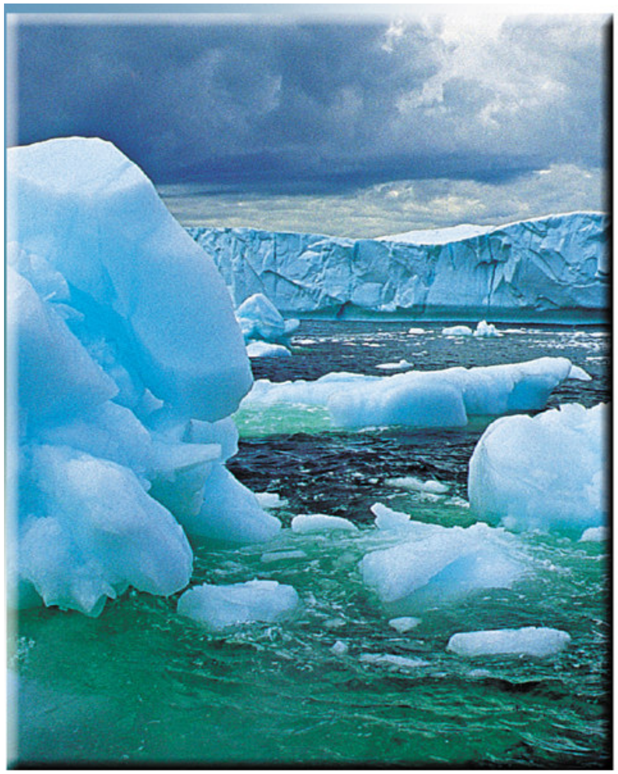


Intermolecular Forces and Liquids and Solids

Chapter 11

A ***phase*** is a homogeneous part of the system in contact with other parts of the system but separated from them by a well-defined boundary.

2 Phases

Solid phase - ice

Liquid phase - water

TABLE 11.1 Characteristic Properties of Gases, Liquids, and Solids

State of Matter	Volume/Shape	Density	Compressibility	Motion of Molecules
Gas	Assumes the volume and shape of its container	Low	Very compressible	Very free motion
Liquid	Has a definite volume but assumes the shape of its container	High	Only slightly compressible	Slide past one another freely
Solid	Has a definite volume and shape	High	Virtually incompressible	Vibrate about fixed positions

Intermolecular Forces

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

Intramolecular 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}

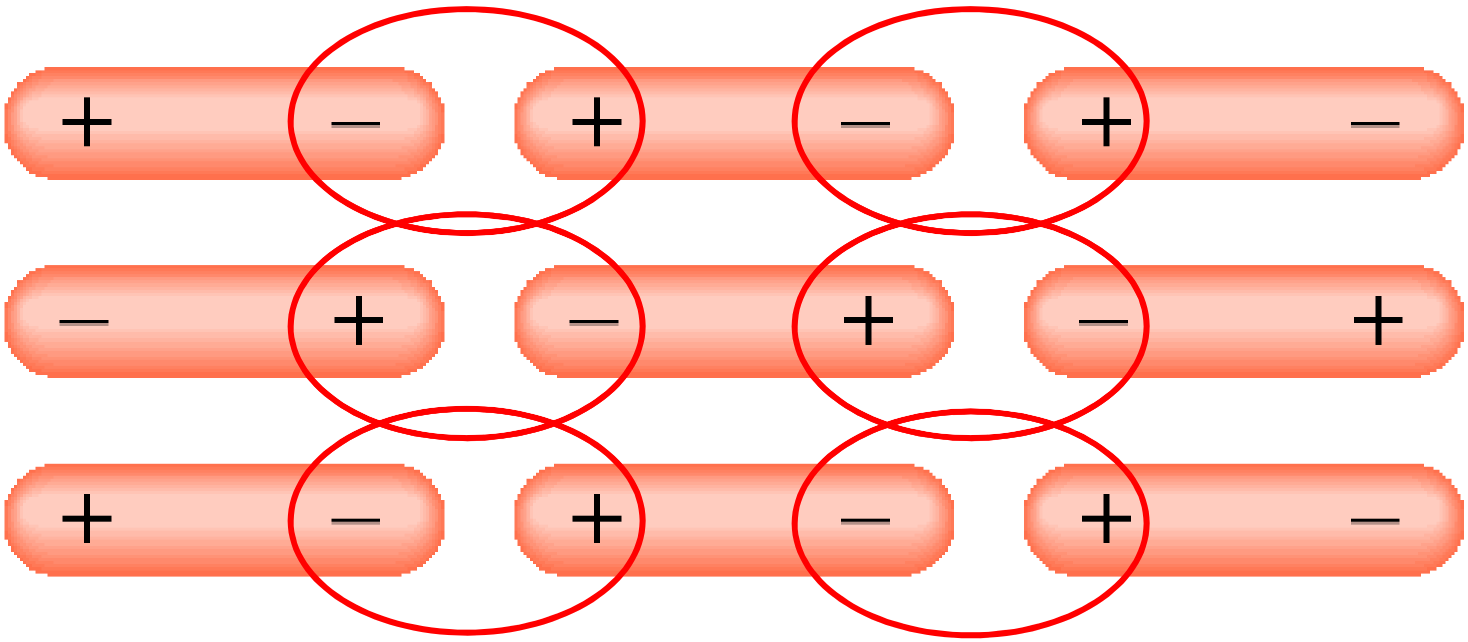
ΔH_{sub}

Intermolecular Forces

Dipole-Dipole Forces

Attractive forces between **polar molecules**

Orientation of Polar Molecules in a Solid

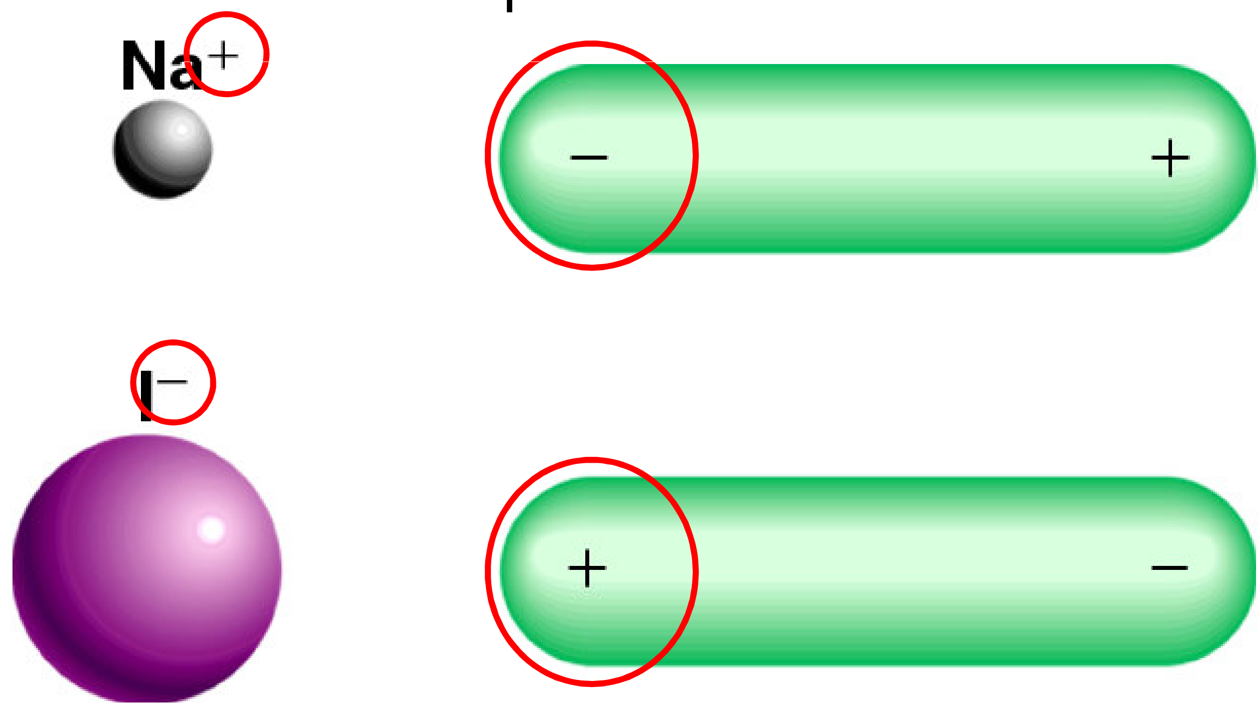


Intermolecular Forces

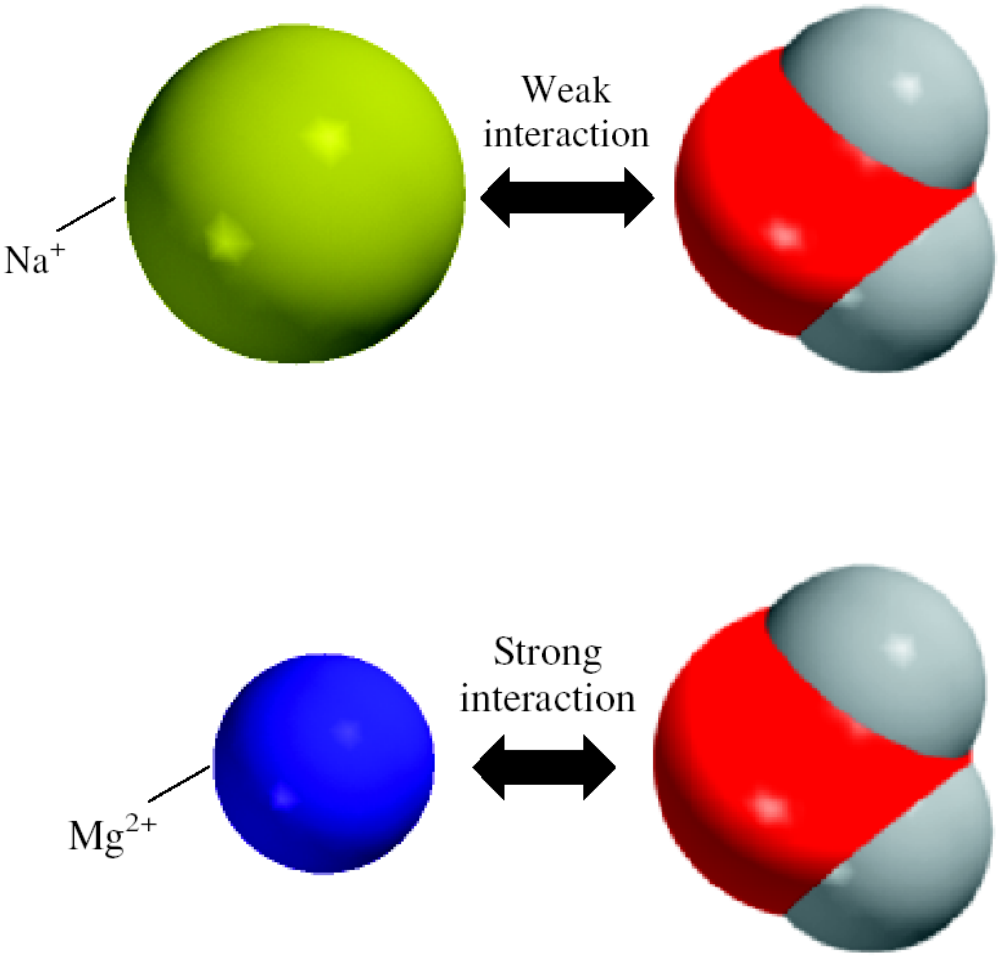
Ion-Dipole Forces

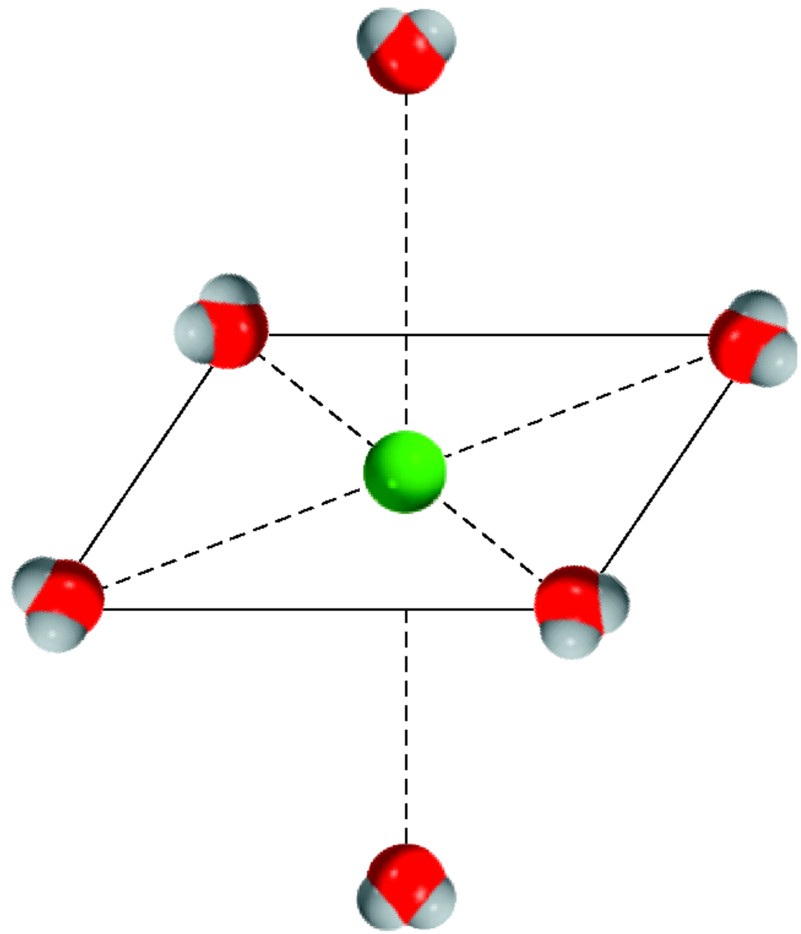
Attractive forces between an **ion** and a **polar molecule**

Ion-Dipole Interaction



Interaction Between Water and Cations



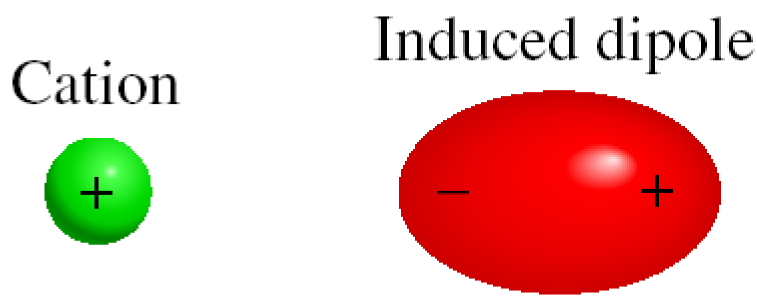


in solution

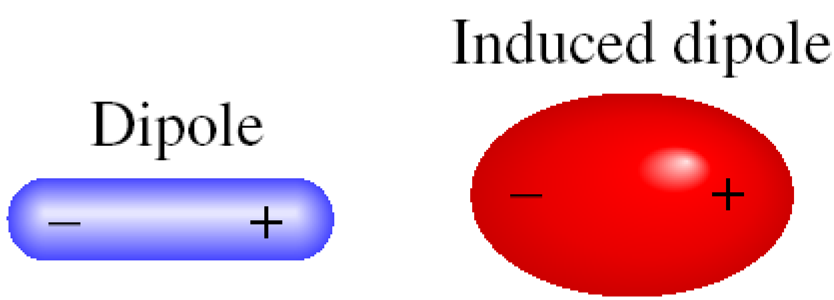
Intermolecular Forces

Dispersion Forces

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

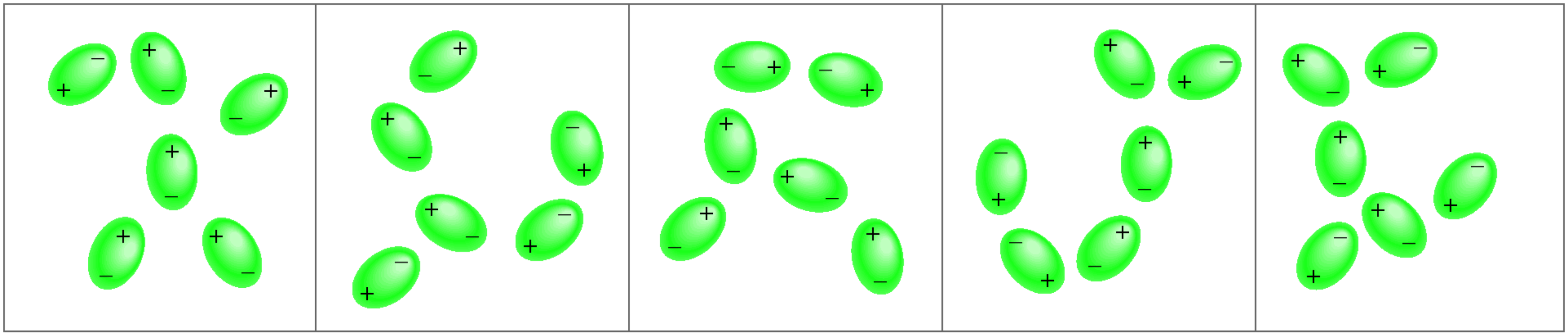


ion-induced dipole interaction



dipole-induced dipole interaction

Induced Dipoles Interacting With Each Other



Intermolecular Forces

Dispersion Forces Continued

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

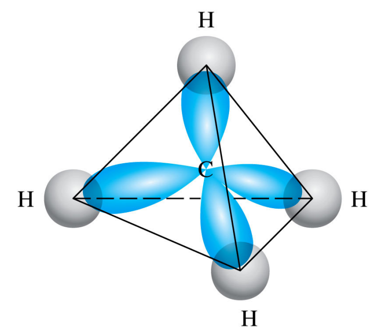
What type(s) of intermolecular forces exist between each of the following molecules?

HBr

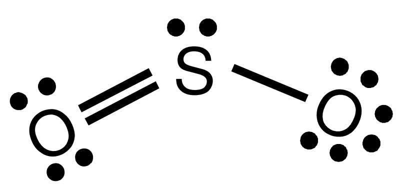
HBr is a polar molecule: dipole-dipole forces. There are also dispersion forces between HBr molecules.

