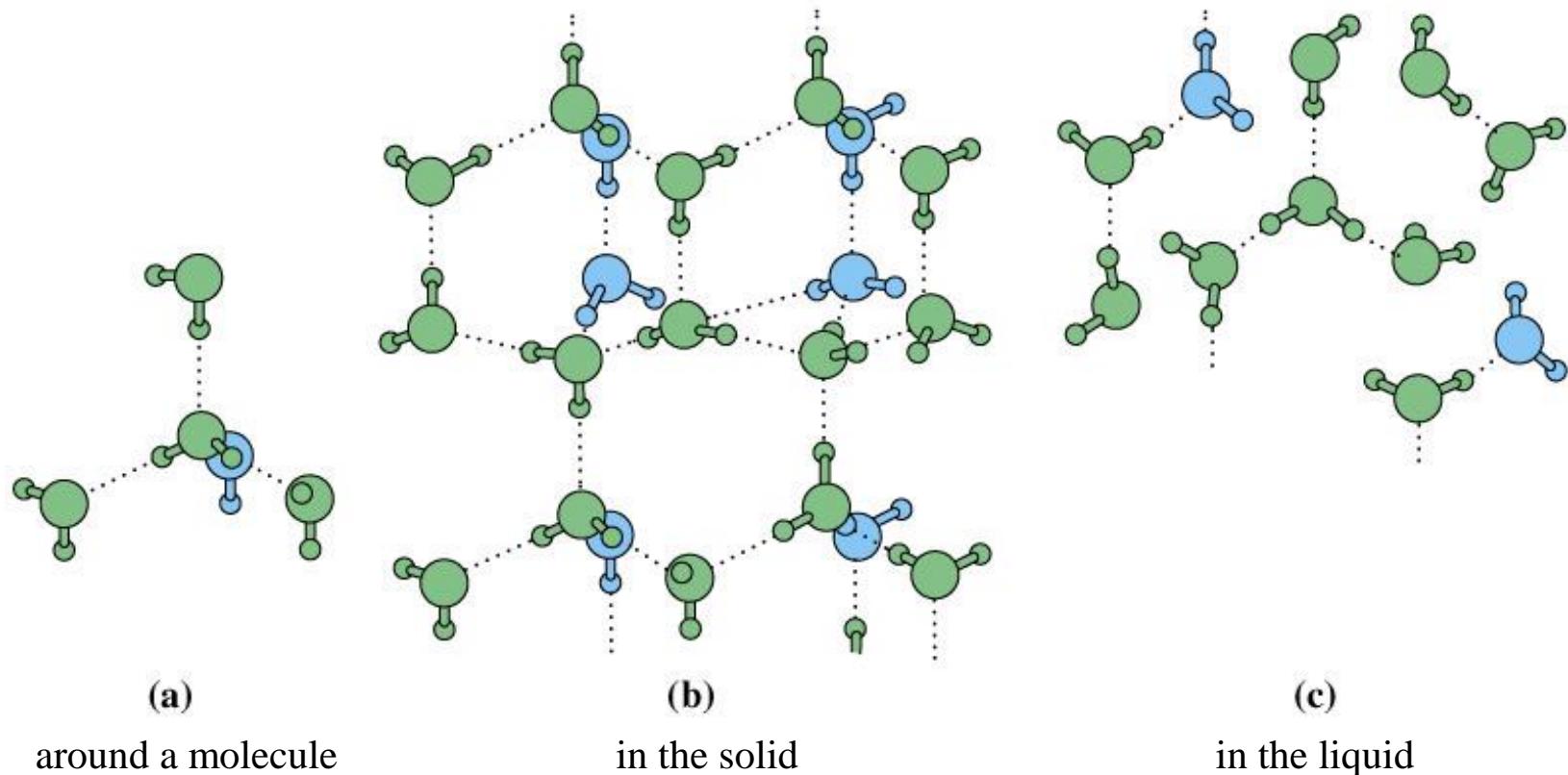
Hydrogen Bonding



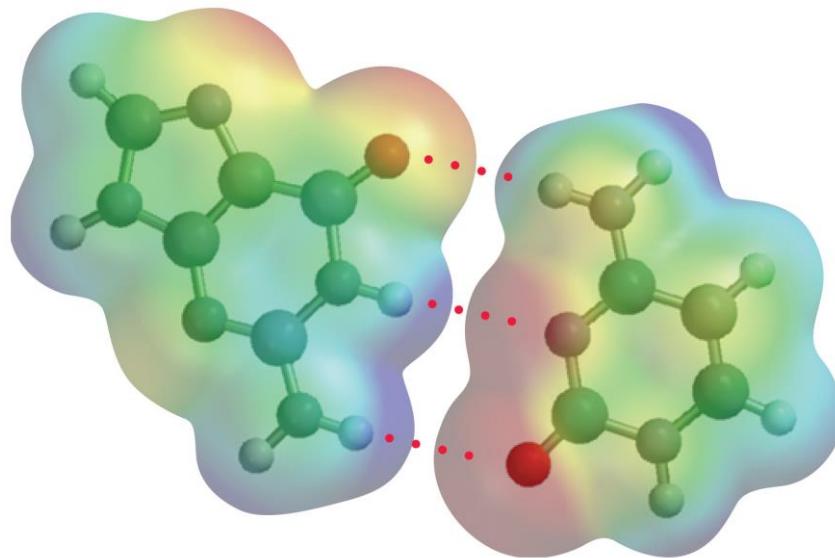
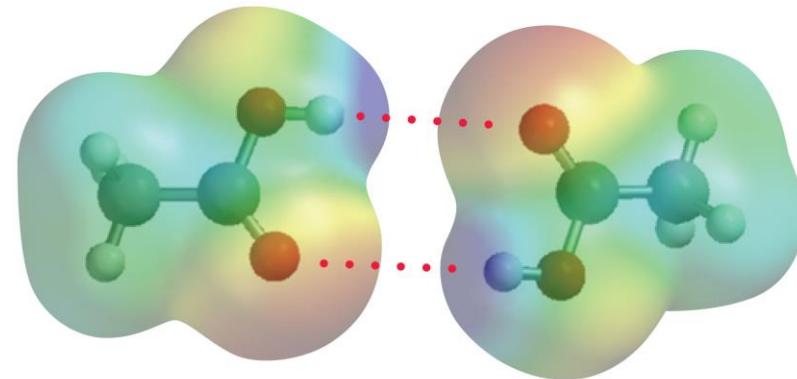
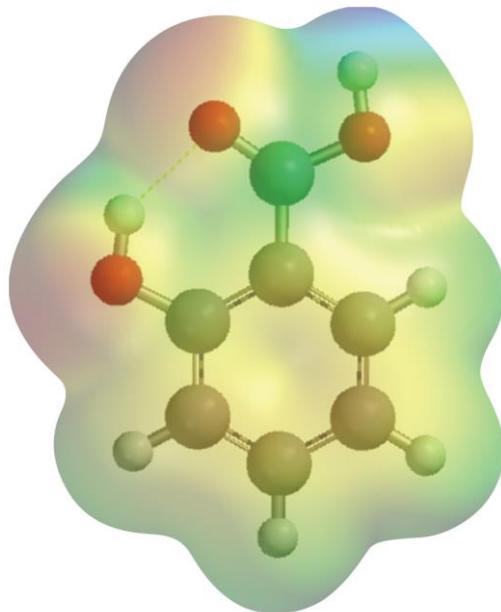
Hydrogen Bonding in HF(g)



