

Liquids, Solids and Phase Changes

12.1 Physical States and Phase Changes

- **Physical states** – gas, liquid and solid
 - **Phases** – physically distinct, homogeneous parts of a sample of matter (can be gaseous, liquid or solid)
 - **Condensed phases** – liquid or solid
 - A sample can contain more than one liquid phases (immiscible) or more than one solid phases
 - **Phase changes** – conversions between the different phases of a substance

- **Intramolecular** (bonding) forces – exist within each molecule or polyatomic ion (influence the chemical properties)
- **Intermolecular** (interparticle) forces – exist between the particles (molecules or ions) of a substance (influence the physical properties)

Kinetic-Molecular View of the Three States

- The physical state of a substance is governed by the relative magnitudes of the potential energy of **intermolecular attraction** and the kinetic energy of **molecular motion**

- **Gas** – the particles are far apart; the energy of motion dominates the energy of attraction
- **Liquid** – the particles are close together; the energies of attraction and motion are comparable
- **Solid** – the particles are close together; the energy of attraction dominates the energy of motion

Table 12.1 A Macroscopic Comparison of Gases, Liquids, and Solids

State	Shape and Volume	Compressibility	Ability to Flow
Gas	Conforms to shape and volume of container	High	High
Liquid	Conforms to shape of container; volume limited by surface	Very low	Moderate
Solid	Maintains its own shape and volume	Almost none	Almost none

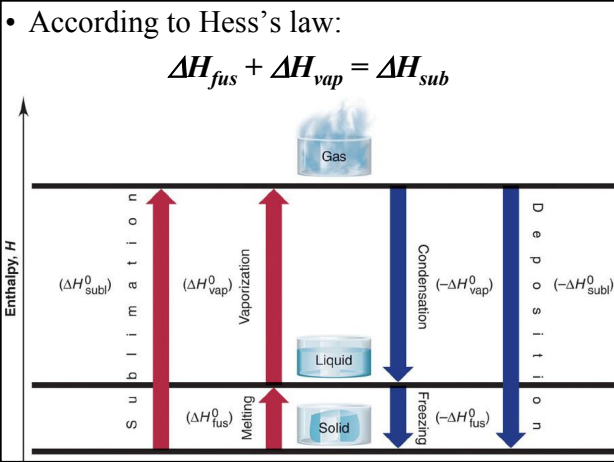
Types of Phase Changes

- Phase changes are caused by changing conditions such as temperature and pressure
 - At high T , the E_k of molecular motion increases
 - At high P , the molecules get closer together and the E_p of intermolecular attraction increases
- **Vaporization** – conversion from liquid to gas
- **Condensation** – conversion from gas to liquid
- **Melting (fusion)** – conversion from solid to liquid
- **Freezing** – conversion from liquid to solid
- **Sublimation** – conversion from solid to gas
- **Deposition** – conversion from gas to solid

Enthalpies (Heats) of Phase Changes

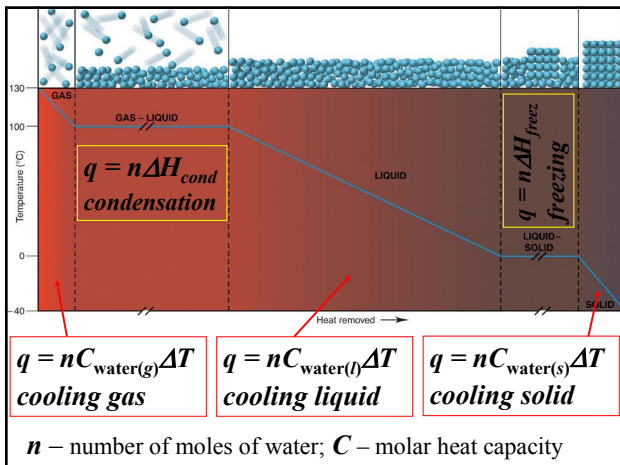
- Phase changes are accompanied by energy and enthalpy changes
 - **Vaporization, melting and sublimation are always endothermic** – energy must be absorbed to overcome the intermolecular forces
 - **Condensation, freezing and deposition are always exothermic** – energy is released as the molecules get closer and attract each other
- **Heat of vaporization (ΔH_{vap})** – enthalpy change for the conversion of **1 mol** of a substance from liquid to gas