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.

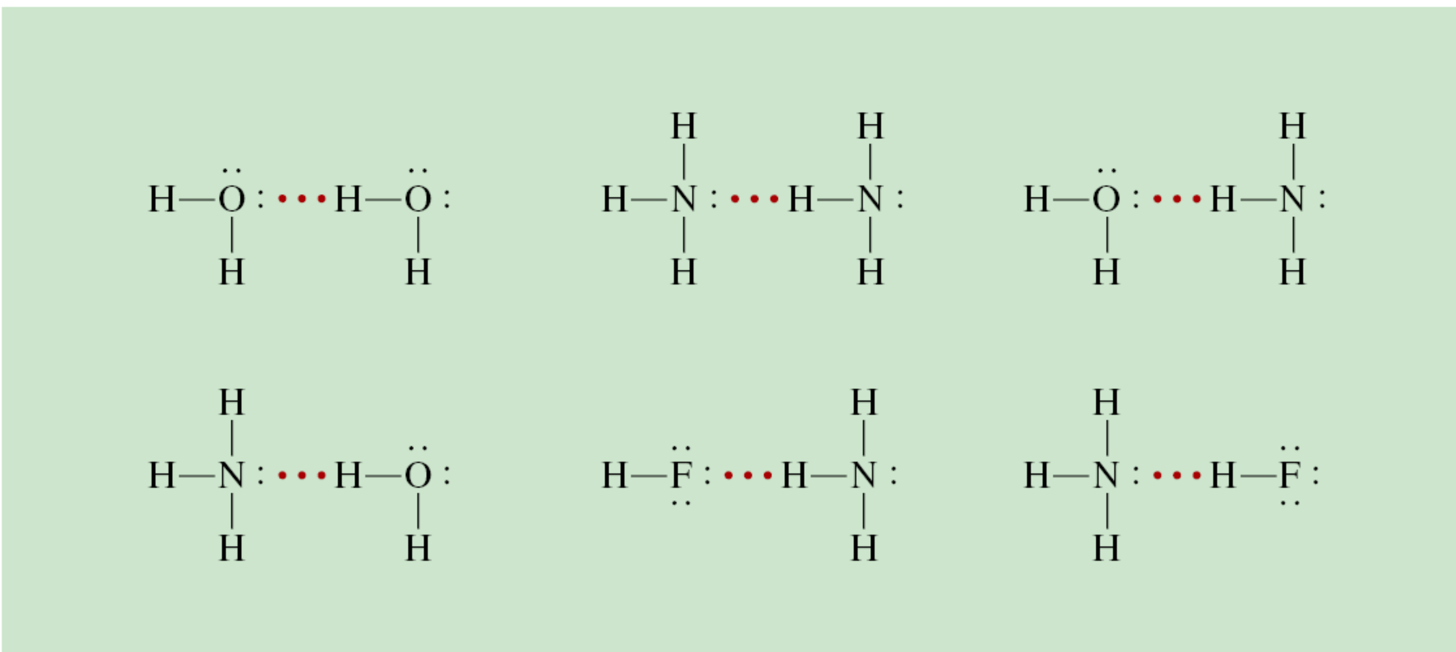
Intermolecular Forces

Hydrogen Bond

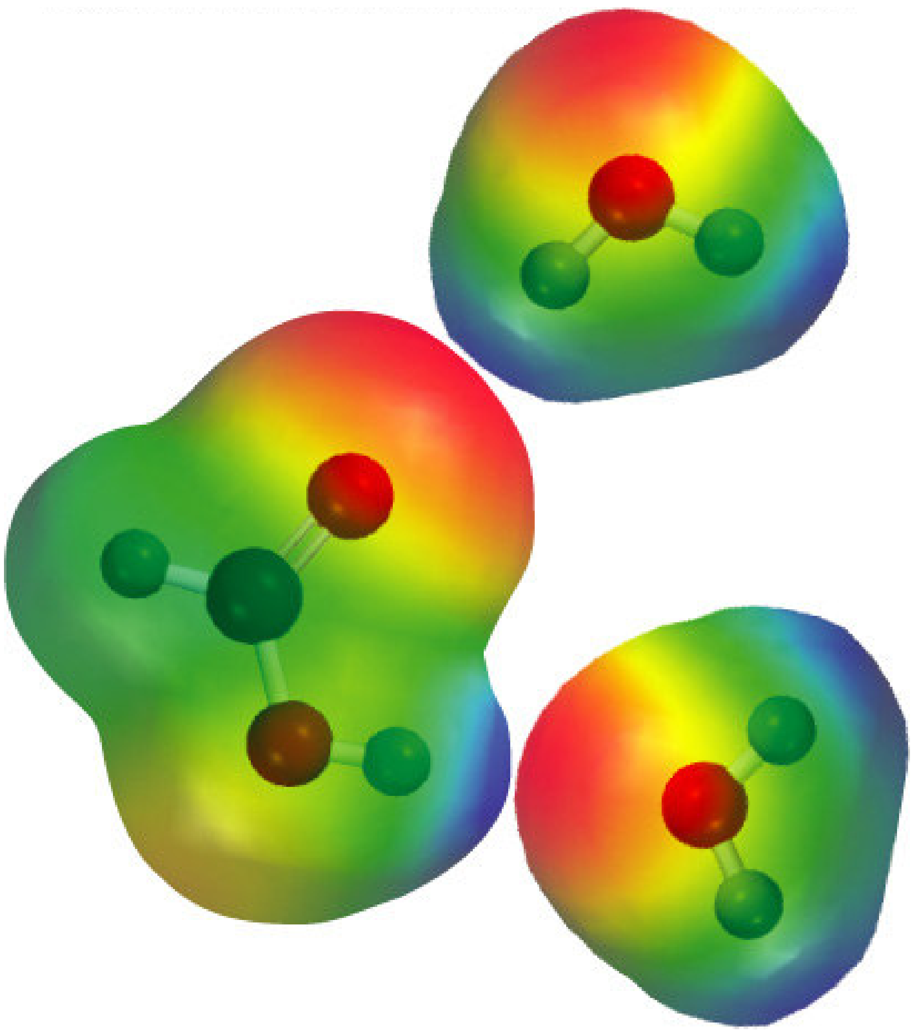
The ***hydrogen bond*** is a special dipole-dipole interaction between they hydrogen atom in a polar N-H, O-H, or F-H bond and an electronegative O, N, or F atom.

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

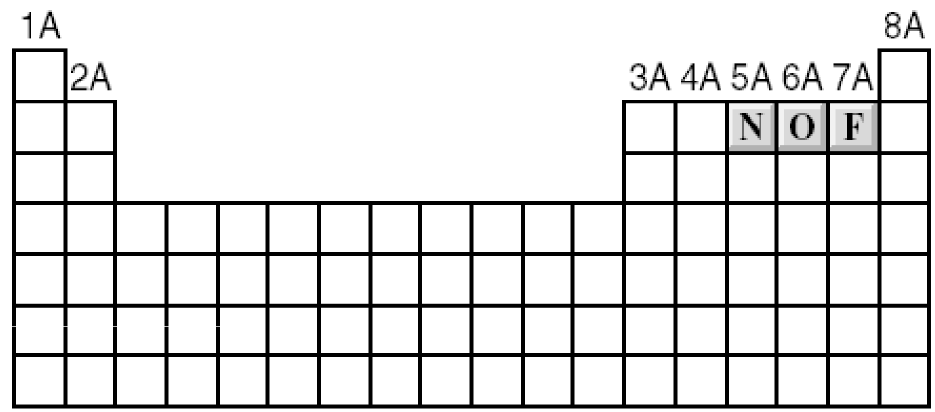
A & B are N, O, or F



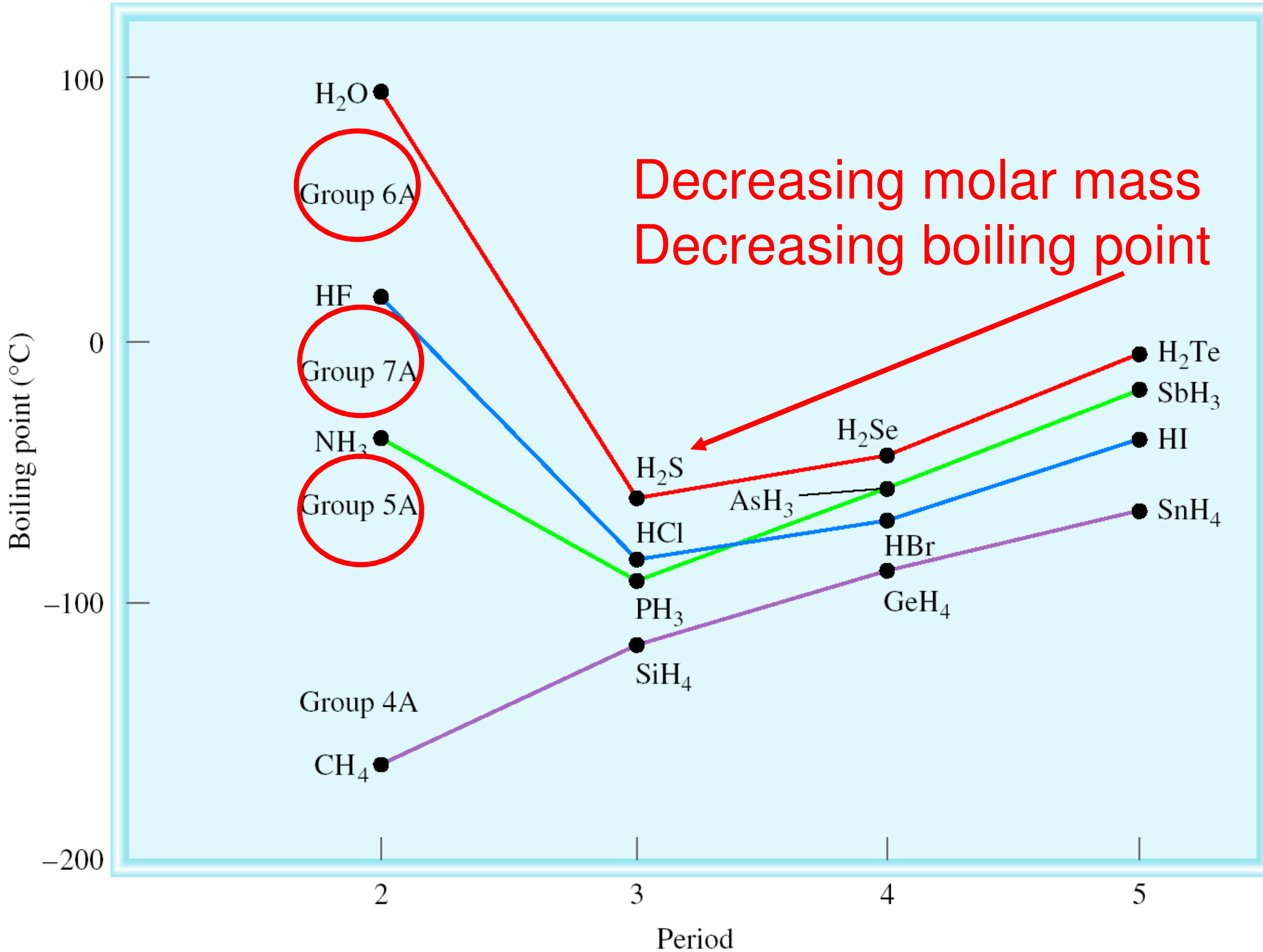
Hydrogen Bond



HCOOH and water



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

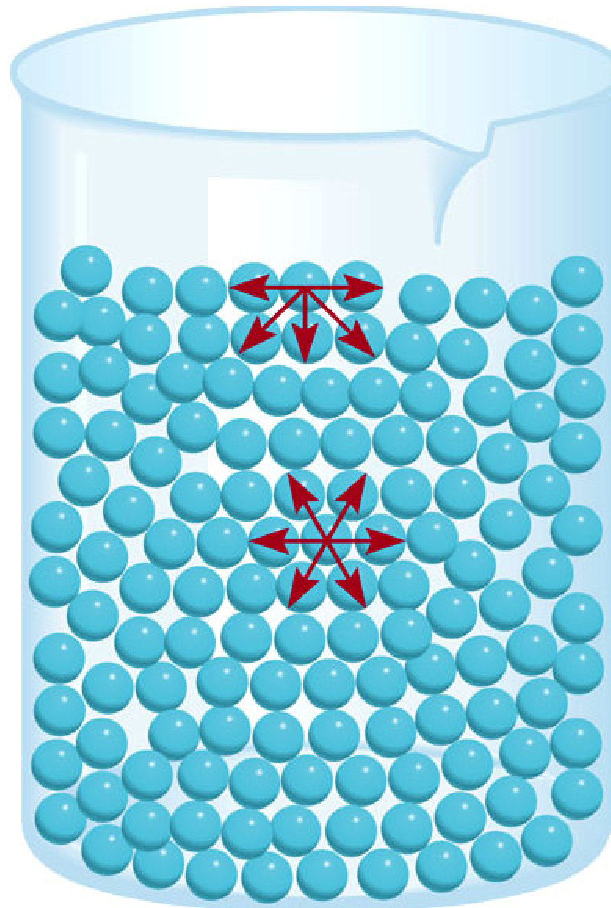


Properties of Liquids

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

Strong intermolecular forces

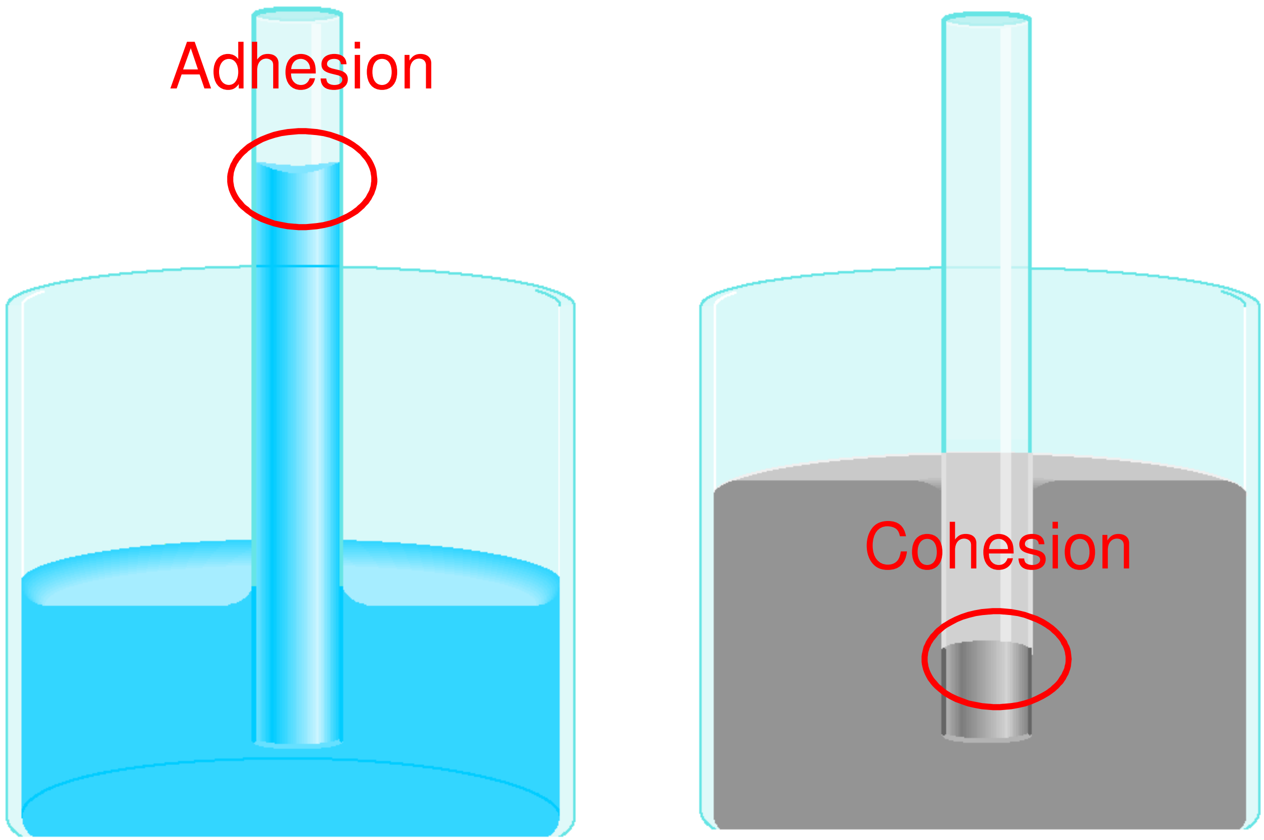
High surface tension



Properties of Liquids

Cohesion is the intermolecular attraction between like molecules

Adhesion is an attraction between unlike molecules



Properties of Liquids

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

Strong intermolecular forces

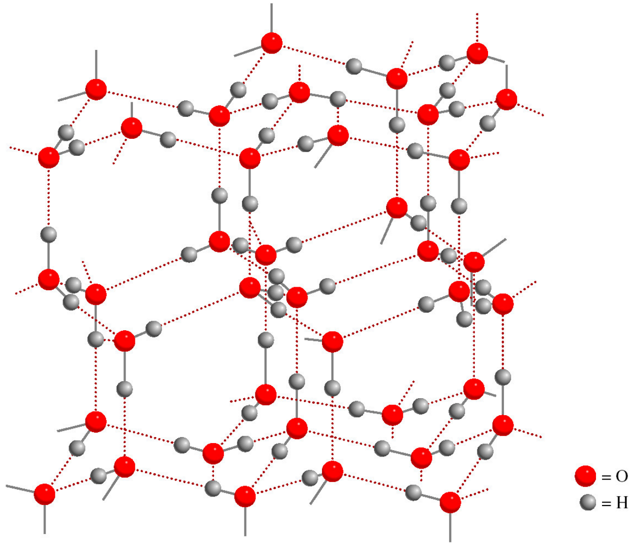
High viscosity

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.