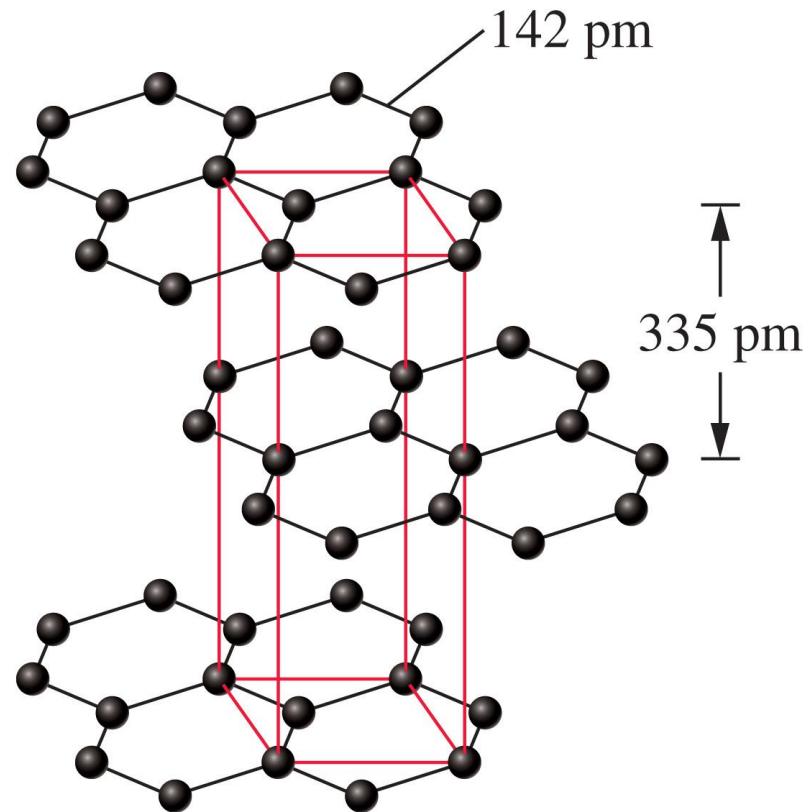
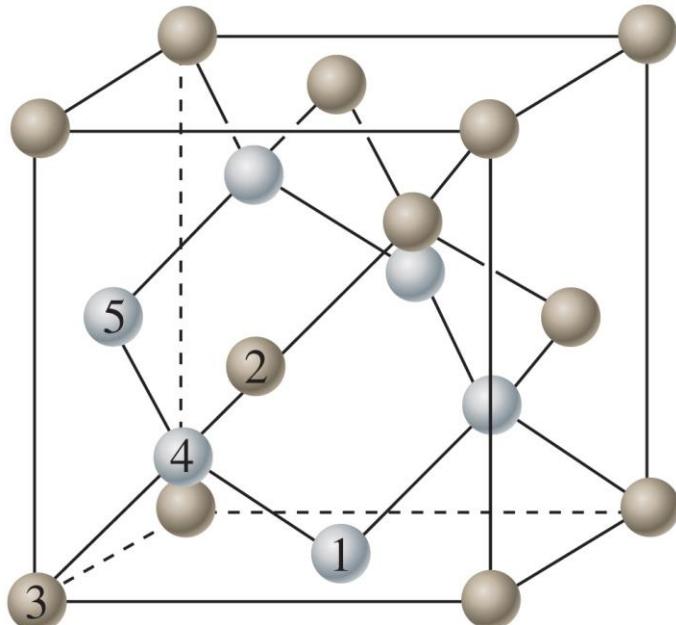
Hydrogen Bonding in Water



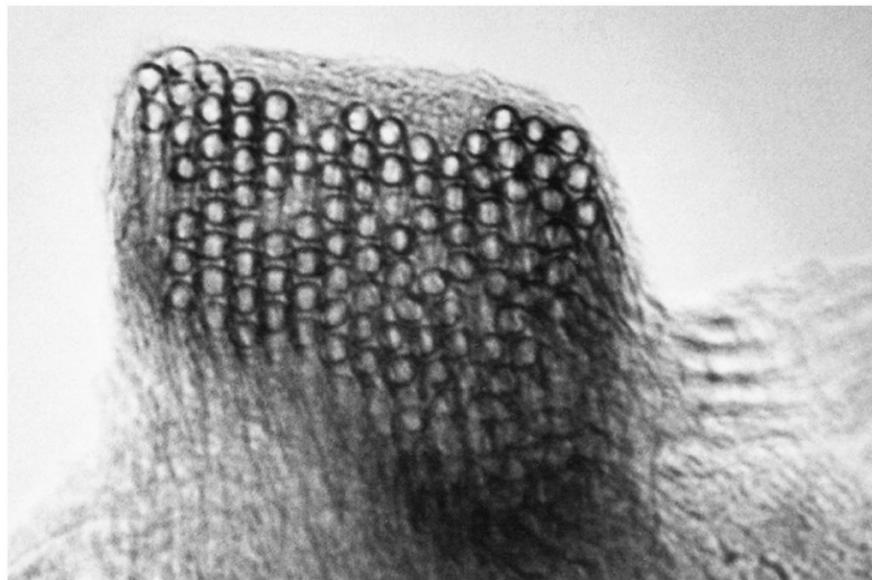
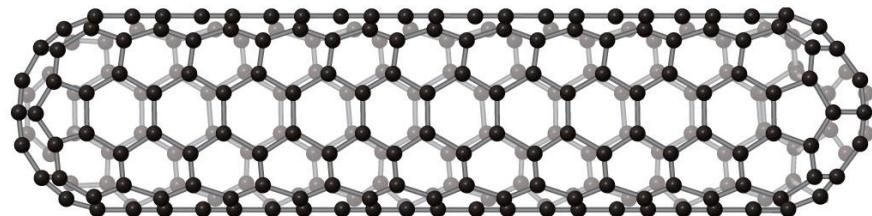
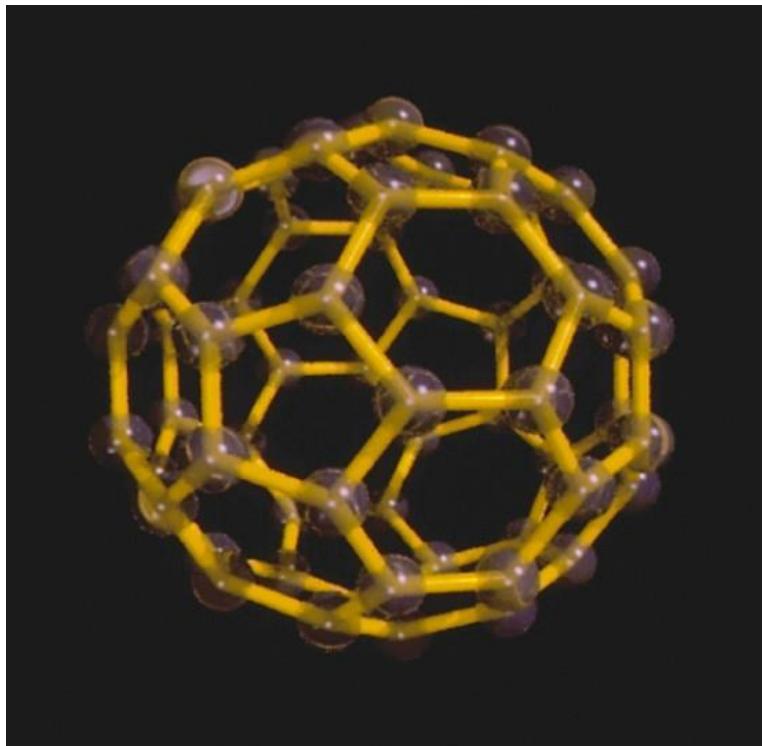
Other examples of H-Bonds