- **Heat of fusion (ΔH_{fus})** – enthalpy change for the conversion of **1 mol** of a substance from solid to liquid
- **Heat of sublimation (ΔH_{sub})** – enthalpy change for the conversion of **1 mol** of a substance from solid to gas
- The heats of the reverse processes (condensation, freezing and deposition) have the same magnitudes but opposite signs (For example: $\Delta H_{cond} = -\Delta H_{vap}$)
- For most substances:
$$0 < \Delta H_{fus} < \Delta H_{vap} < \Delta H_{sub}$$



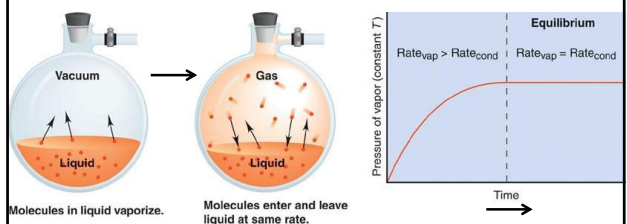
12.2 Quantitative Aspects of Phase Changes

- **Heating-cooling curves** – show the variation of the temperature of a sample as it is heated or cooled at a constant rate
- Regions in the heating-cooling curves
 - **Sloped regions** – correspond to temperature changes in the pure solid, liquid or gas phases (slope depends on the heat capacity of each phase; E_k of molecular motion changes)
 - **Flat regions** – correspond to phase changes (temperature remains constant; E_p of intermolecular attraction changes)



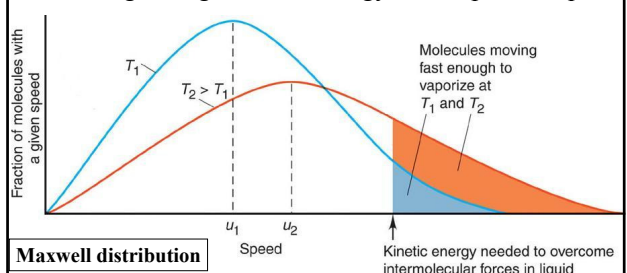
The Equilibrium Nature of Phase Changes

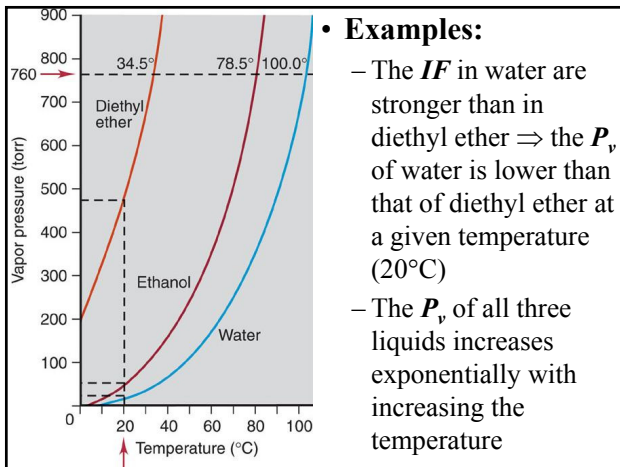
- Liquid-gas equilibria (**liquid \leftrightarrow gas**)
 - At constant temperature in a closed container a **dynamic equilibrium** is established between vaporization and condensation
 - At equilibrium the rate of vaporization equals the rate of condensation



- **Vapor pressure (P_v)** – the pressure exerted by the vapors over a liquid at equilibrium
 - P_v depends only on the nature of the liquid and T (if P_v is disturbed by compression or expansion, the equilibrium shifts to restore the original P_v)
 - In the presence of other gases over the liquid, P_v is the **partial pressure** of the vapors
- P_v increases with decreasing the strength of the intermolecular forces (**IF**)
 - In order to vaporize, a molecule must escape the forces of attraction, **IF**, between the molecules in the liquid

- P_v increases with increasing temperature
 - In order to vaporize, a molecule must have enough kinetic energy to escape the liquid
 - Increasing T increases the fraction of molecules having enough kinetic energy to escape the liquid