3-D Structure of Water

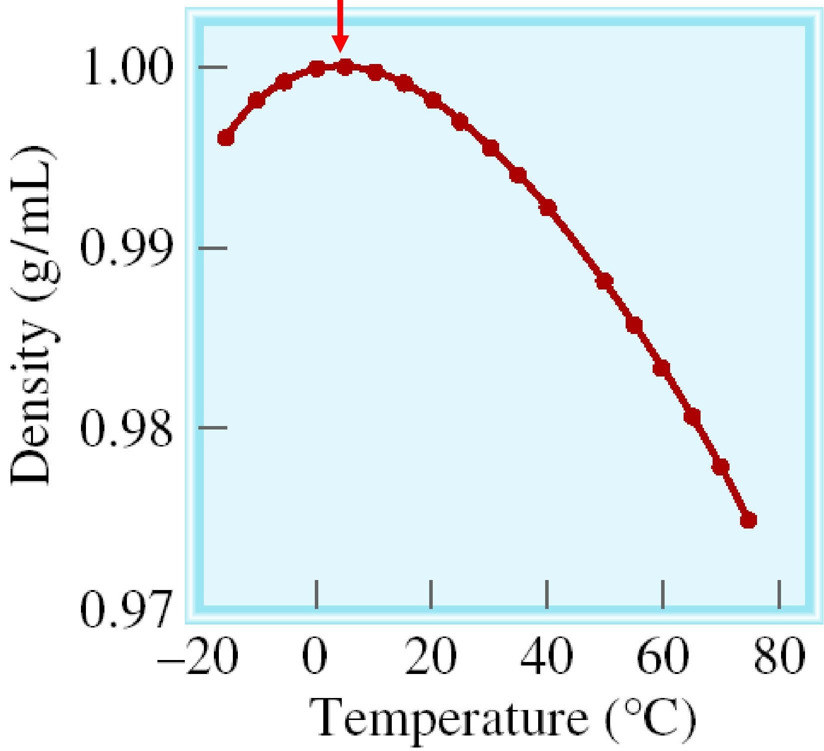


Ice is less dense than water

Water is a Unique Substance

Maximum Density
4^0C

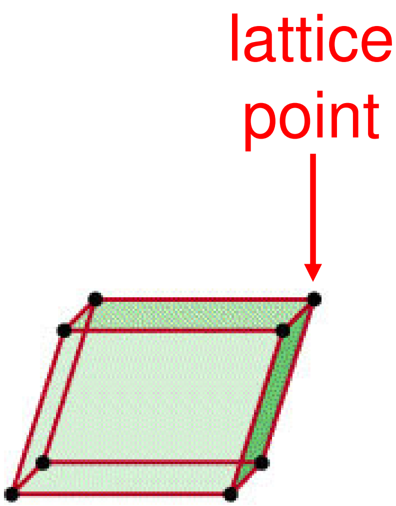
Density of Water



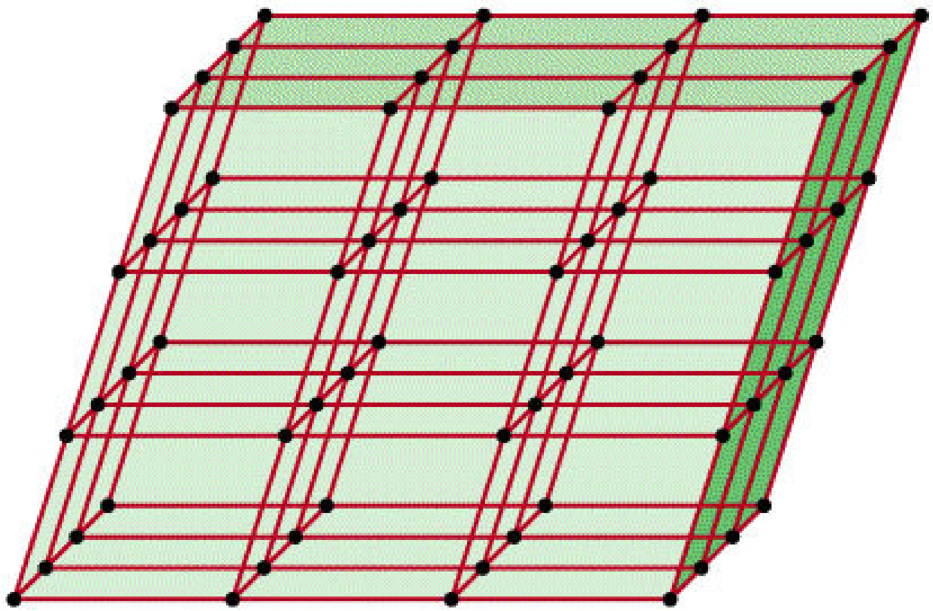
A ***crystalline solid*** possesses rigid and long-range order. In a crystalline solid, atoms, molecules or ions occupy specific (predictable) positions.

An ***amorphous solid*** does not possess a well-defined arrangement and long-range molecular order.

A ***unit cell*** is the basic repeating structural unit of a crystalline solid.



Unit Cell

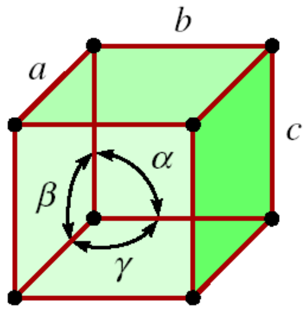


Unit cells in 3 dimensions

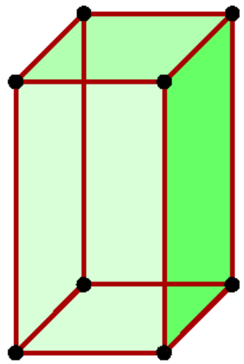
At lattice points:

- Atoms
- Molecules
- Ions

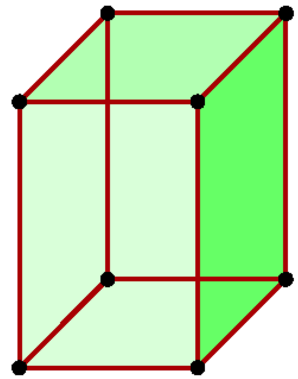
Seven Basic Unit Cells



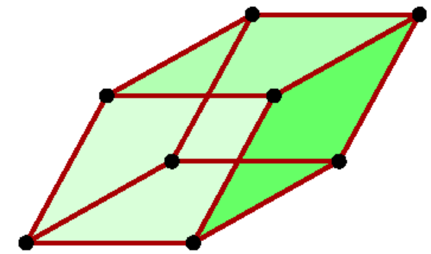
Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$



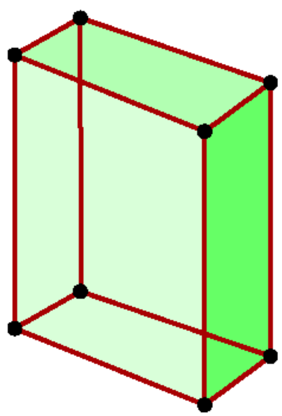
Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$



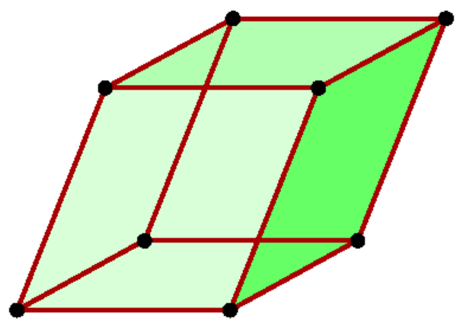
Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



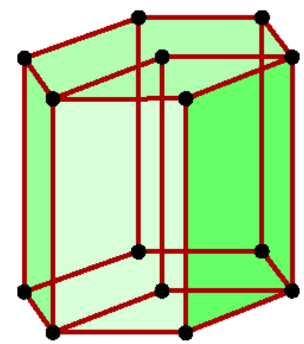
Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$



Monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90°$

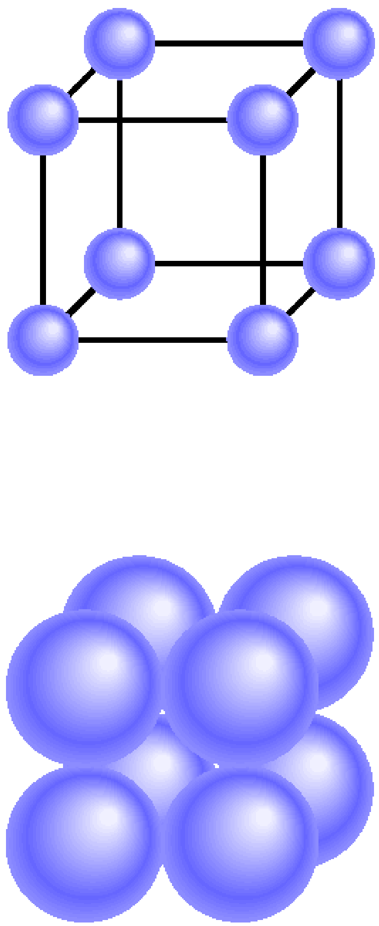


Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

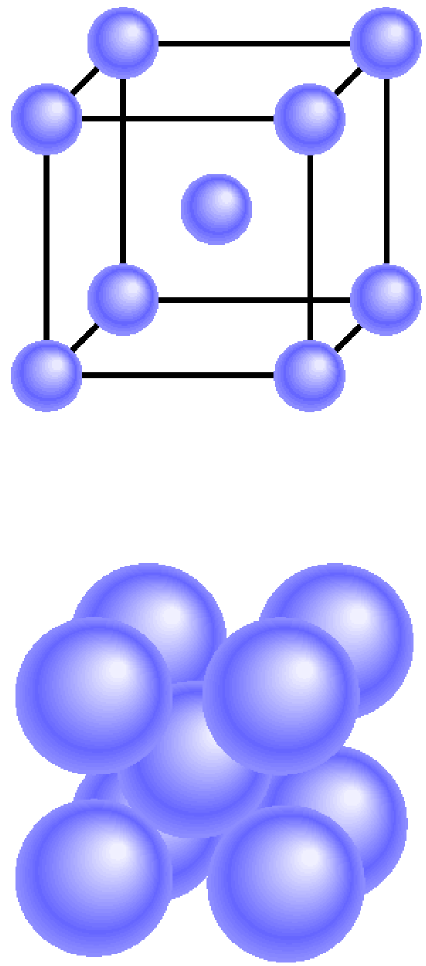


Hexagonal
$a = b \neq c$
$\alpha = \beta = 90°,\ \gamma = 120°$

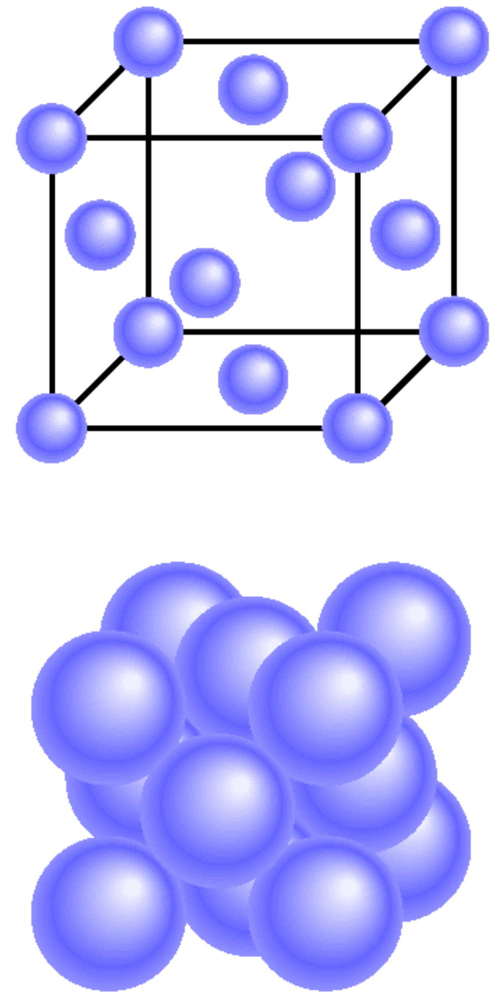
Three Types of Cubic Unit Cells



Simple cubic

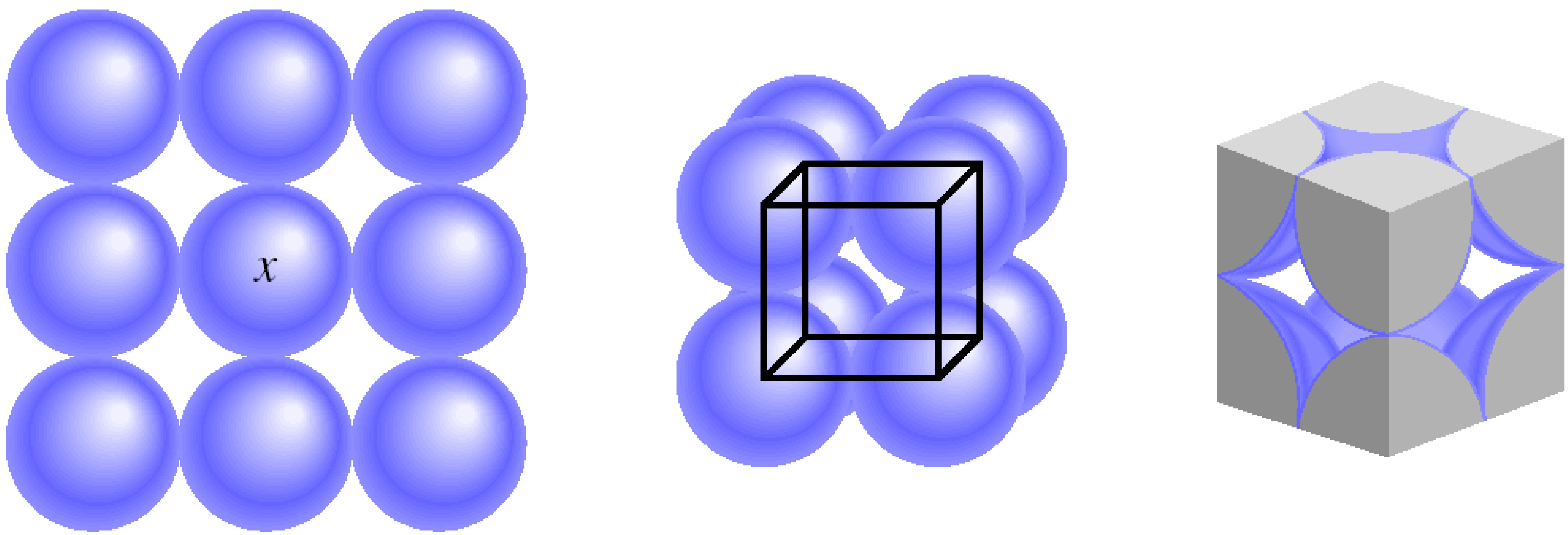


Body-centered cubic

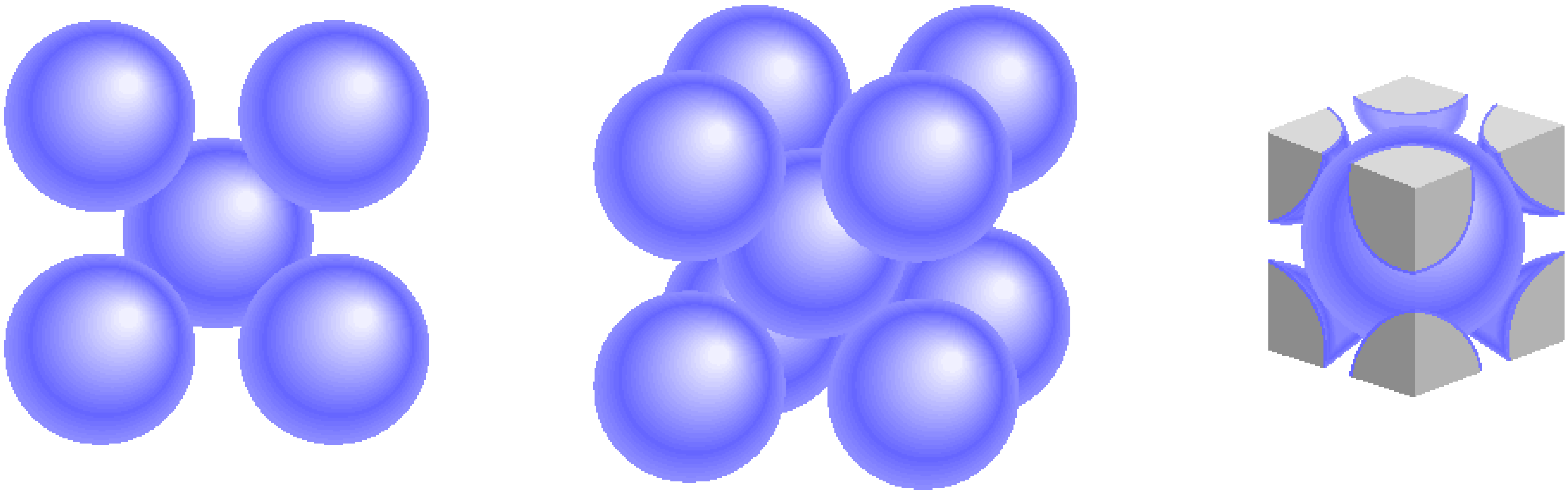


Face-centered cubic

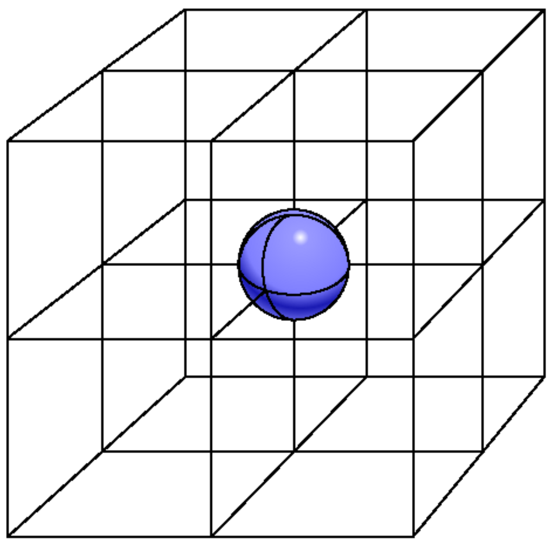
Arrangement of Identical Spheres in a Simple Cubic Cell