12-7 Network Covalent Solids and Ionic Solids

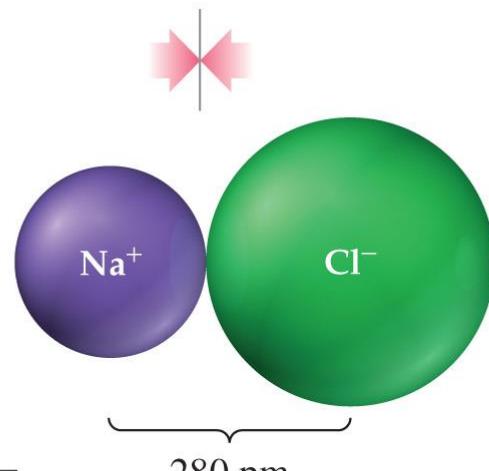


Other Carbon Allotropes



Interionic Forces

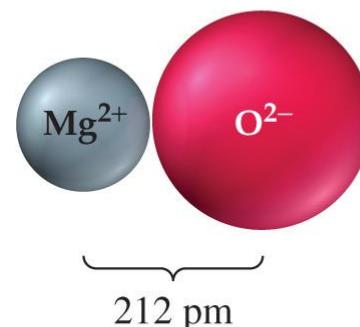
Attractive force



Radius sum =
distance between
center of ions:

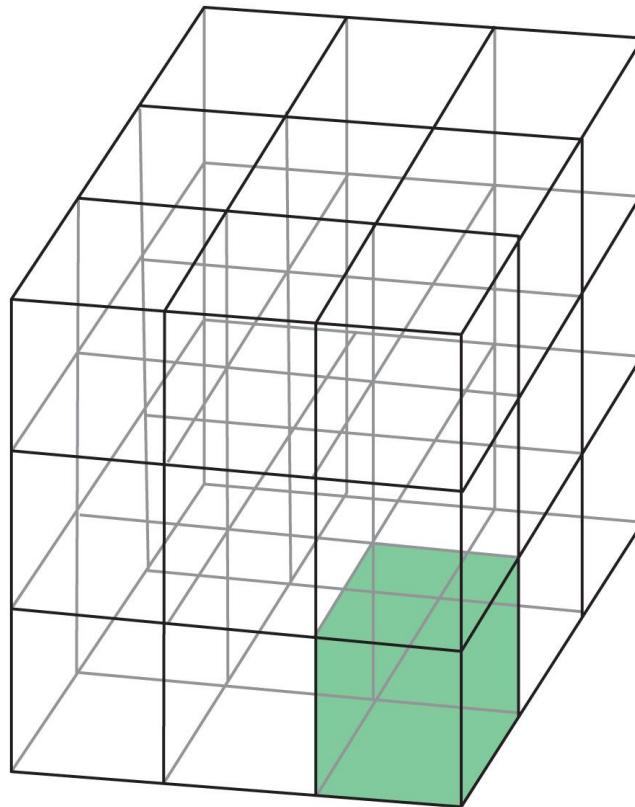
Radius:
 $\text{Na}^+ = 99 \text{ pm}$
 $\text{Cl}^- = 181 \text{ pm}$

Attractive force

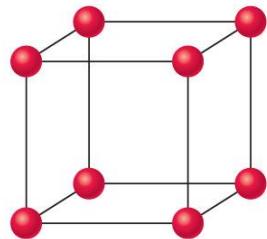


$$\begin{aligned}\text{Mg}^{2+} &= 72 \text{ pm} \\ \text{O}^{2-} &= 140 \text{ pm}\end{aligned}$$

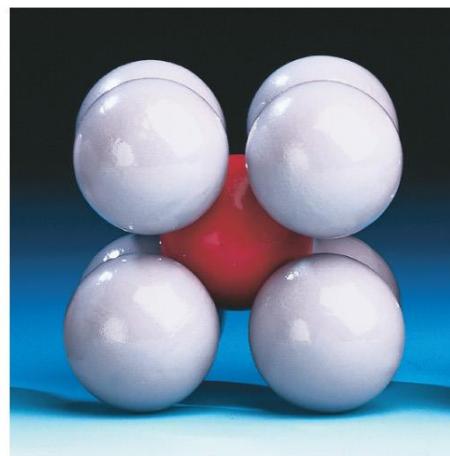
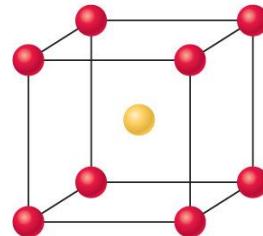
12-8 Crystal Structures



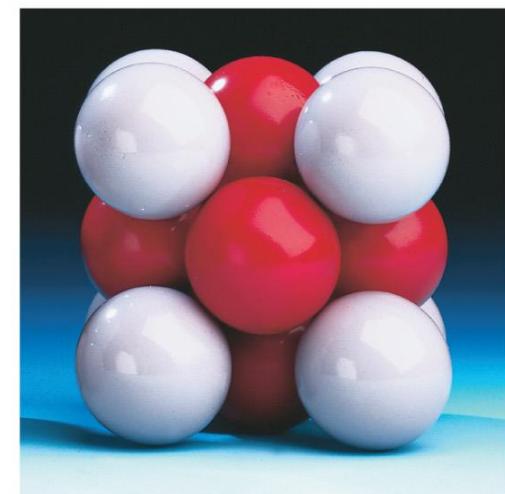
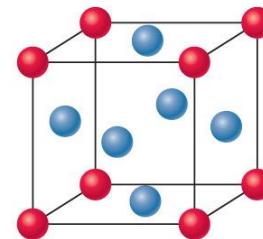
Unit Cells in the Cubic Crystal System