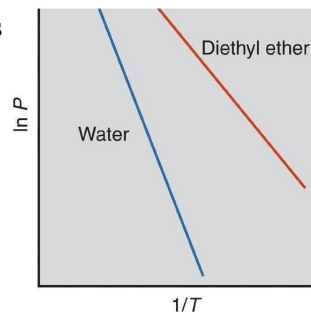




• **Clausius-Clapeyron equation** – relates P_v , T and ΔH_{vap} :

$$\ln P_v = \frac{-\Delta H_{vap}}{R} \left(\frac{1}{T} \right) + const.$$

- A plot of $\ln P_v$ versus $(1/T)$ should yield a straight line with **slope** = $-\Delta H_{vap}/R$
- \Rightarrow Can be used to determine ΔH_{vap} by measuring P_v at different T s



- If two equations are written for two different T s, T_1 and T_2 , at which the P_v s are P_1 and P_2 and the 1st equation is subtracted from the 2nd, one gets:

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

- **Boiling** – in an open container a liquid starts boiling (forming bubbles inside) when P_v reaches the external pressure, P_{atm}
- **Boiling point** (T_b) – the T at which $P_v = P_{atm}$
- $\Rightarrow T_b$ increases with increasing P_{atm} since at higher P_{atm} , higher P_v must be achieved for boiling to occur, so higher T is needed
- **Normal boiling point** – the T_b at $P_{atm} = 760$ torr

Example: Estimate the T_b of water on Mt. Everest where P_{atm} is ~ 270 torr, if its ΔH_{vap} is 40.7 kJ/mol.

- \rightarrow Use the Clausius-Clapeyron equation for two T s:
- Normal boiling point $\rightarrow T_1 = 100^\circ\text{C} \rightarrow P_1 = 760$ torr
- Boiling point Everest $\rightarrow T_2 = ??? \rightarrow P_2 = 270$ torr

$$\ln \frac{270 \text{ torr}}{760 \text{ torr}} = \frac{-40.7 \text{ kJ/mol}}{8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}} \left(\frac{1}{T_2} - \frac{1}{373 \text{ K}} \right)$$

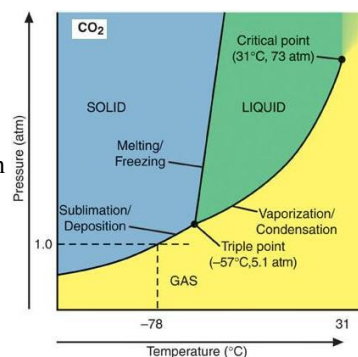
$$\frac{1}{T_2} - \frac{1}{373} = \frac{8.314 \times 10^{-3}}{-40.7} \ln \frac{270}{760} = 2.11 \times 10^{-4}$$

$$\frac{1}{T_2} = 2.11 \times 10^{-4} + \frac{1}{373} = 2.89 \times 10^{-3} \quad T_2 = 346 \text{ K} = 73^\circ\text{C}$$

- **Solid-liquid equilibria (solid \leftrightarrow liquid)**
 - At constant temperature a **dynamic equilibrium** is established as the rate of melting equals the rate of freezing
 - **Melting (freezing) point** (T_m) – pressure affects T_m only very slightly
- **Solid-gas equilibria (solid \leftrightarrow gas)**
 - At constant temperature a **dynamic equilibrium** is established as the rate of sublimation equals the rate of deposition
 - Since the vapor pressure of solids is typically quite low, solid-gas equilibria are not very common at normal T and P conditions

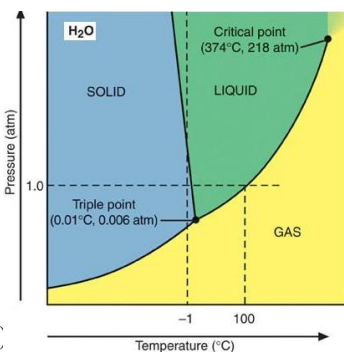
Phase Diagrams

- Specify the stability of the various phases at different T and P
- \triangleright Solid lines – phase boundaries
- \triangleright Between the lines – **one** stable phase
- \triangleright On the lines – **two** phases in equilibrium
- \triangleright At the **triple point** – **three** phases in equilibrium
- \triangleright **Critical point** – the end of the liquid/gas phase boundary



- The slope of the solid/liquid boundary is normally positive, but in a few cases like H_2O , it's negative \Rightarrow ice melts at lower T when the P is higher

- **Critical temperature (T_c)** – vapors can't be liquefied at any P if T is greater than T_c
- **Critical pressure (P_c)** – P at the critical point
- **Supercritical fluid** – above T_c and P_c – the liquid and vapor merge into a single phase (resembles both phases)