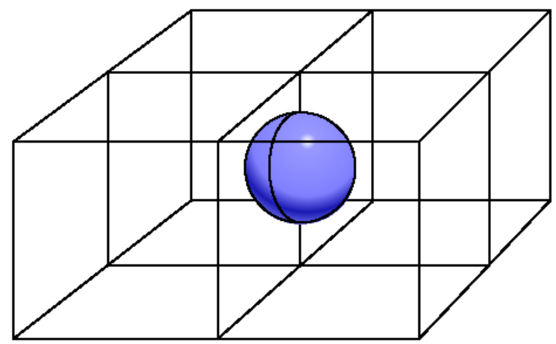
Arrangement of Identical Spheres in a Body-Centered Cubic Cell



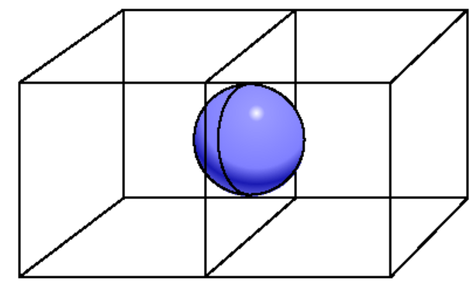
A Corner Atom, a Edge-Centered Atom and a Face-Centered Atom



Shared by 8 unit cells

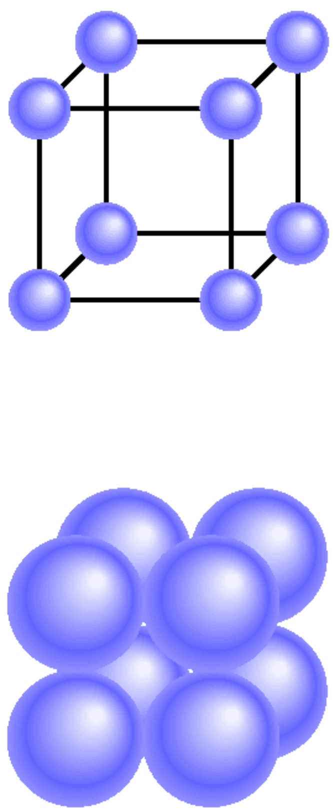


Shared by 4 unit cells



Shared by 2 unit cells

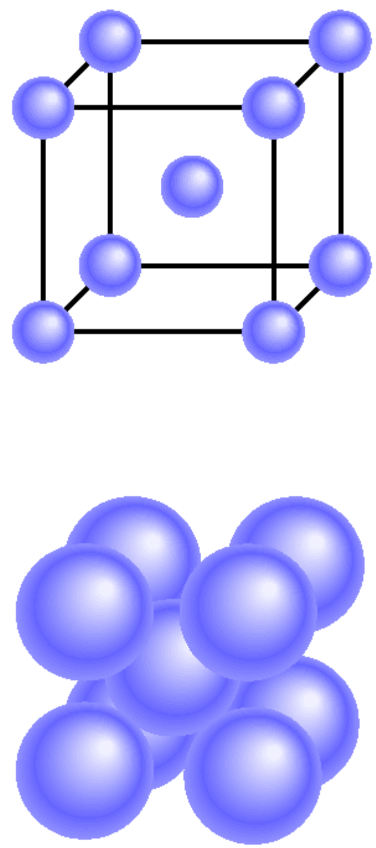
Number of Atoms Per Unit Cell



Simple cubic

1 atom/unit cell

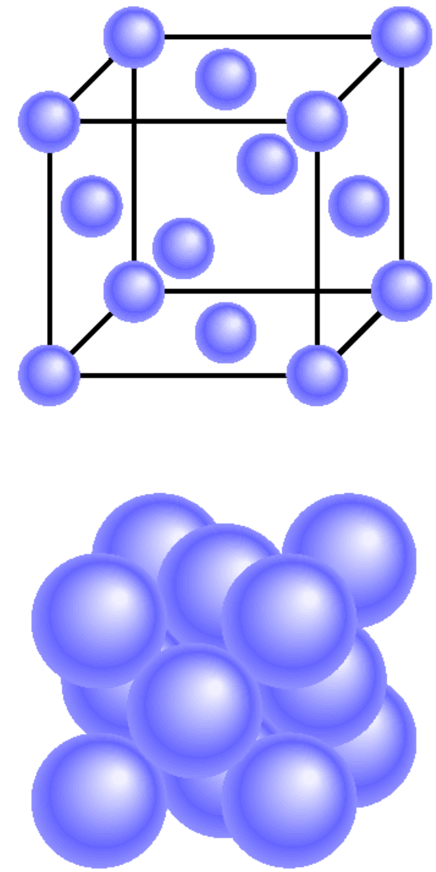
(8 x 1/8 = 1)



Body-centered cubic

2 atoms/unit cell

(8 x 1/8 + 1 = 2)

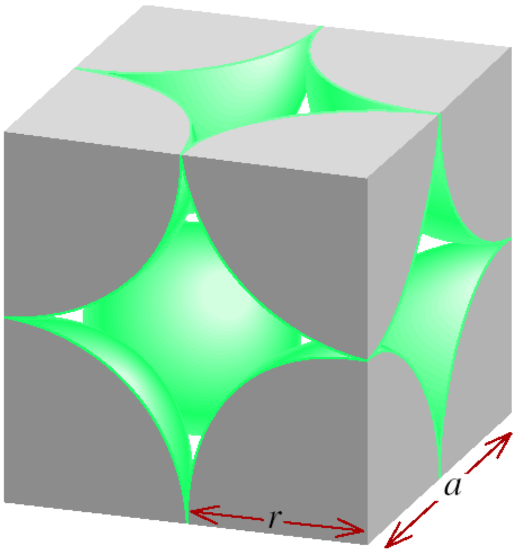


Face-centered cubic

4 atoms/unit cell

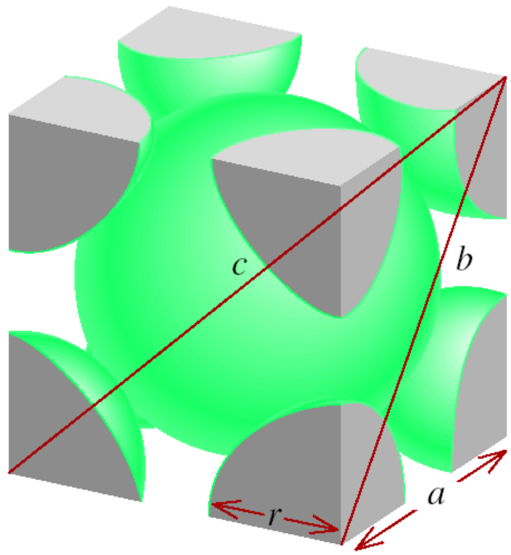
(8 x 1/8 + 6 x 1/2 = 4)

Relation Between Edge Length and Atomic Radius



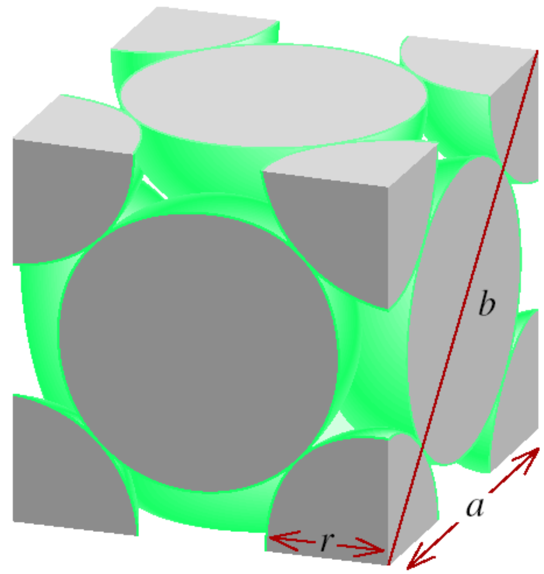
scc

$$a = 2r$$



bcc

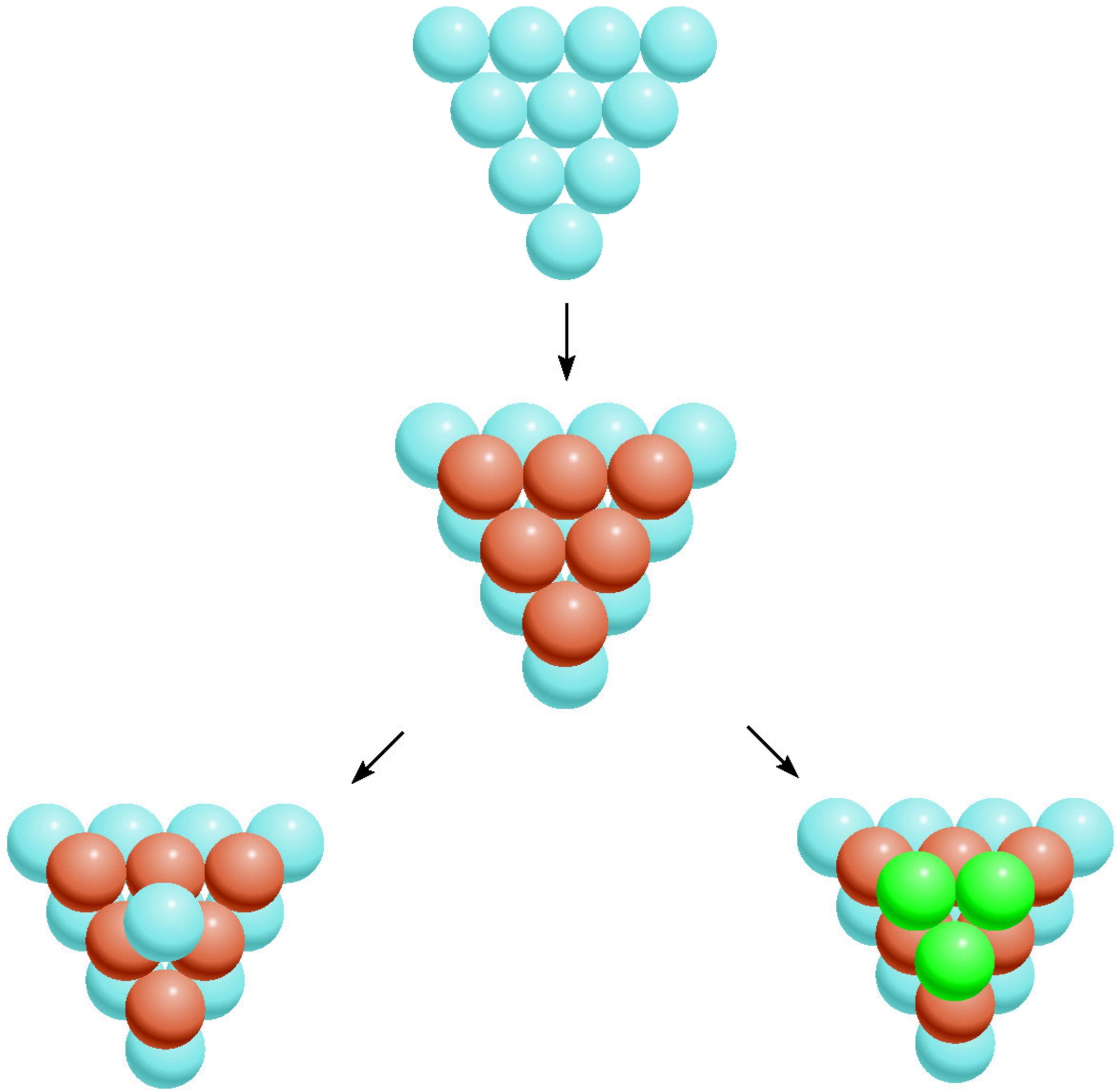
$$\begin{aligned} b^2 &= a^2 + a^2 \\ c^2 &= a^2 + b^2 \\ &= 3a^2 \\ c &= \sqrt{3}a = 4r \\ a &= \frac{4r}{\sqrt{3}} \end{aligned}$$



fcc

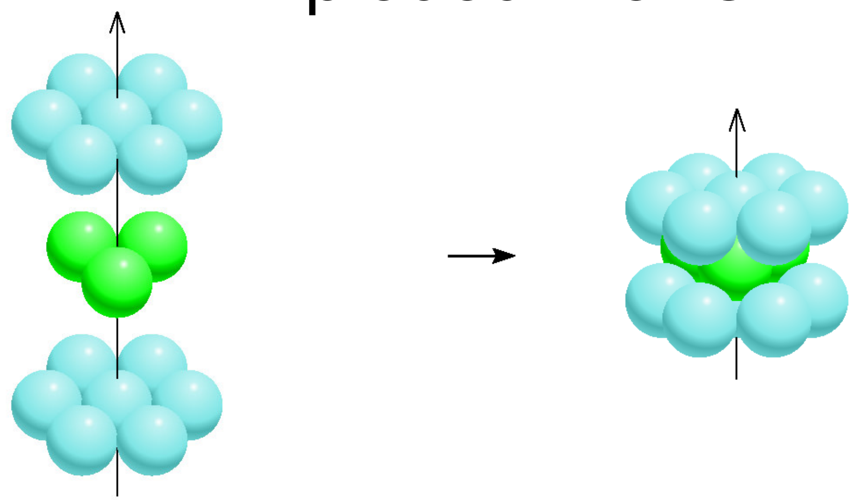
$$\begin{aligned} b &= 4r \\ b^2 &= a^2 + a^2 \\ 16r^2 &= 2a^2 \\ a &= \sqrt{8}r \end{aligned}$$

Closet Packing: Hexagonal and Cubic



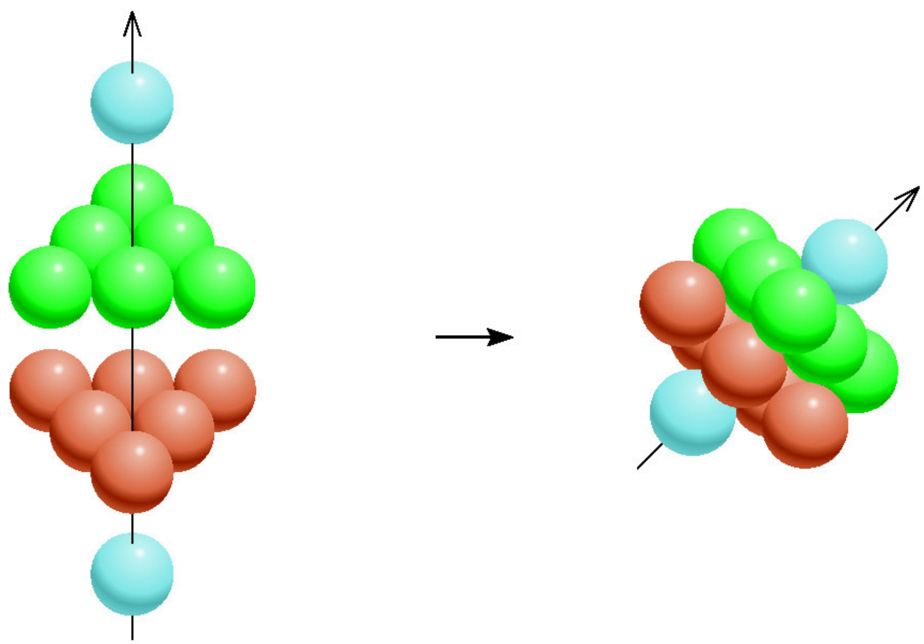
hexagonal cubic

Exploded Views



Exploded view

Hexagonal close-packed structure



Exploded view

Cubic close-packed structure

When silver crystallizes, it forms face-centered cubic cells. The unit cell edge length is 409 pm. Calculate the density of silver.