Simple cubic

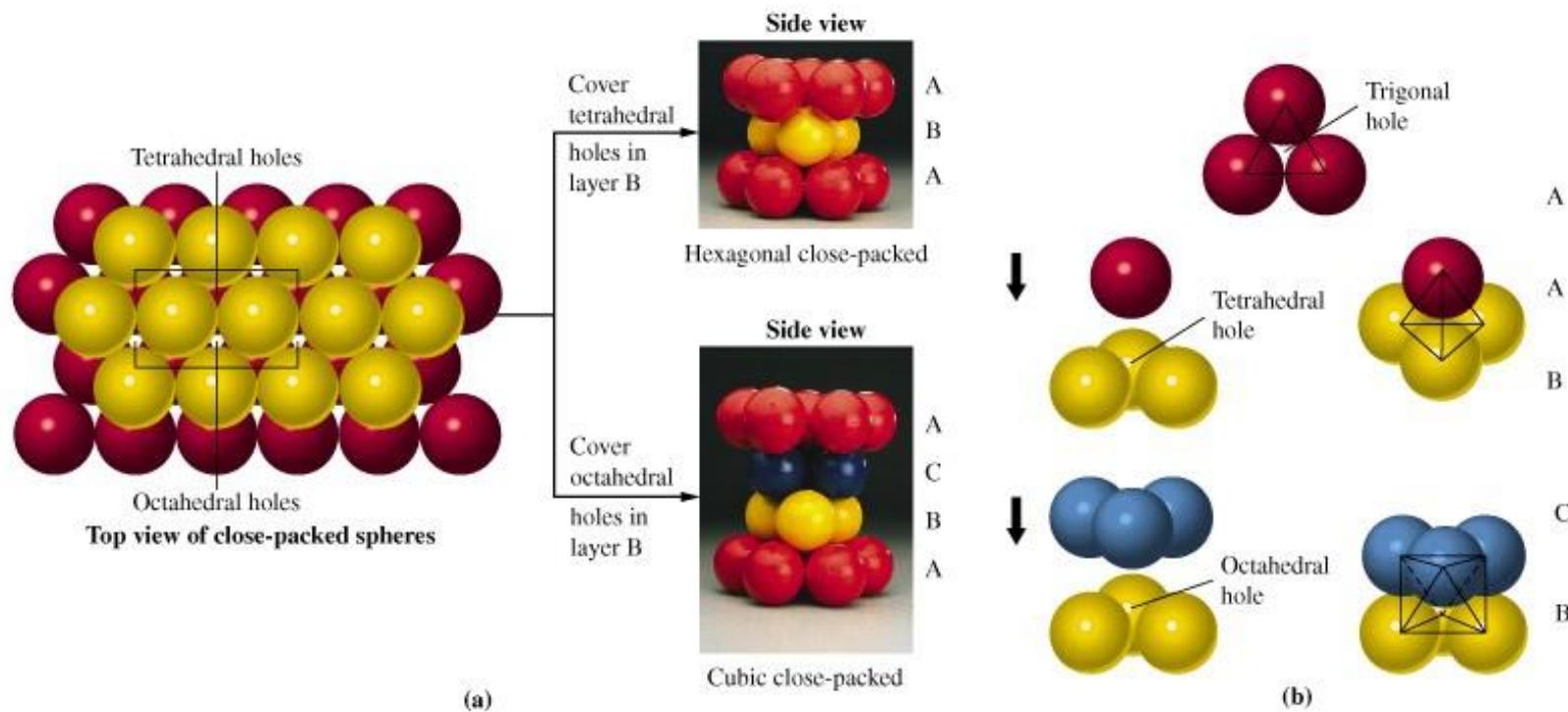


Body-centered cubic

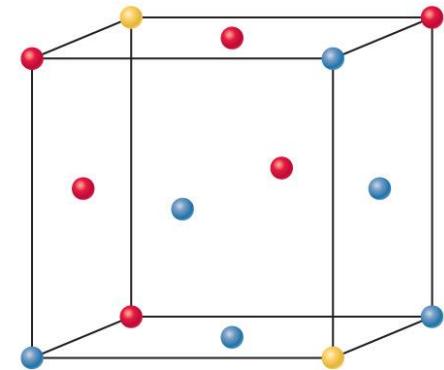
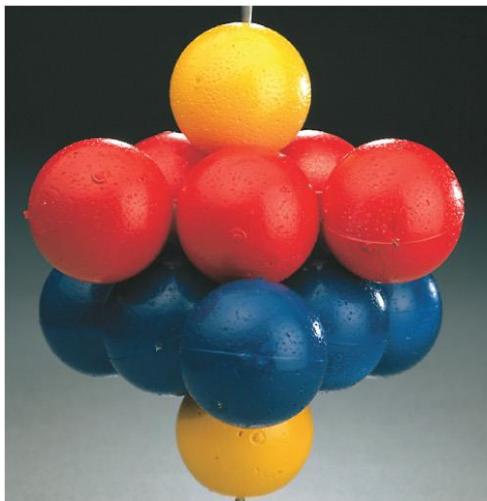


Face-centered cubic

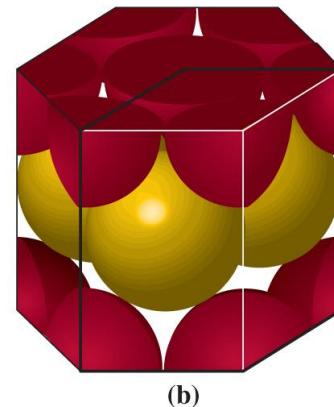
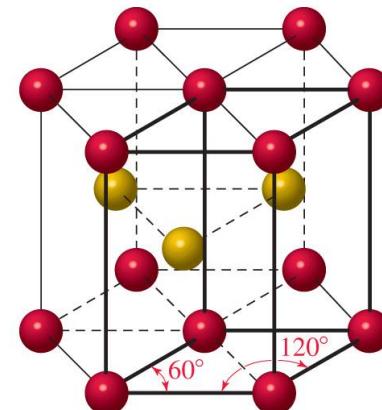
Holes in Crystals