12.3 Types of Intermolecular Forces (IF)

- IFs** are based on electrostatic interactions between opposite charges, but they are much weaker than chemical bonds for two reasons:
 - Smaller el. charges are involved
 - The distances between the el. charges are longer
- **Covalent radius** – $\frac{1}{2}$ the distance between two identical bonded atoms
- **van der Waals radius** – $\frac{1}{2}$ the distance between two adjacent, identical (nonbonded) atoms from different molecules \rightarrow *The van der Waals radius of an atom is always longer than its covalent radius*
- **IFs** are also called **van der Waals forces**
- Stronger **IFs** lead to higher T_b and T_m values

- **Ion-Dipole forces** – **IFs** between an ion and a nearby polar molecule (ionic compounds like NaCl dissolved in polar solvents like H_2O)
- **Dipole-Dipole forces** – **IFs** between two polar molecules (δ^+ of one molecule attracts δ^- of the other)
 - Increase with increasing the dipole moment

Example:

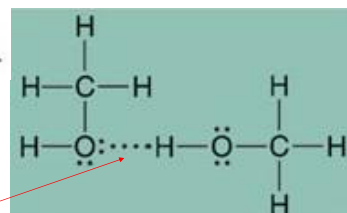
$\text{CH}_3\text{CH}_2\text{CH}_3$ and CH_3CN have almost the same molecular weight and size. Since CH_3CN is much more polar, its dipole-dipole forces are much stronger and its boiling and melting points, T_b and T_m , are much higher.

- **Hydrogen Bonding** – **IF** between molecules containing **H**-atoms connected to highly electronegative small atoms with lone pairs like **F**, **O** and **N**
 - Due to the very high polarity of the **H-F**, **H-O** and **H-N** bonds (the δ^+ of **H** is attracted to the δ^- of the lone pair of **F**, **O** or **N**)



Example:

CH_3OH has an O-H bond \Rightarrow H-bonding



- **Charge-Induced Dipole forces**

- **Induced dipole** – a dipole induced in a particle through a distortion of its electron cloud by an electric field such as a nearby charge or another dipole
- **Polarizability** – the ease with which the electron cloud of a particle can be distorted (increases with increasing the size of the electron cloud and therefore with the molar mass of the particle)
- **Ion-Induced Dipole forces** – **IFs** between an ion and a dipole it induces in a nearby particle
- **Dipole-Induced Dipole forces** – **IFs** between a dipole and a dipole it induces in a nearby particle

- **Dispersion (London) forces**

- **Instantaneous dipole** – a dipole that results from an instantaneous fluctuation of the electron cloud in a particle
- The instantaneous dipole can induce a dipole in a nearby particle and create an **induced dipole** in it
- **Dispersion (London) forces** – **IFs** between an **instantaneous dipole** and an **induced dipole** in a nearby particle
- Dispersion forces *exist between any particles*, but they are *the only type of IFs for non-polar molecules and atoms of noble gases*
- Examples:** CH_4 , Cl_2 , CO_2 , Ar, Kr, Xe ... are all non-polar \Rightarrow only dispersion forces are present

– The **strength** of the dispersion forces depends on:

- The **polarizability** (size, molar mass) of the particles
 \uparrow size, molar mass $\Rightarrow \uparrow$ dispersion forces
- The **shape** of the particles – dispersion forces between rod-shaped molecules are stronger compared to spherical molecules of the same size (rod-shapes provide more points of contact)

Example:

The boiling points of the noble gases increase down the group as the molar mass increases

Noble gases \rightarrow He Ne Ar Kr Xe
 T_b ($^{\circ}\text{C}$) \rightarrow -269 -246 -186 -153 -108
 Molar mass $\uparrow \Rightarrow$ Dispersion forces $\uparrow \Rightarrow T_b \uparrow$

Force	Model	Energy (kJ/mol)	Example
Ion-dipole		40–600	$\text{Na}^+ \cdots \text{O} \begin{matrix} \text{H} \\ \diagup \\ \text{H} \end{matrix}$
H bond		10–40	$\begin{matrix} \text{H} \\ \diagup \\ \text{O} \cdots \text{H} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{matrix}$
Dipole-dipole		5–25	$\text{I}-\text{Cl} \cdots \text{I}-\text{Cl}$
Ion-induced dipole		3–15	$\text{Fe}^{2+} \cdots \text{O}_2$
Dipole-induced dipole		2–10	$\text{H}-\text{Cl} \cdots \text{Cl}-\text{Cl}$
Dispersion (London)		0.05–40	$\text{F}-\text{F} \cdots \text{F}-\text{F}$