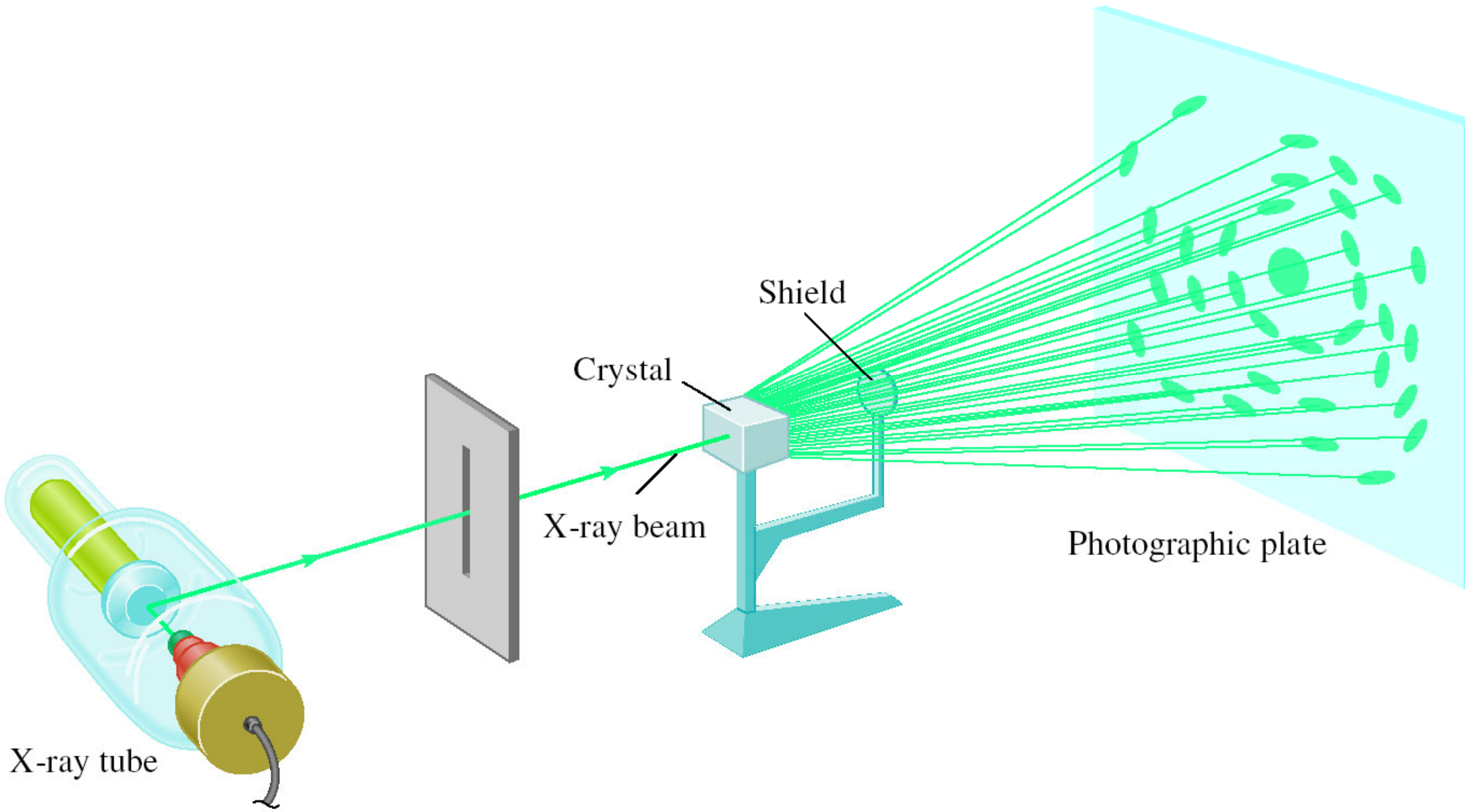
$$d = \frac{m}{V} \qquad V = a^3 = (409\text{ pm})^3 = 6.83 \times 10^{-23}\text{ cm}^3$$

4 atoms/unit cell in a face-centered cubic cell

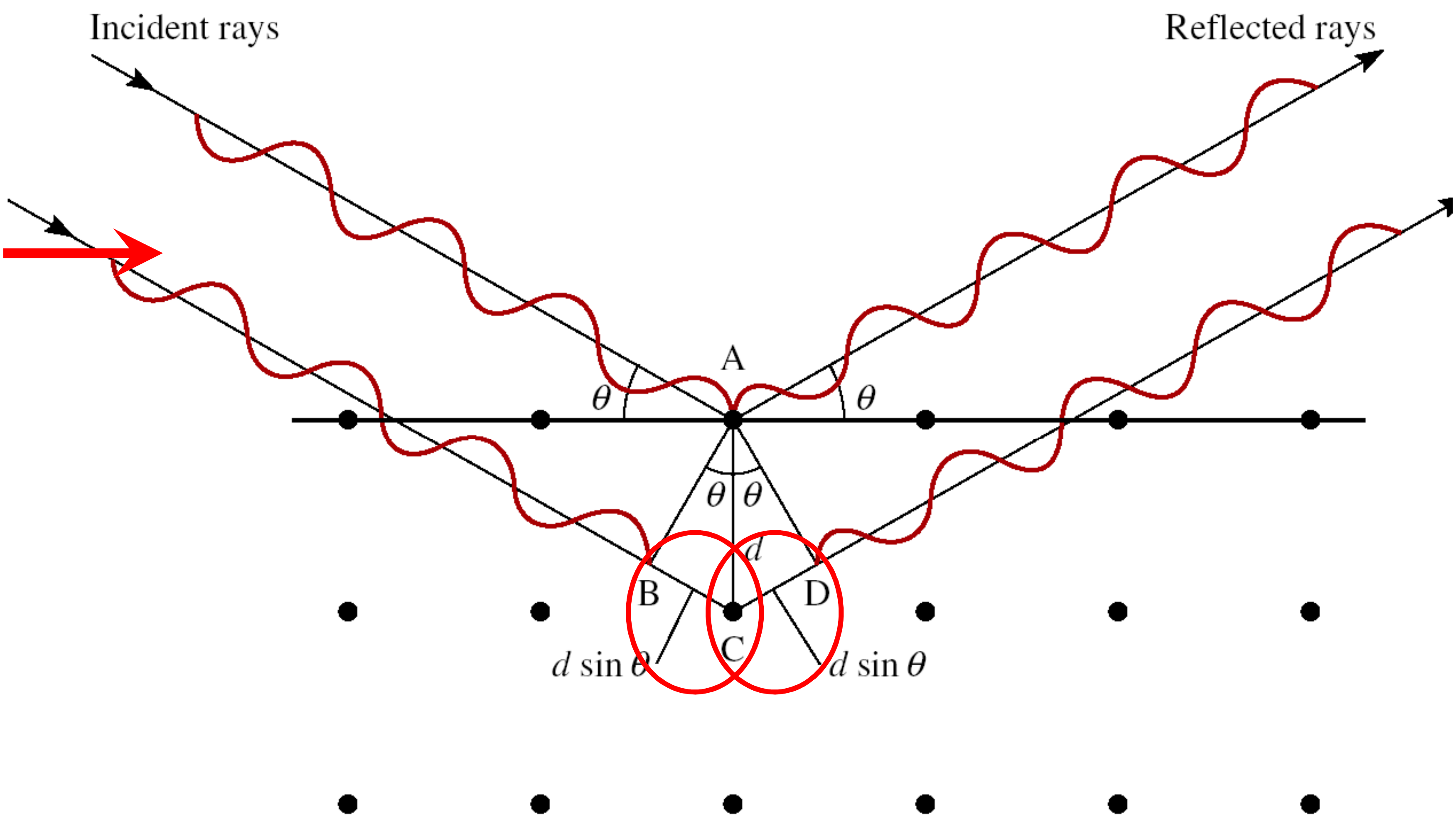
$$m = 4\text{ Ag }\cancel{\text{atoms}} \times \frac{107.9\text{ g}}{\cancel{\text{mole}}\text{ Ag}} \times \frac{1\ \cancel{\text{mole}}\text{ Ag}}{6.022 \times 10^{23}\ \cancel{\text{atoms}}} = 7.17 \times 10^{-22}\text{ g}$$

$$d = \frac{m}{V} = \frac{7.17 \times 10^{-22}\text{ g}}{6.83 \times 10^{-23}\text{ cm}^3} = 10.5\text{ g/cm}^3$$

An Arrangement for Obtaining the X-ray Diffraction Pattern of a Crystal.



Reflection of X rays from Two Layers of Atoms.



Extra distance = BC + CD = $2d\sin\theta = n\lambda$ (Bragg Equation)

X rays of wavelength 0.154 nm are diffracted from a crystal at an angle of 14.17°. Assuming that n = 1, what is the distance (in pm) between layers in the crystal?

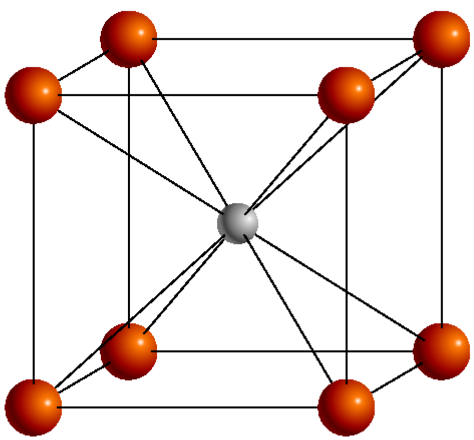
$$n\lambda = 2d \sin\theta \qquad n = 1 \qquad \theta = 14.17^{o} \quad \lambda = 0.154 \text{ nm} = 154 \text{ pm}$$

$$d = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 154 \text{ pm}}{2 \times \sin 14.17} = 314.0 \text{ pm}$$

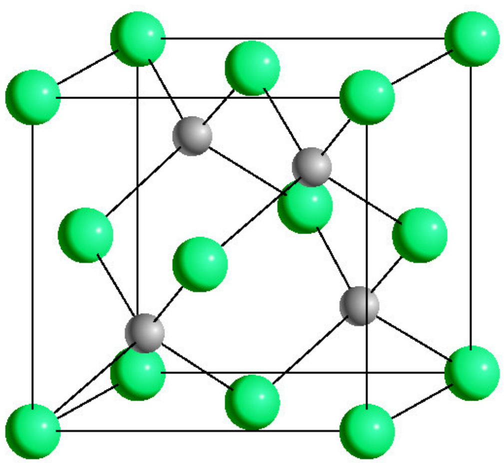
Types of Crystals

<u>Ionic Crystals</u>

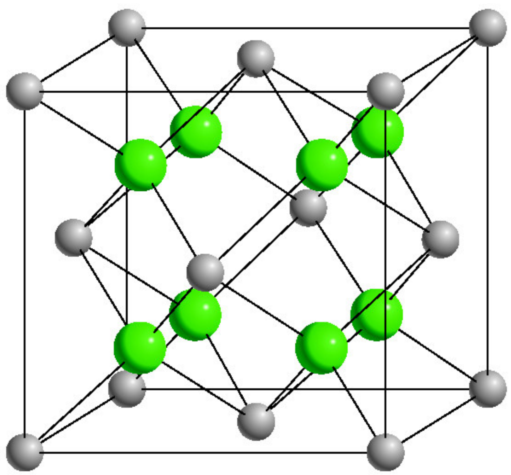
- Lattice points occupied by cations and anions
- Held together by electrostatic attraction
- Hard, brittle, high melting point
- Poor conductor of heat and electricity



CsCl



ZnS

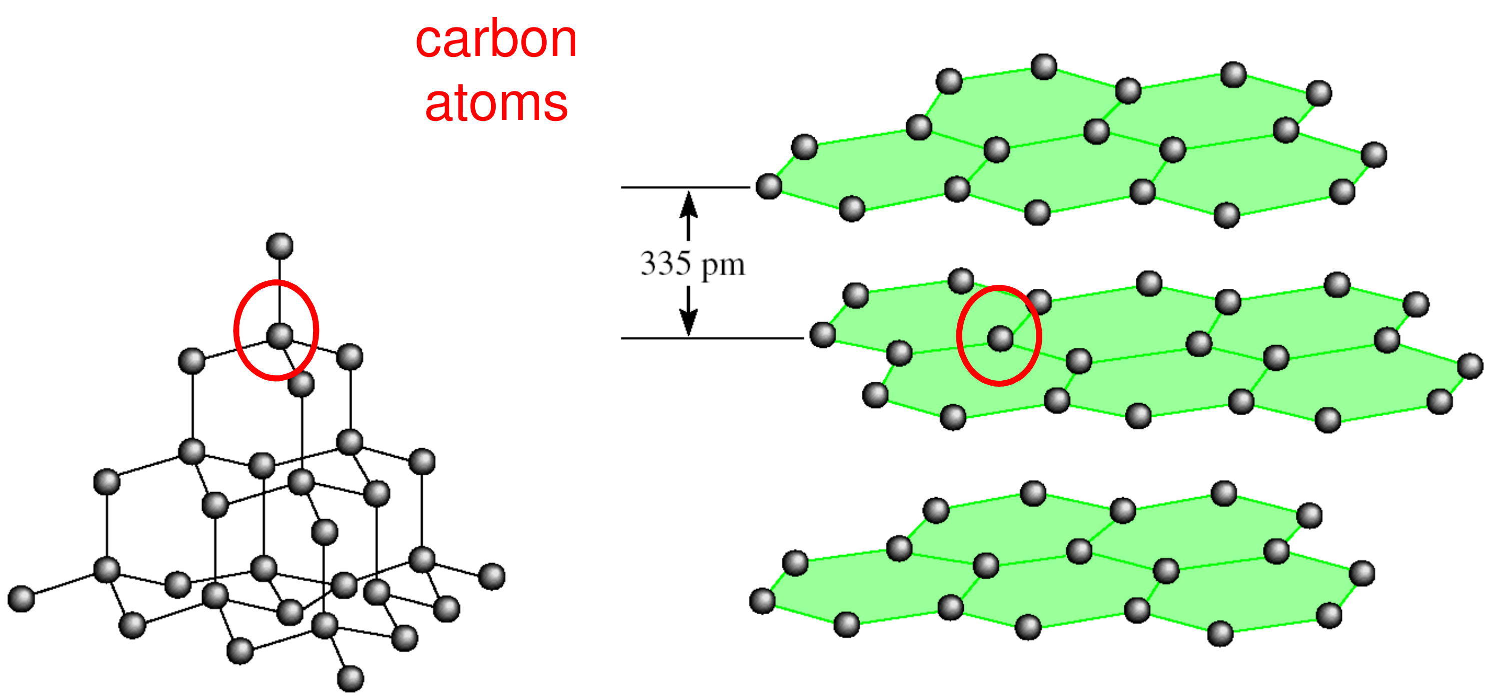


CaF_2

Types of Crystals

<u>Covalent Crystals</u>

- Lattice points occupied by atoms
- Held together by covalent bonds
- Hard, high melting point
- Poor conductor of heat and electricity



diamond graphite

Types of Crystals

Molecular Crystals

- Lattice points occupied by molecules
- Held together by intermolecular forces
- Soft, low melting point
- Poor conductor of heat and electricity

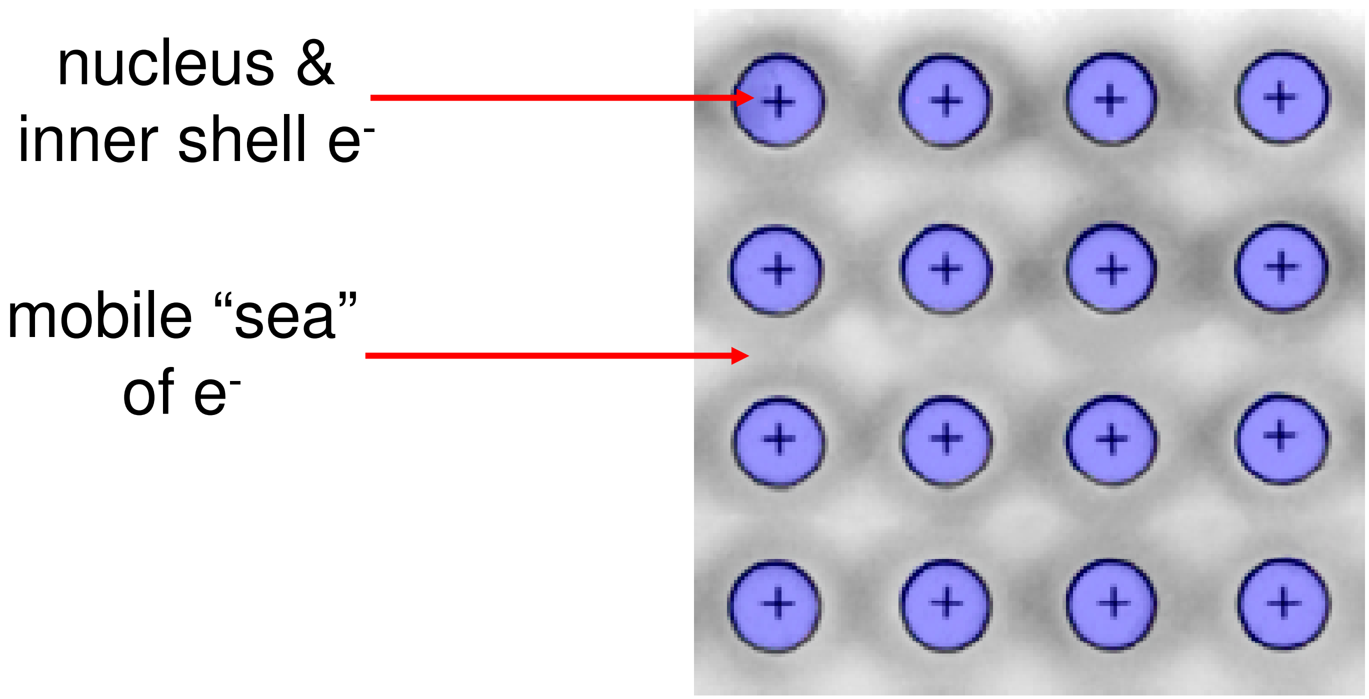
water  benzene

Types of Crystals

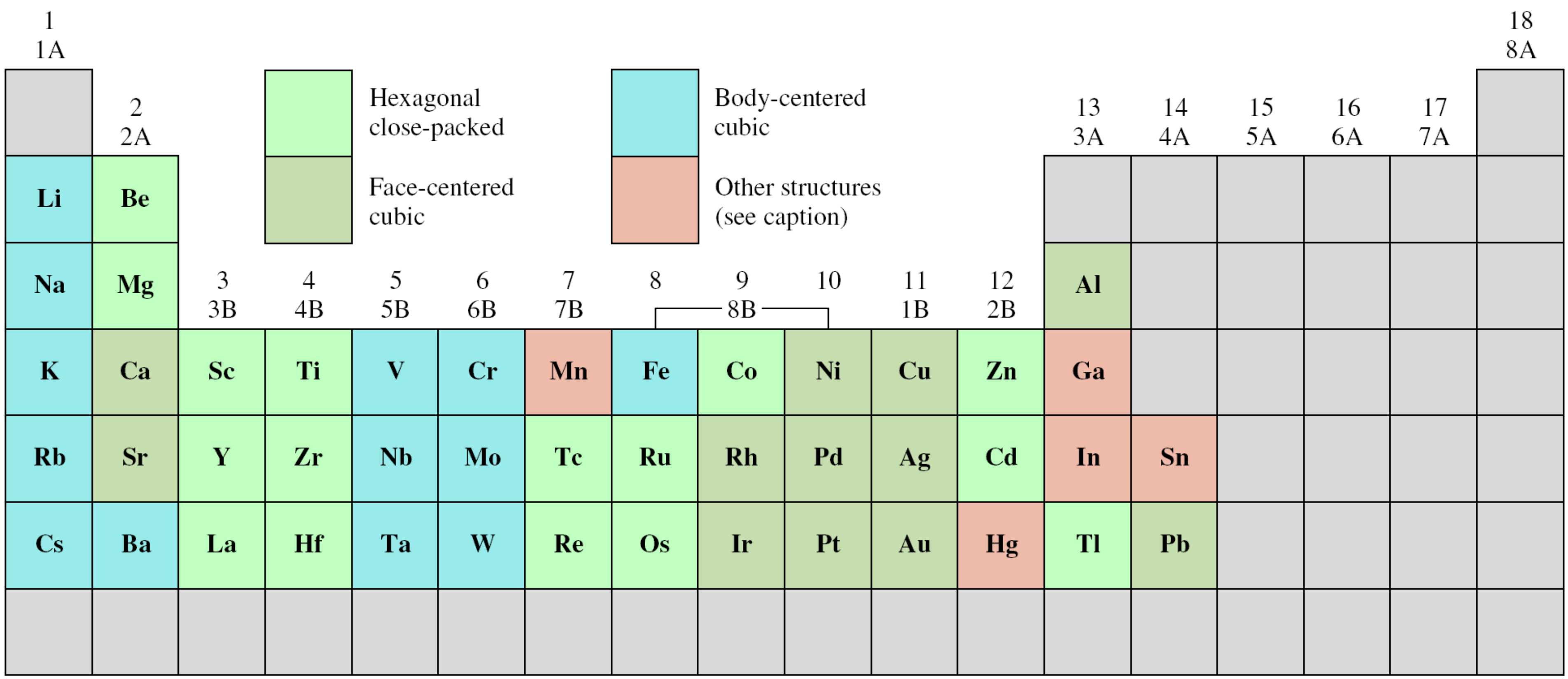
<u>Metallic Crystals</u>

- Lattice points occupied by metal atoms
- Held together by metallic bonds
- Soft to hard, low to high melting point
- Good conductors of heat and electricity