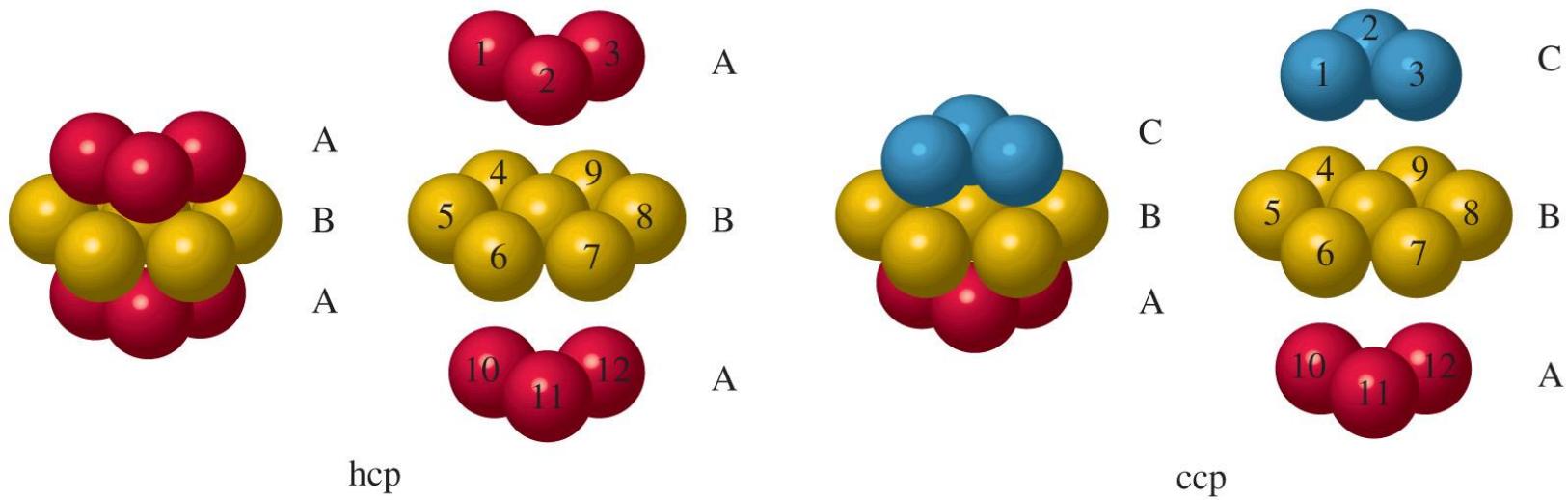
Face Centered Cubic Unit Cell



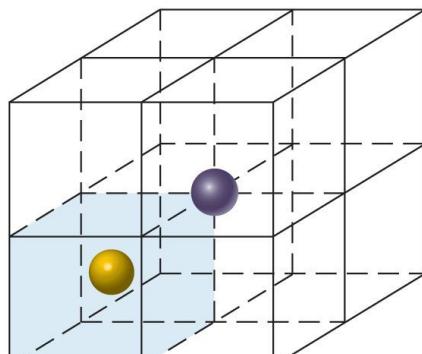
Hexagonal Close Packed (hcp)



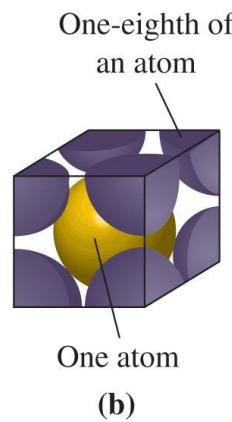
Coordination Number



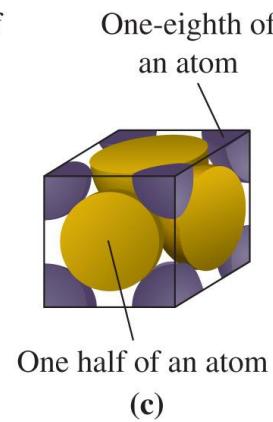
Counting Cell Occupancy



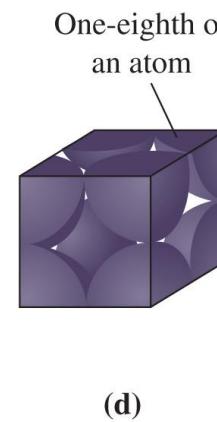
(a)



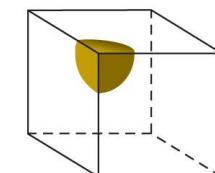
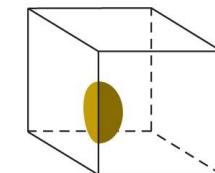
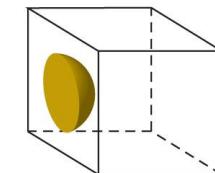
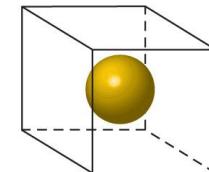
(b)
Body-centered
cubic