Intermolecular

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H–H
Metallic		Cations–delocalized electrons	75–1000	Fe

Intramolecular

- Comparing the different types of **IFs**

- The most common **IFs** in substances are H-bonding, dipole-dipole and dispersion forces
- Dispersion forces are typically more important than dipole-dipole forces, and if they have opposite trends, the dispersion forces dominate

Example:

H-halides \rightarrow HCl HBr HI
 T_b (K) \rightarrow 188 206 237
 Dipole moment $\downarrow \Rightarrow$ Dipole-dipole forces \downarrow
 Molar mass $\uparrow \Rightarrow$ Dispersion forces \uparrow
 The dispersion forces dominate the trend and $T_b \uparrow$

- Comparing the different types of **IFs**
- H-bonding is typically much stronger than dipole-dipole and dispersion forces for particles of similar sizes

Example:

Hydrogen halides \rightarrow HF HCl HBr HI
 T_b (K) \rightarrow 293 188 206 237
 Molar mass $\uparrow \Rightarrow$ Dispersion forces \uparrow

HF breaks the trend and has an anomalously high T_b due to the much stronger H-bonding forces which are not present in HCl, HBr and HI

Example: Identify the types of **IFs** and rank the following substances in order of increasing boiling point, T_b :

CH_3CH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{-O-CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

$\uparrow T_b$

$\text{CH}_3\text{CH}_2\text{OH} \rightarrow$ O-H bond \rightarrow **H-bonding**
 \rightarrow dispersion forces
 \rightarrow polar \rightarrow dipole-dipole forces

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow$ non-polar \rightarrow **dispersion**

$\text{CH}_3\text{-O-CH}_3 \rightarrow$ no O-H bonds
 \rightarrow **dispersion**
 \rightarrow slightly polar \rightarrow **dipole-dipole**

$\text{CH}_3\text{CH}_3 \rightarrow$ non-polar \rightarrow **dispersion forces**

12.3 Properties of Liquids

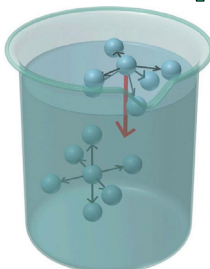
- **Surface tension** (σ) – the energy needed to increase the surface area of a liquid by a unit amount (units \rightarrow J/m²)

➤ Surface molecules experience a **net inward force** ↩

➤ To create more surface (surface molecules), energy is needed to work against this inward force

⇒ Liquids tend to assume shapes that **minimize the surface area** (spherical drops)

➤ $\sigma \uparrow$ with increasing the strength of the **IFs**

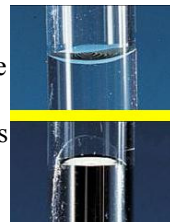


- **Capillary action** – the rising of liquids in narrow tubes (capillaries) against the force of gravity (results from the competition of two types of forces)

➤ **Adhesive forces** – between the molecules of the liquid and the walls of the capillary

➤ **Cohesive forces** – between the molecules within the liquid (**IFs**)

Examples: The **H₂O** level rises inside a narrow glass tube \rightarrow the adhesive forces are stronger; The **Hg** level drops inside a narrow glass tube \rightarrow the cohesive forces are stronger



- **Viscosity** (η) – the resistance to flow

– $\eta \uparrow$ with increasing the strength of the **IFs**

– $\eta \downarrow$ with increasing the temperature (the kinetic energy of the molecules increases relative to the **IFs** of attraction between them)

Examples:

CH₃CH₂OH is more viscous than **CH₃CH₂CH₃**

H-bonding ↩

London forces ↩

Oil and honey flow easier at higher **T**

12.5 The Unique Properties of Water

- **Solvent** properties of water

– Dissolves ionic compounds through ion-dipole forces (salts, minerals, acids, bases, ...)

– Dissolves molecular compounds

• Through H-bonding and dipole-dipole forces (sugars, alcohols, proteins, ...)

• Through Dipole-induced dipole forces (O₂, CO₂, ...)