Cross Section of a Metallic Crystal



Crystal Structures of Metals



Types of Crystals

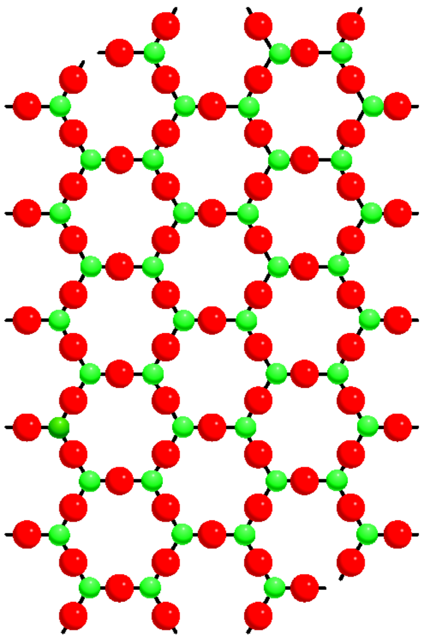
TABLE 11.4 Types of Crystals and General Properties

Type of Crystal	Force(s) Holding the Units Together	General Properties	Examples
Ionic	Electrostatic attraction	Hard, brittle, high melting point, poor conductor of heat and electricity	NaCl, LiF, MgO, $CaCO_3$
Covalent	Covalent bond	Hard, high melting point, poor conductor of heat and electricity	C (diamond),† SiO_2 (quartz)
Molecular*	Dispersion forces, dipole-dipole forces, hydrogen bonds	Soft, low melting point, poor conductor of heat and electricity	Ar, CO_2, I_2, H_2O, $C_{12}H_{22}O_{11}$ (sucrose)
Metallic	Metallic bond	Soft to hard, low to high melting point, good conductor of heat and electricity	All metallic elements; for example, Na, Mg, Fe, Cu

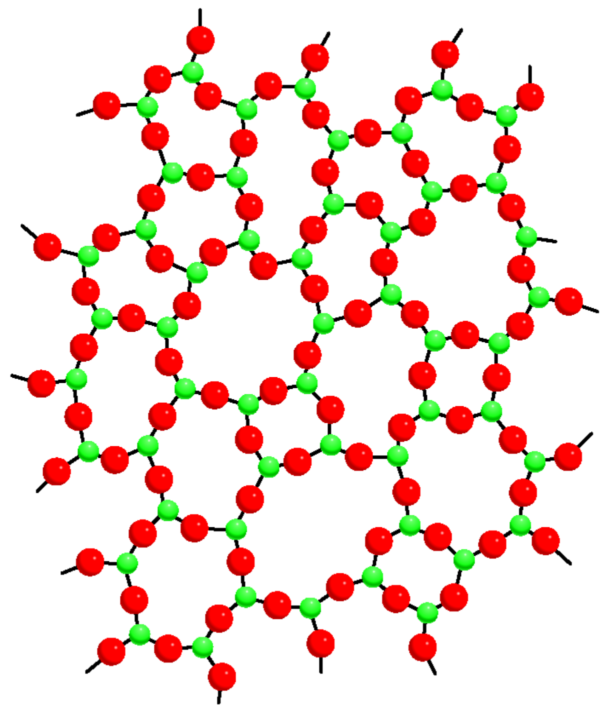
*Included in this category are crystals made up of individual atoms.
†Diamond is a good thermal conductor.

An ***amorphous solid*** does not possess a well-defined arrangement and long-range molecular order.

A ***glass*** is an optically transparent fusion product of inorganic materials that has cooled to a rigid state **without crystallizing**

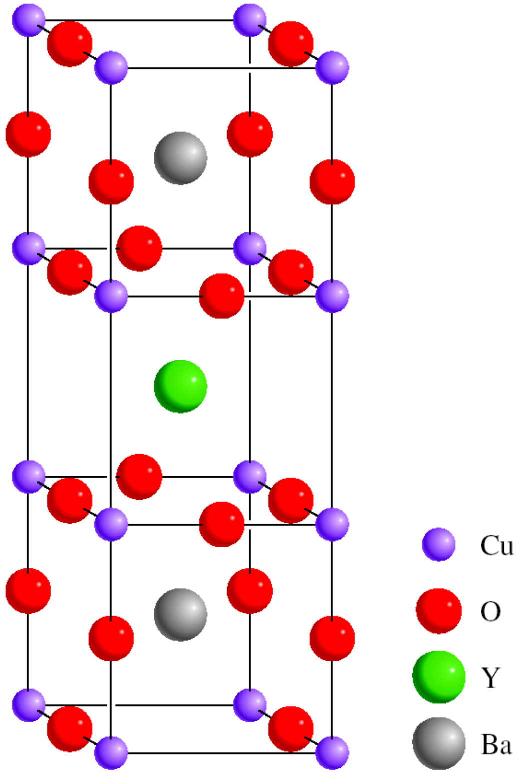


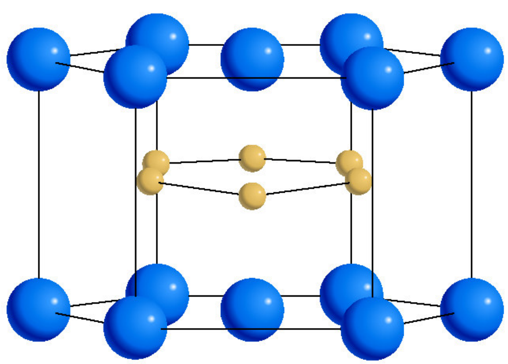
Crystalline quartz (SiO_2)



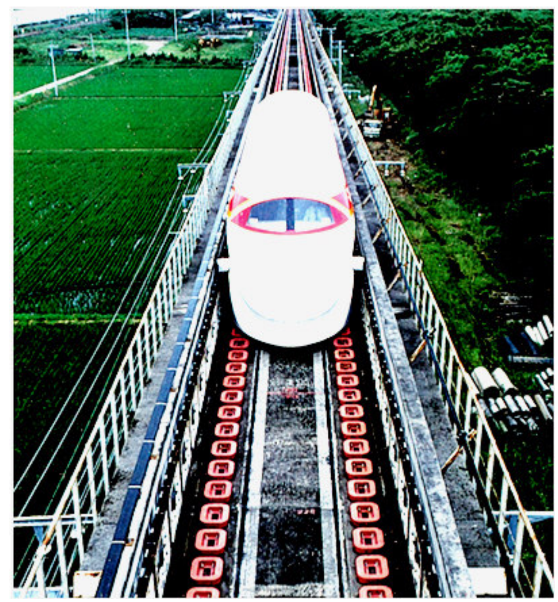
Non-crystalline quartz glass

Chemistry In Action: High-Temperature Superconductors





MgB_2

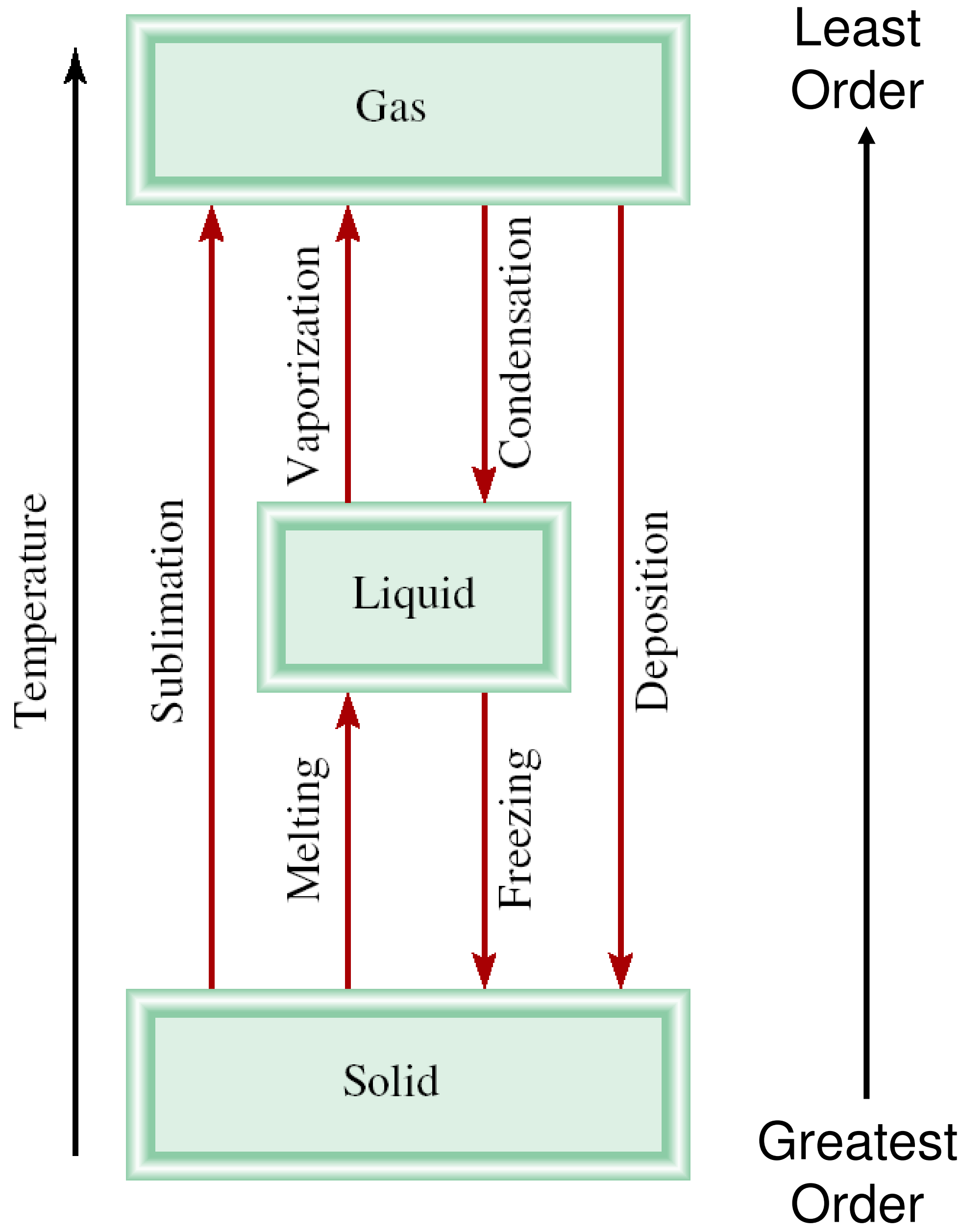


Chemistry In Action: And All for the Want of a Button

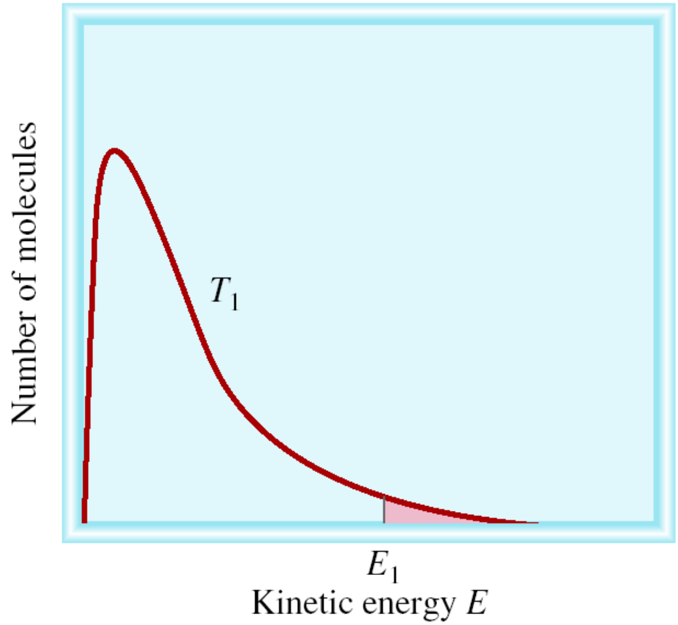
$$\text{white tin} \xrightarrow{T < 13\ ^0C} \text{grey tin}$$

stable weak

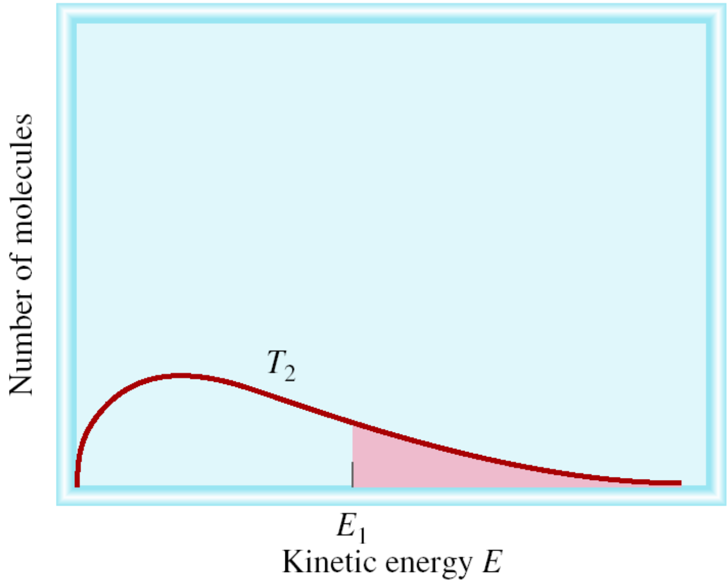
Phase Changes



Effect of Temperature on Kinetic Energy



$T_2 > T_1$

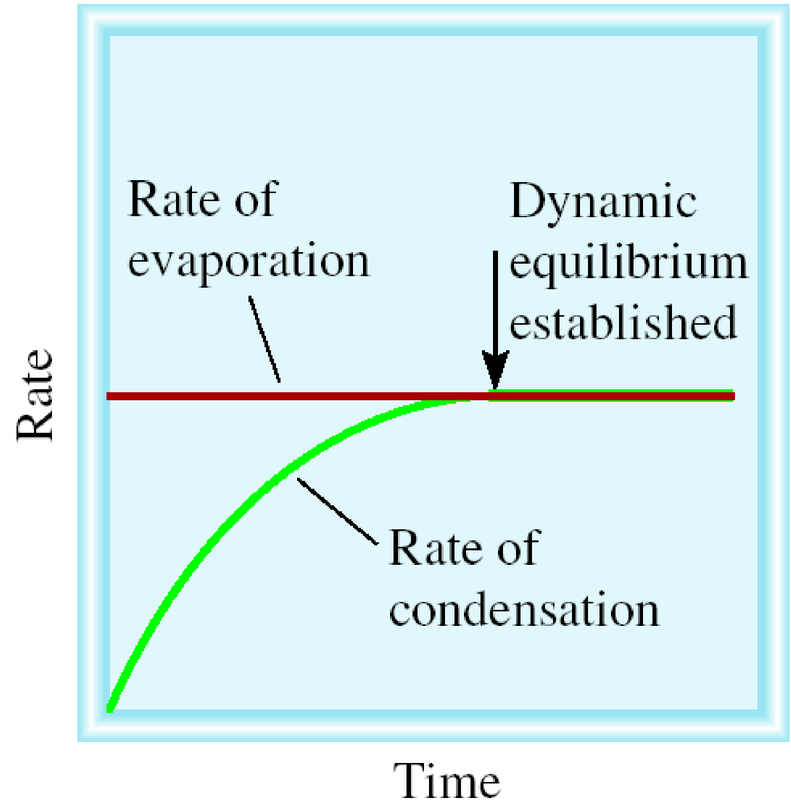


The ***equilibrium vapor pressure*** is the vapor pressure measured when a dynamic equilibrium exists between condensation and evaporation

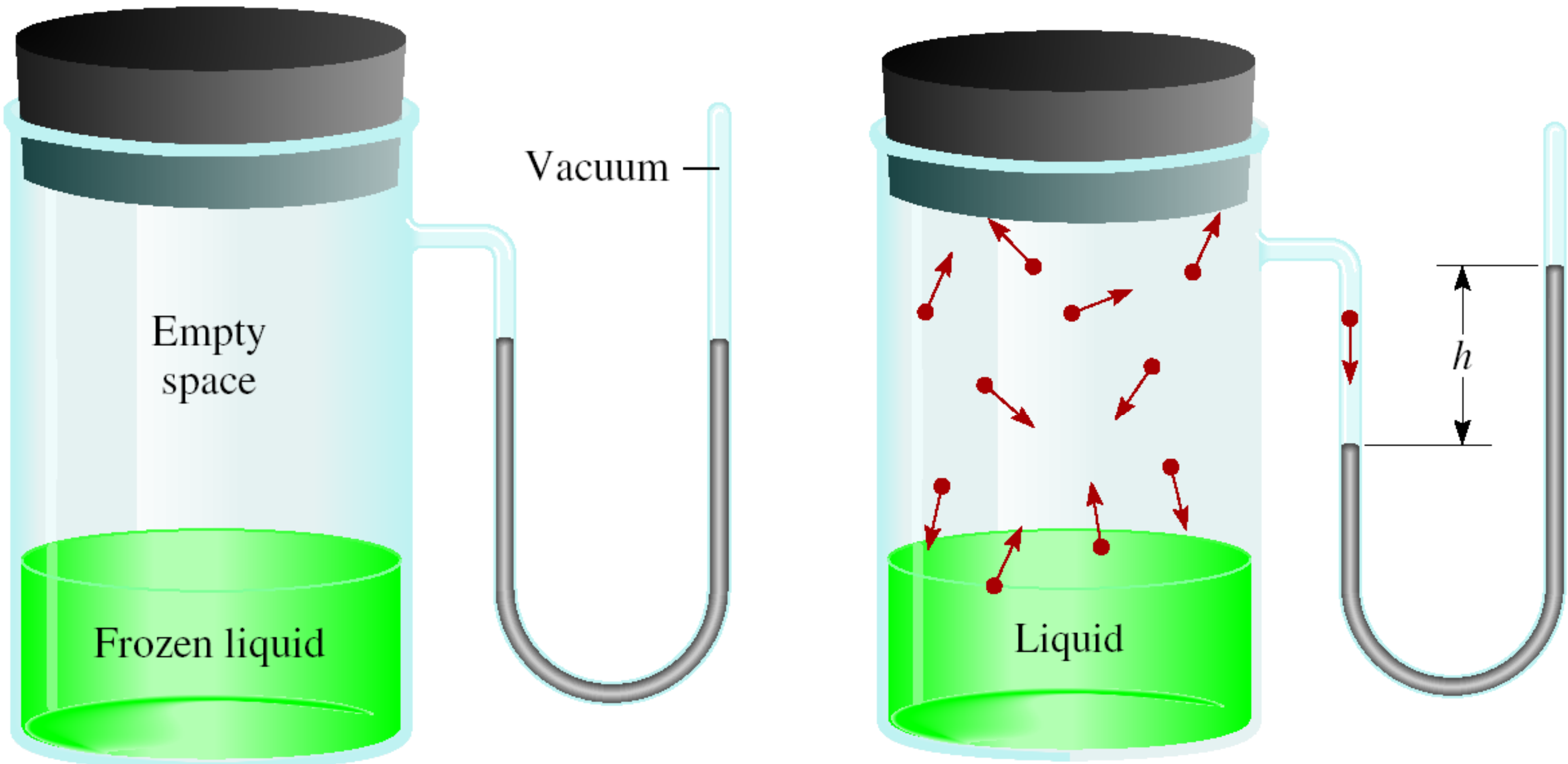
$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

Dynamic Equilibrium

Rate of condensation = Rate of evaporation



Measurement of Vapor Pressure



Before Evaporation

At Equilibrium

Molar heat of vaporization (ΔH_{vap}) is the energy required to vaporize 1 mole of a liquid at its boiling point.