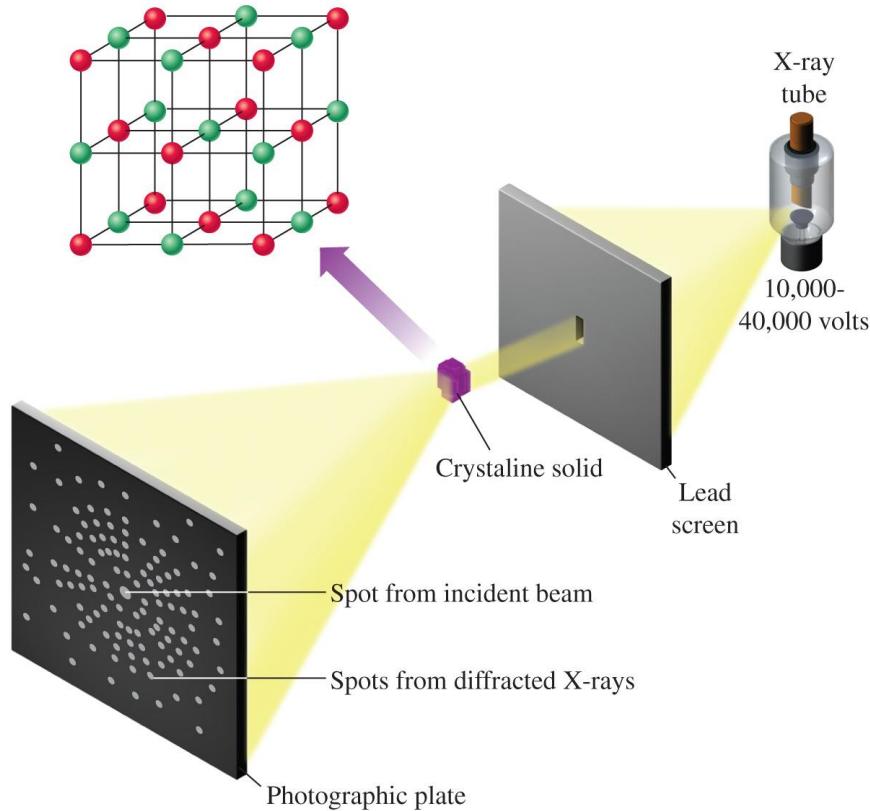
(c)
Face-centered
cubic



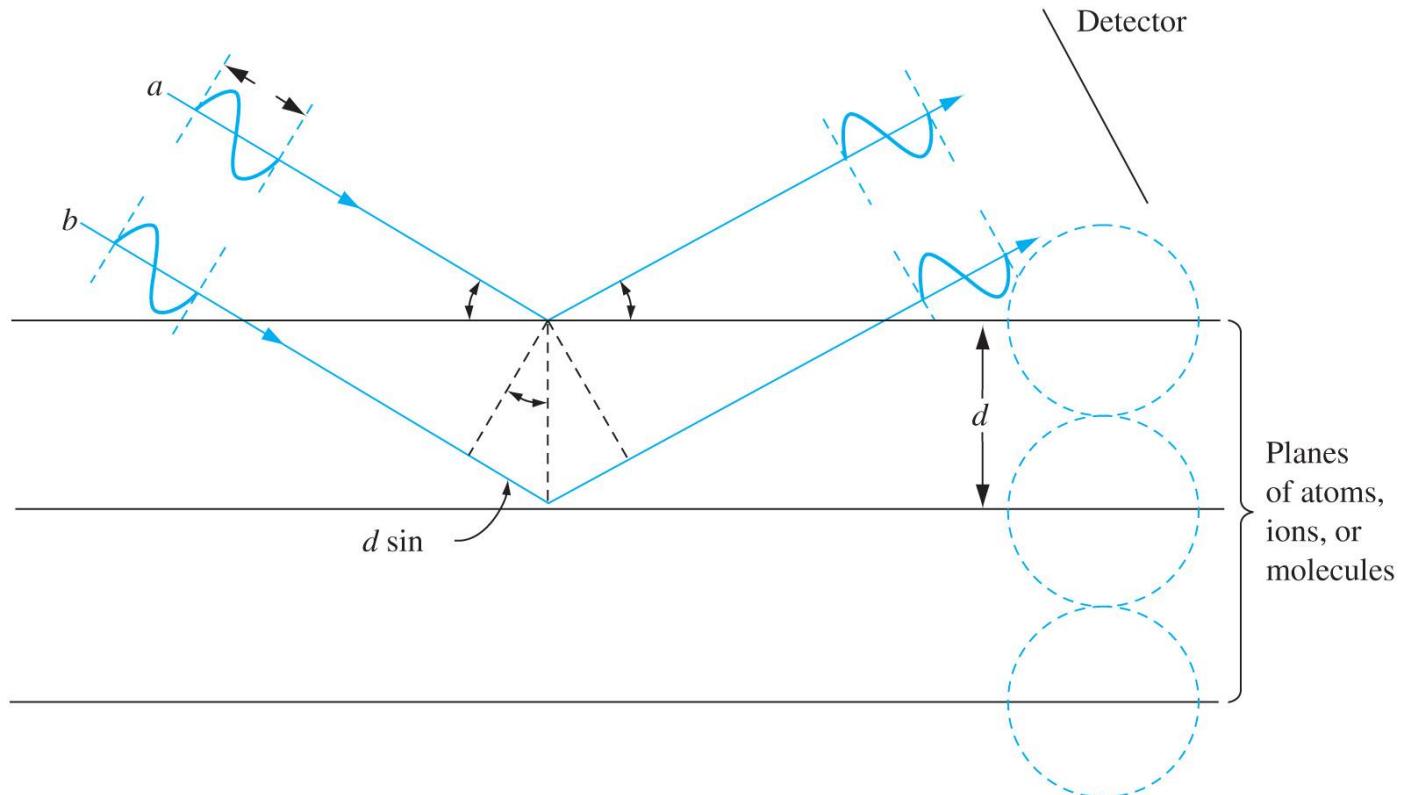
(d)
Simple
cubic



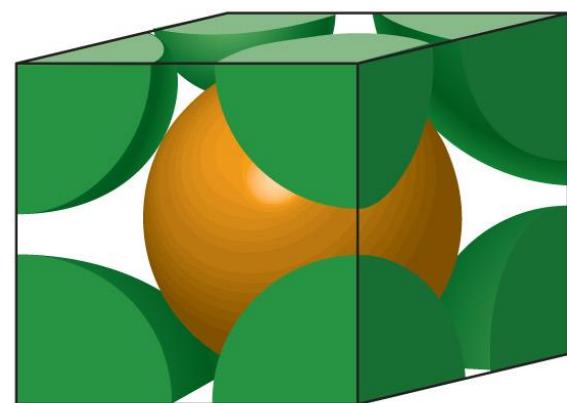
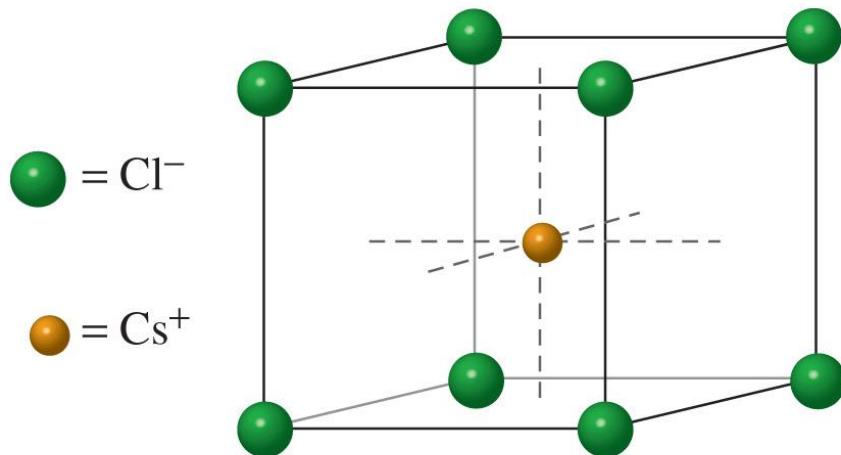
X-Ray Diffraction



X-Ray Diffraction

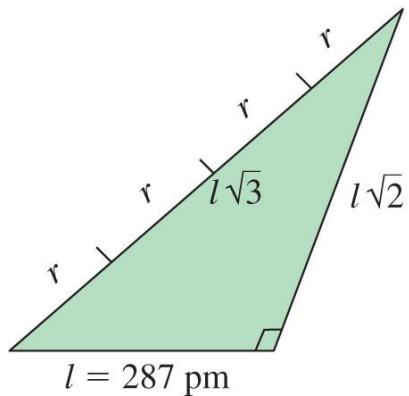
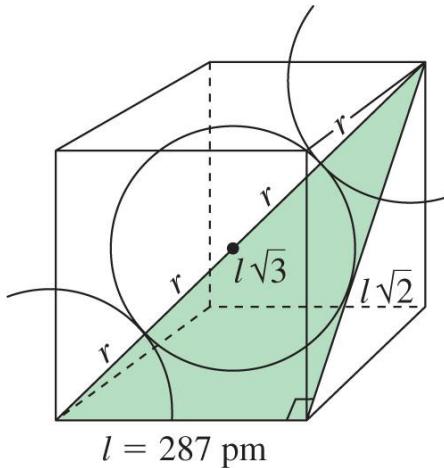