<u>Clausius-Clapeyron Equation</u>

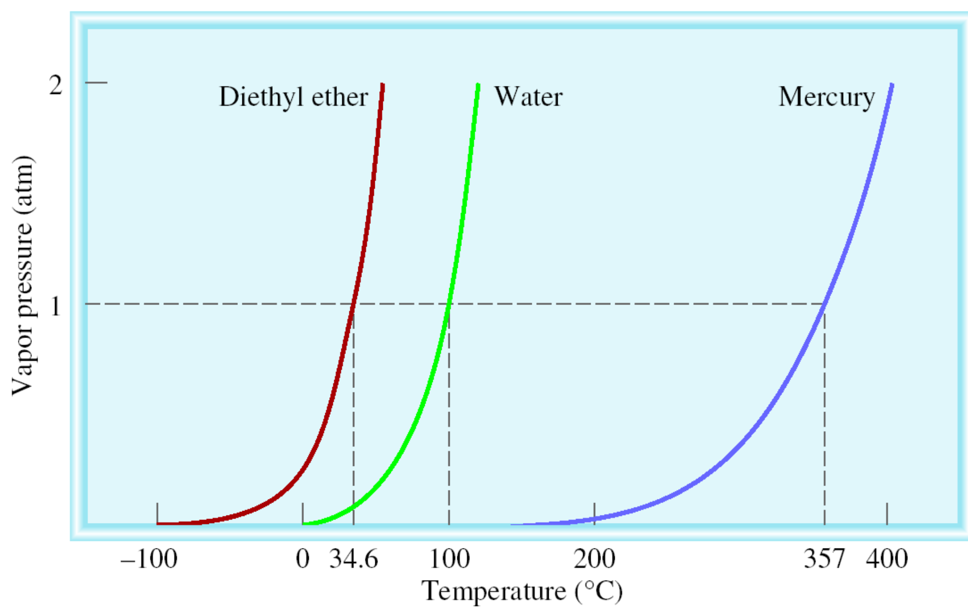
$$\ln P = -\frac{\Delta H_{vap}}{RT} + C$$

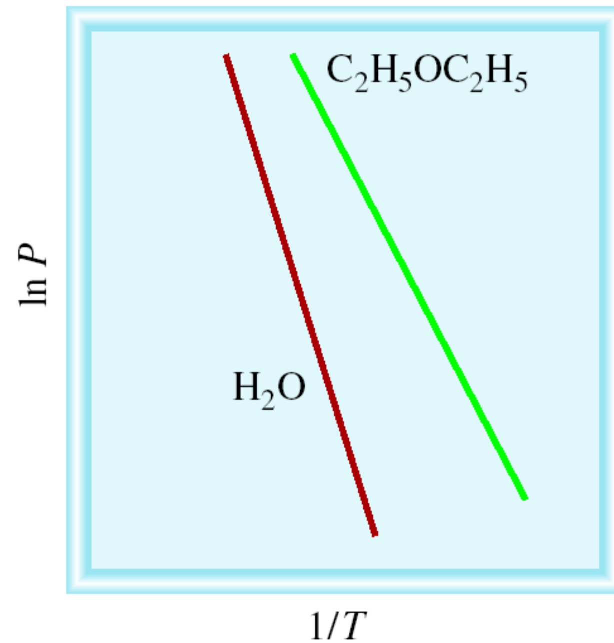
P = (equilibrium) vapor pressure

T = temperature (K)

R = gas constant (8.314 J/K•mol)

Vapor Pressure Versus Temperature





Alternate Forms of the Clausius-Clapeyron Equation

At two temperatures

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

or

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

The ***boiling point*** is the temperature at which the (equilibrium) vapor pressure of a liquid is equal to the external pressure.

The ***normal boiling point*** is the temperature at which a liquid boils when the external pressure is 1 atm.

TABLE 11.6 Molar Heats of Vaporization for Selected Liquids

Substance	Boiling Point* (°C)	ΔH_{vap} (kJ/mol)
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	80.1	31.0
Diethyl ether ($C_2H_5OC_2H_5$)	34.6	26.0
Ethanol (C_2H_5OH)	78.3	39.3
Mercury (Hg)	357	59.0
Methane (CH_4)	−164	9.2
Water (H_2O)	100	40.79

*Measured at 1 atm.

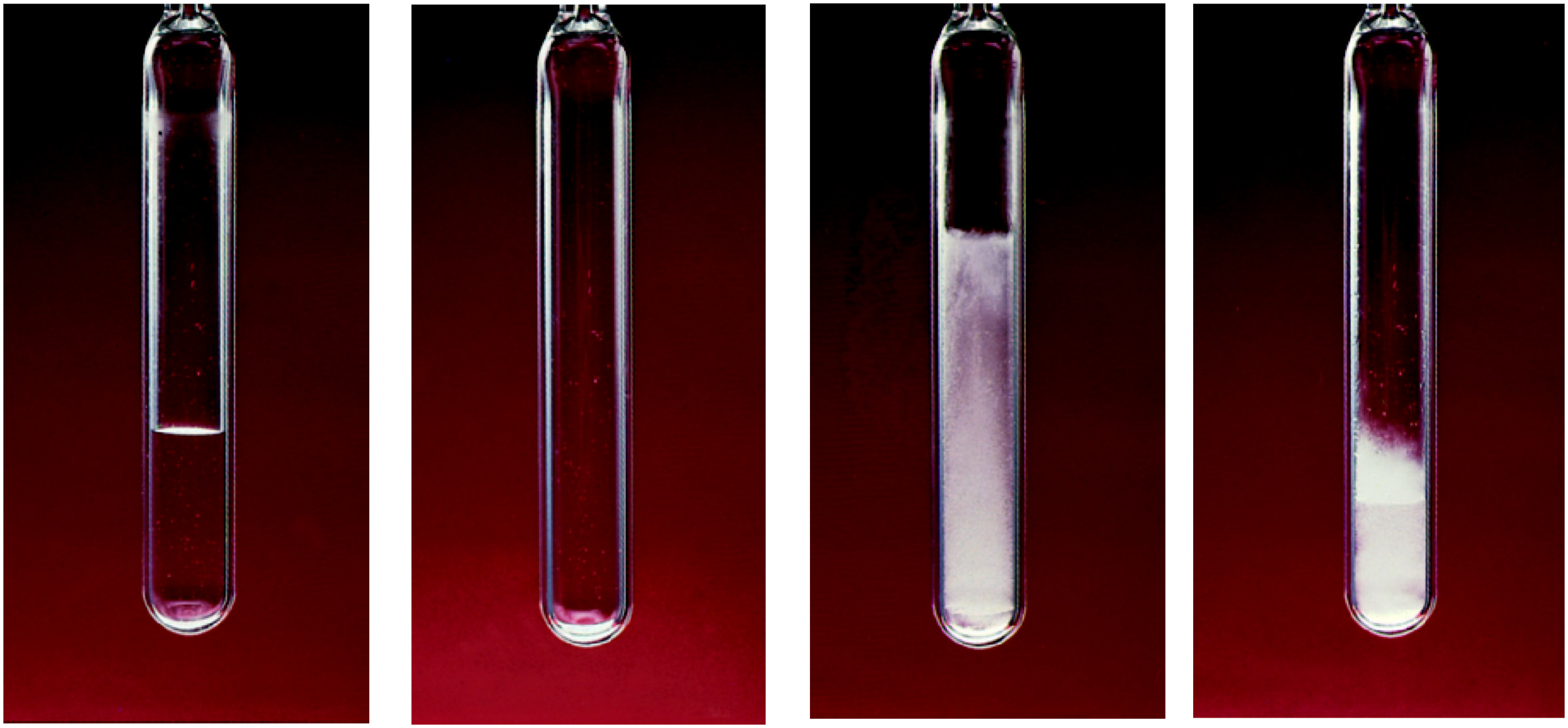
The ***critical temperature*** (***T_c***) is the temperature above which the gas cannot be made to liquefy, no matter how great the applied pressure.

The ***critical pressure*** (***P_c***) is the minimum pressure that must be applied to bring about liquefaction at the critical temperature.

TABLE 11.7 Critical Temperatures and Critical Pressures of Selected Substances

Substance	T_c (°C)	P_c (atm)
Ammonia (NH_3)	132.4	111.5
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	288.9	47.9
Carbon dioxide (CO_2)	31.0	73.0
Ethanol (C_2H_5OH)	243	63.0
Diethyl ether ($C_2H_5OC_2H_5$)	192.6	35.6
Mercury (Hg)	1462	1036
Methane (CH_4)	−83.0	45.6
Molecular hydrogen (H_2)	−239.9	12.8
Molecular nitrogen (N_2)	−147.1	33.5
Molecular oxygen (O_2)	−118.8	49.7
Sulfur hexafluoride (SF_6)	45.5	37.6
Water (H_2O)	374.4	219.5

The Critical Phenomenon of SF_6

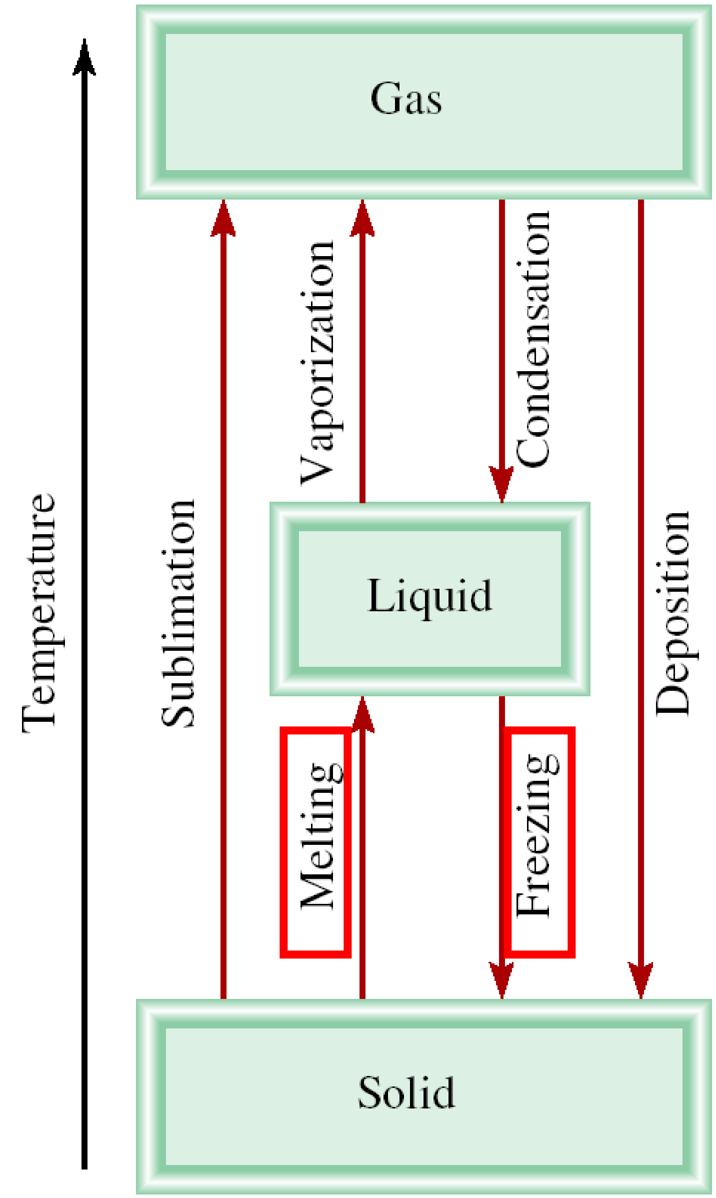


$T < T_c$ $T > T_c$ $T \sim T_c$ $T < T_c$

Solid-Liquid Equilibrium

$$H_2O\ (s) \rightleftharpoons H_2O\ (l)$$

The ***melting point*** of a solid or the ***freezing point*** of a liquid is the temperature at which the solid and liquid phases coexist in equilibrium



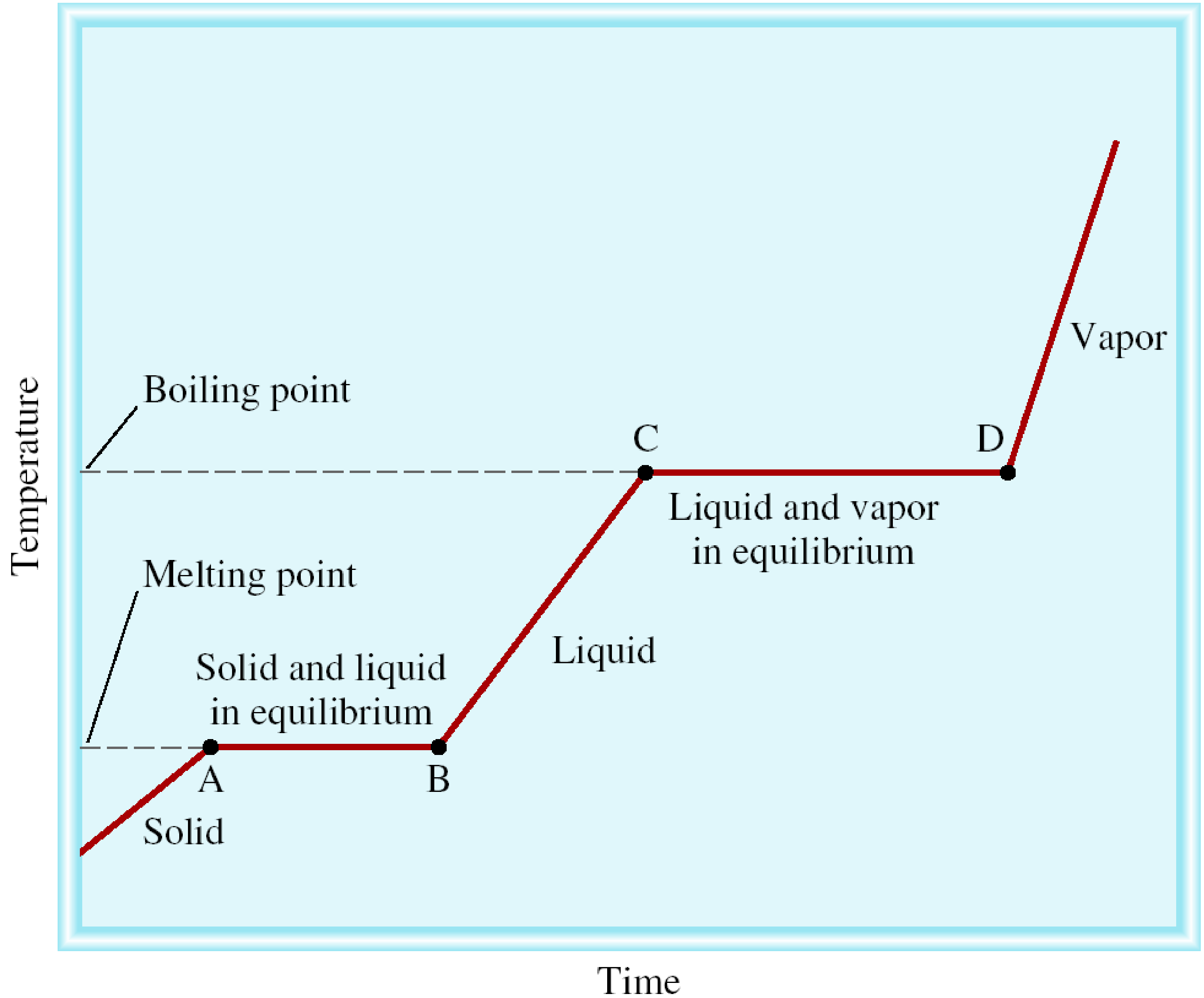
Molar heat of fusion (ΔH_{fus}) is the energy required to melt 1 mole of a solid substance at its freezing point.