Cesium Chloride

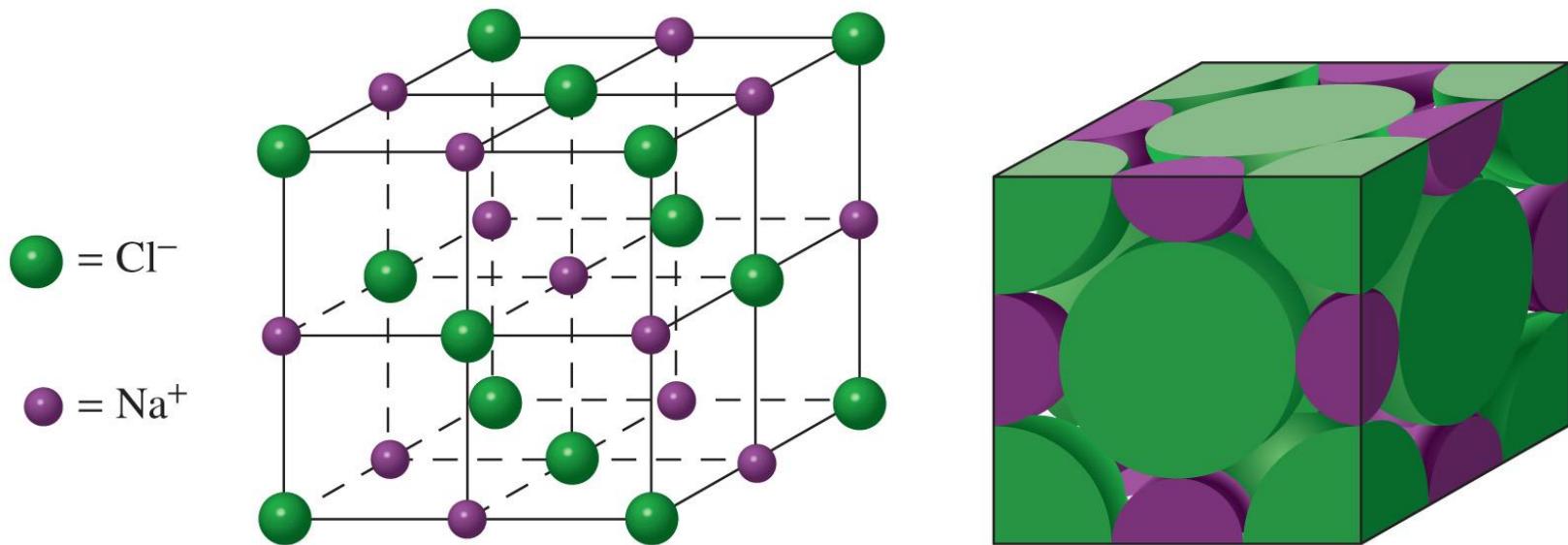


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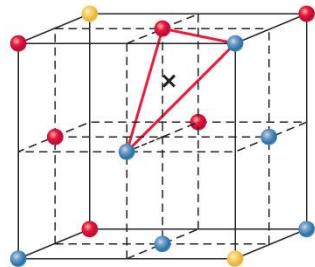
Atomic Radii from Crystal Structures



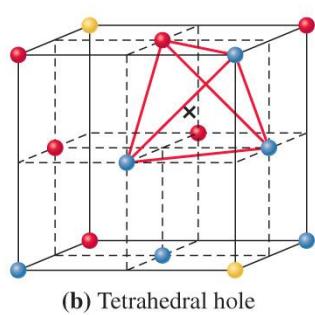
Sodium Chloride



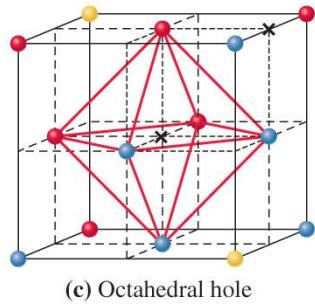
Holes in Crystals



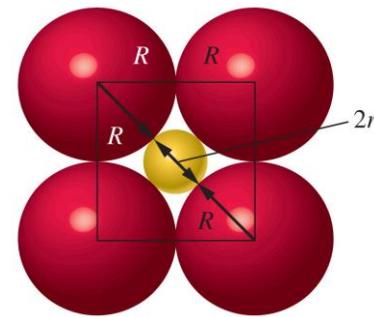
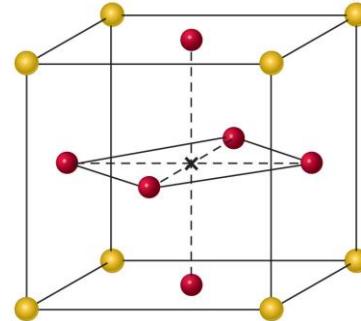
(a) Trigonal hole



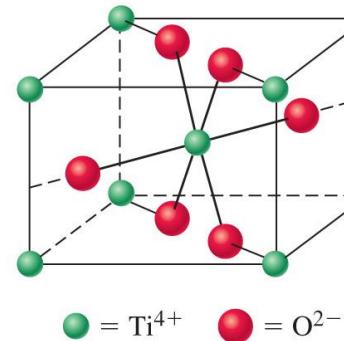
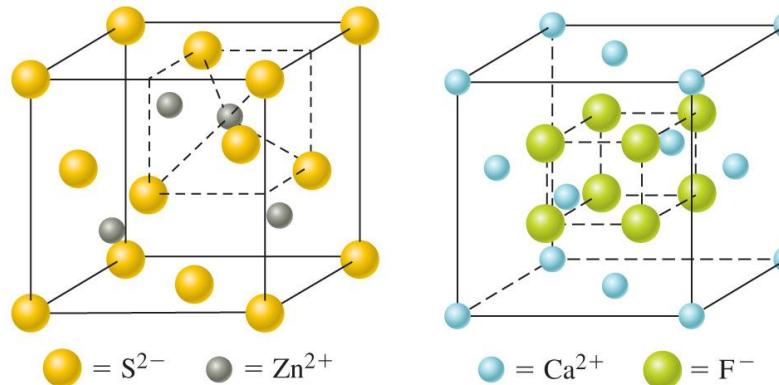
(b) Tetrahedral hole



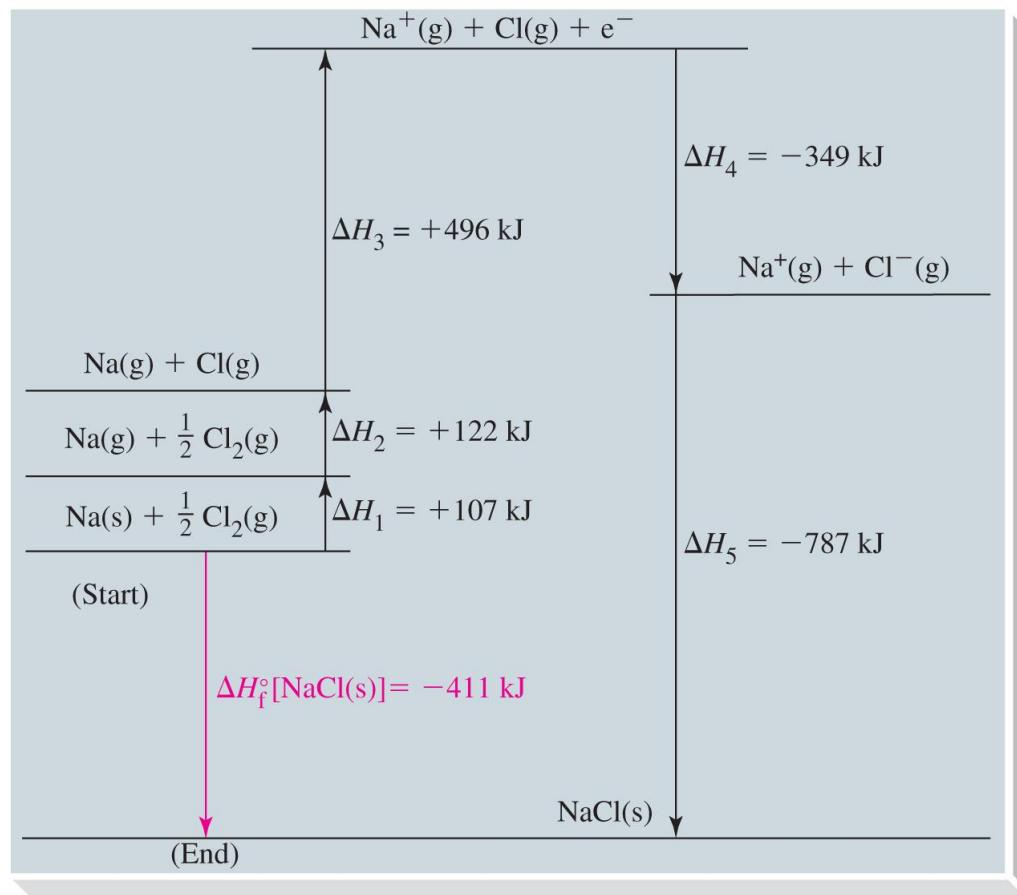
(c) Octahedral hole



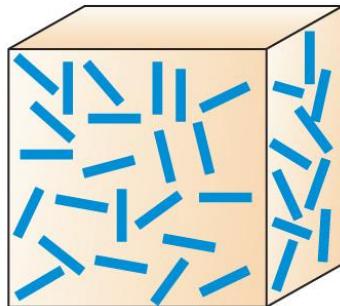
More Complex Unit Cells



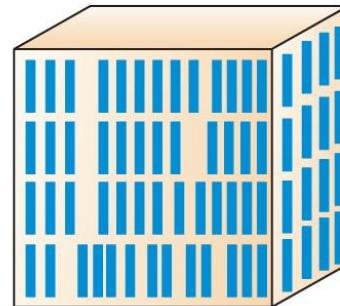
12-9 Energy Changes in the Formation of Ionic Crystals



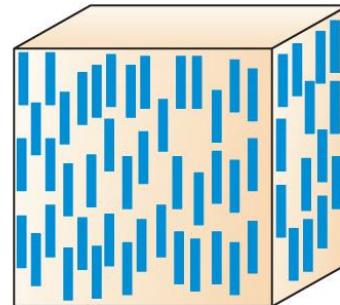
Focus On Liquid Crystals



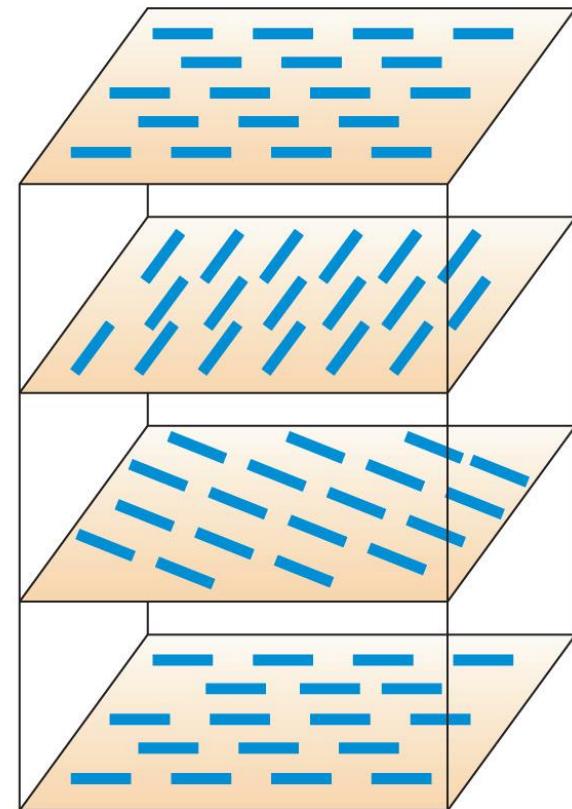
(a) Orientation of molecules in liquid



Smectic liquid crystal



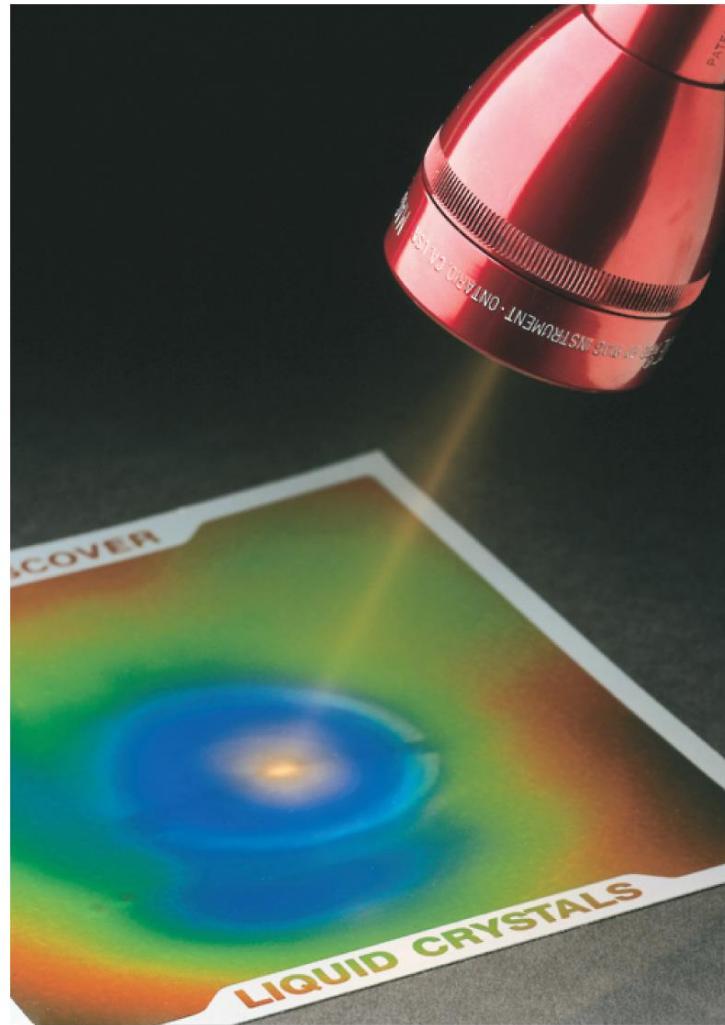
Nematic liquid crystal



Cholesteric liquid crystal

(b) Orientation of molecules in liquid crystals

Liquid Crystal Thermometers



End of Chapter Questions

- ◆ You can think about problems in reverse to help sort out a strategy.