TABLE 11.8 Molar Heats of Fusion for Selected Substances

Substance	Melting Point* (°C)	ΔH_{fus} (kJ/mol)
Argon (Ar)	−190	1.3
Benzene (C_6H_6)	5.5	10.9
Diethyl ether ($C_2H_5OC_2H_5$)	−116.2	6.90
Ethanol (C_2H_5OH)	−117.3	7.61
Mercury (Hg)	−39	23.4
Methane (CH_4)	−183	0.84
Water (H_2O)	0	6.01

*Measured at 1 atm.

Heating Curve



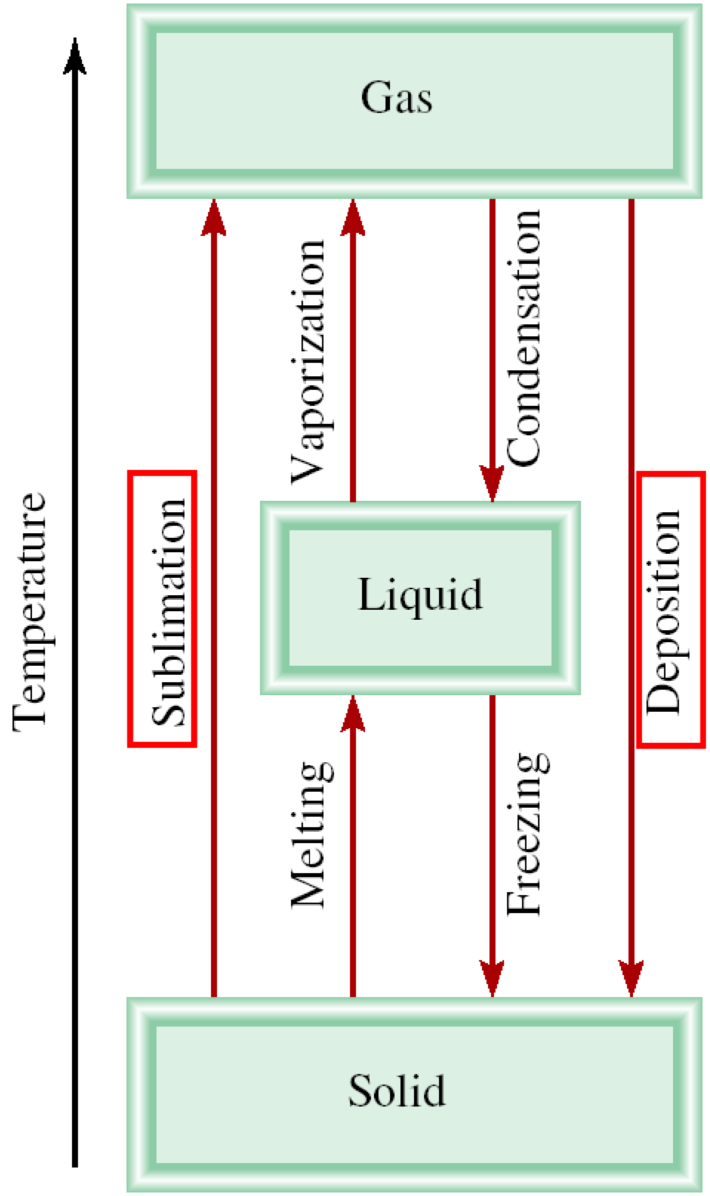
Solid-Gas Equilibrium

$$H_2O\ (s) \rightleftharpoons H_2O\ (g)$$

Molar heat of sublimation (ΔH_{sub}) is the energy required to sublime 1 mole of a solid.

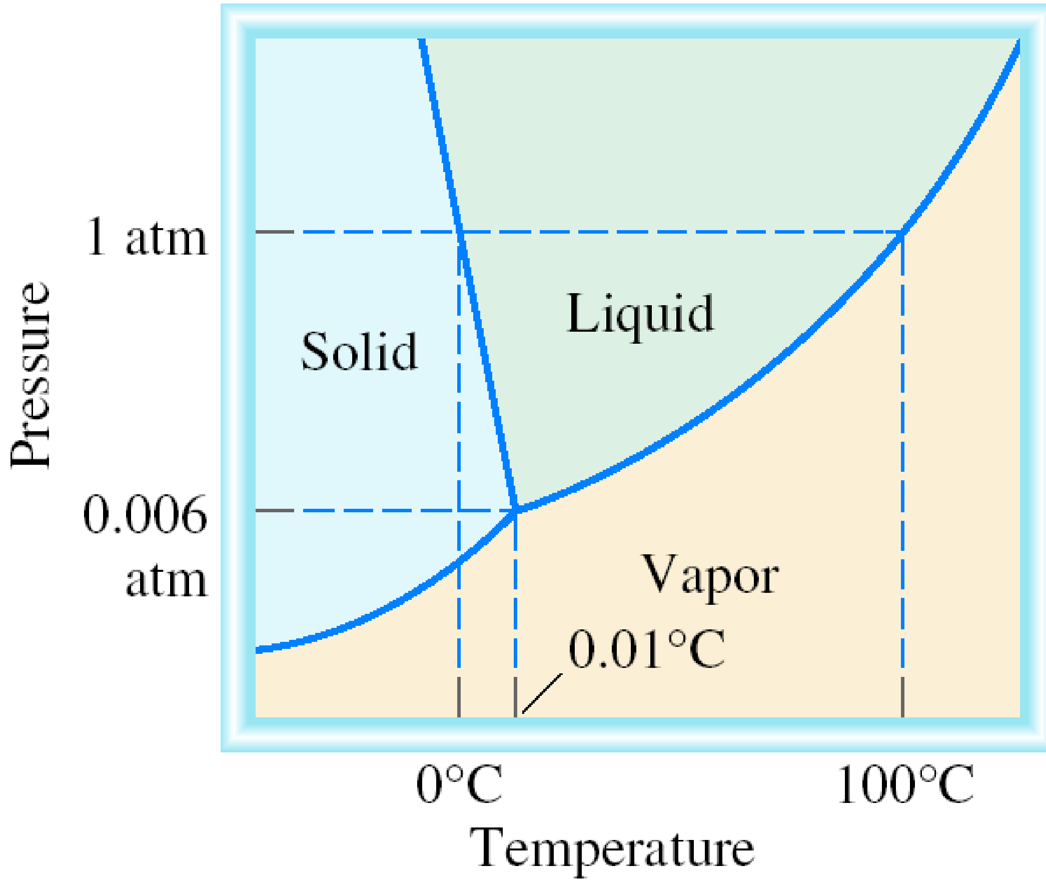
$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

(Hess's Law)

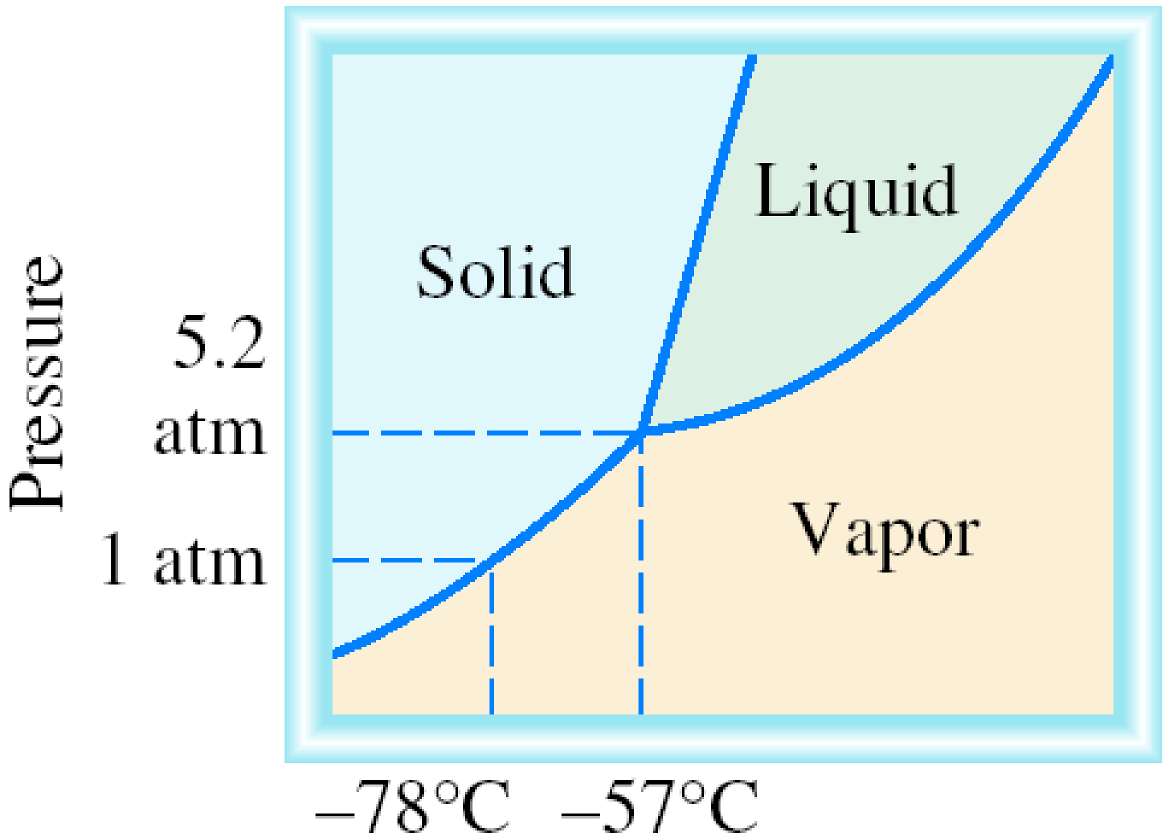


A ***phase diagram*** summarizes the conditions at which a substance exists as a solid, liquid, or gas.

Phase Diagram of Water



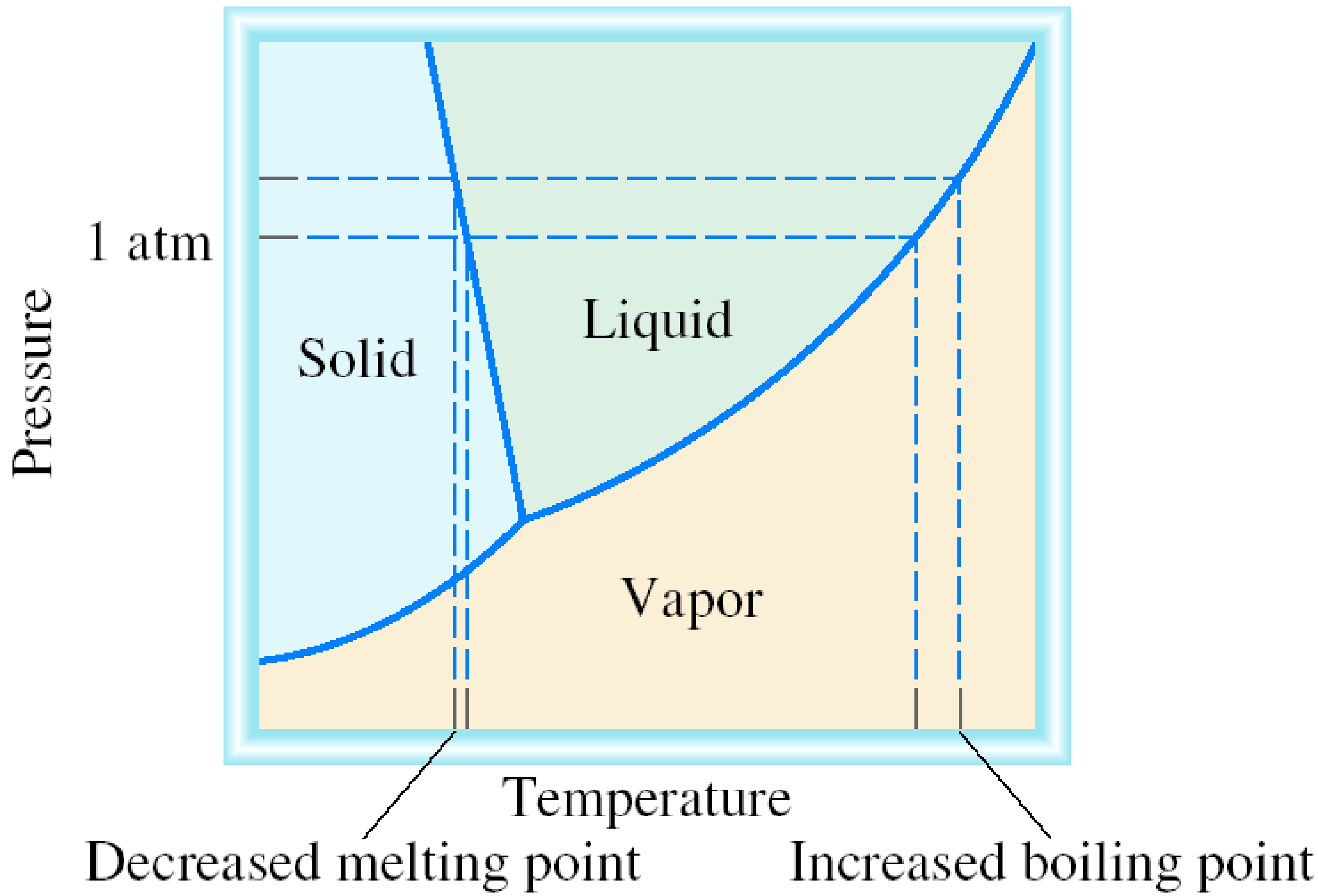
Phase Diagram of Carbon Dioxide



At 1 atm

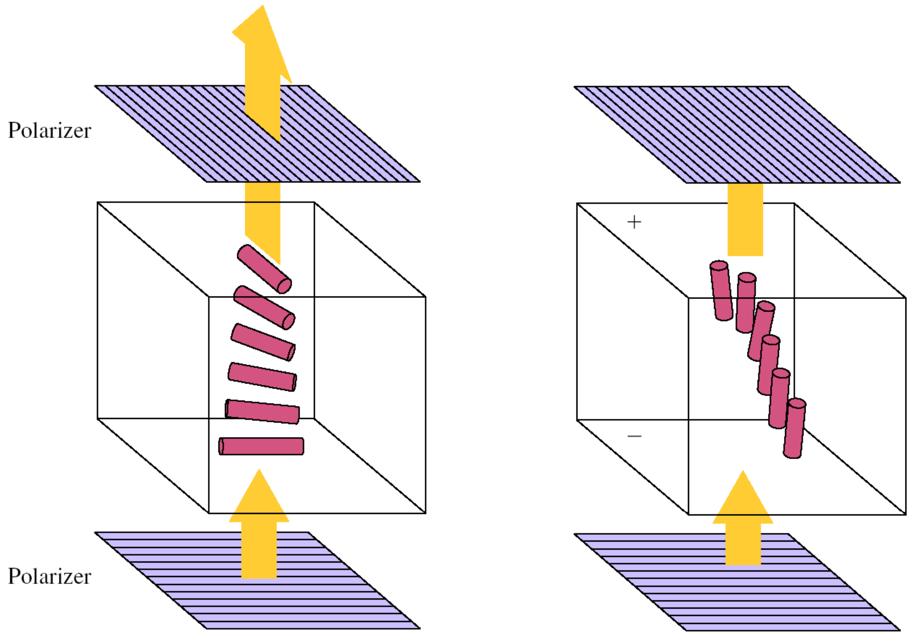
$CO_2\ (s) \longrightarrow CO_2\ (g)$

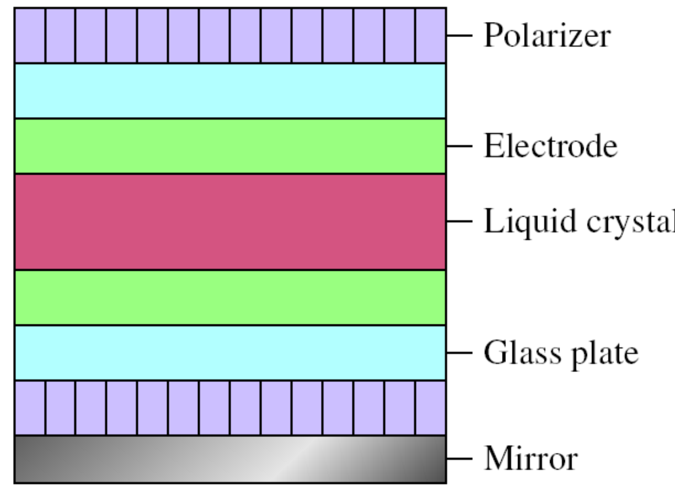
Effect of Increase in Pressure on the Melting Point of Ice and the Boiling Point of Water

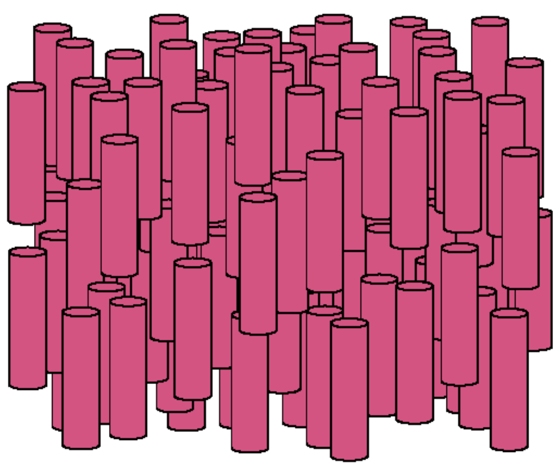


Chemistry In Action: Ice Skating

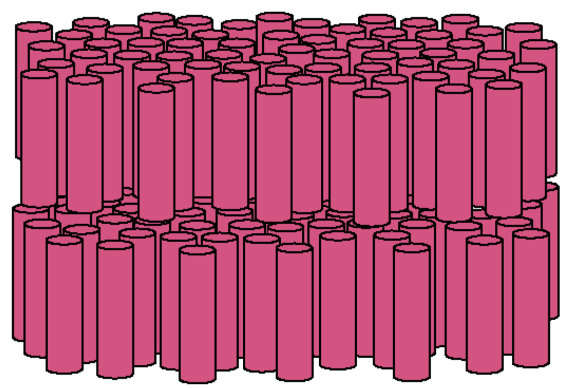
Chemistry In Action: Liquid Crystals







Nematic



Smectic