- **Thermal** properties of water

– Very high **heat capacity** – it takes a lot of heat to warm or cool water (due to strong H-bonding)

• Oceans help maintain a narrow **T** range on Earth

– Very high ΔH_{vap} – it takes a lot of heat to vaporize water (due to strong H-bonding)

• Sweating helps maintain body temperature

- **Surface** properties of water

– Very high **surface tension** (strong H-bonding)

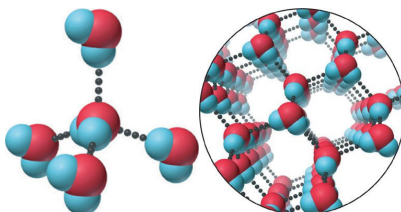
• Provides excellent capillary action (moisture in soil)

- **Density** of water

– Ice has lower density than liquid water due to the open ice structure (hexagonal network of H-bonds); the liquid is packed more efficiently

• Negative slope of solid liquid-phase boundary (rare)

• Ice floats on the surface of lakes and prevents total freezing



12.6 The Solid State

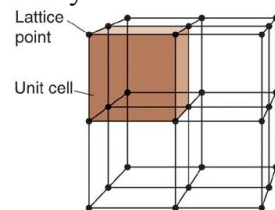
– **Amorphous solids** – random arrangement of structural units (rubber, plastics, ...)

– **Crystalline solids** – structural units arranged in regular arrays (crystals with well defined shapes and surfaces)

- **Crystal lattice** – a system of points defining the geometric pattern of the crystal

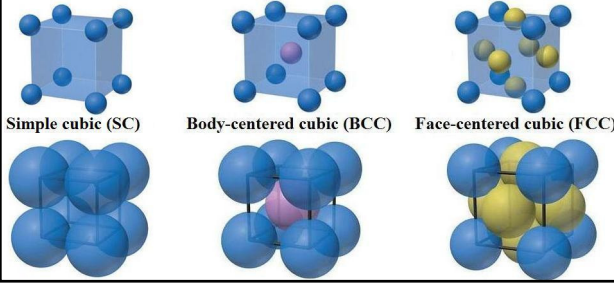
➤ **Lattice points** – points with identical surroundings (can be occupied by atoms, ions or molecules)

➤ **Unit cell** – a small set of lattice points sufficient to reproduce the entire lattice



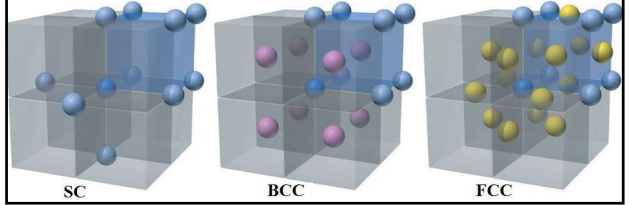
➤ There are 7 **crystallographic systems** with different lattices occurring in nature

- **Cubic system** – the unit cell is a cube
 - There are three types of cubic unit cells
 - Let's assume that a spherical particle occupies each lattice point (not always the case)



➤ **Coordination number** – the number of nearest neighbors of a particle in the lattice

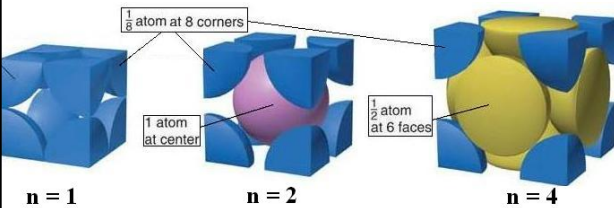
- SC → **coord. # = 6** → each particle touches 6 other particles (4 in the same layer, 1 above and 1 below)
- BCC → **coord. # = 8** → each corner particle touches 8 particles in the body centers of the 8 cells it belongs to
- FCC → **coord. # = 12** → each corner particle touches 12 particles in the face centers (4 in the same layer, 4 above and 4 below)



➤ **Lattice points per unit cell (n)**

- Corner points belong to 8 cells → $1/8$ of the corner points
- Face points belong to 2 cells → $1/2$ of the corner points
- Body points belong to 1 cell → all body points

- SC → $n = (1/8) * 8$ corners = 1
- BCC → $n = (1/8) * 8$ corners + 1 body point = $1 + 1 = 2$
- FCC → $n = (1/8) * 8$ corners + $(1/2) * 6$ face points = $1 + 3 = 4$

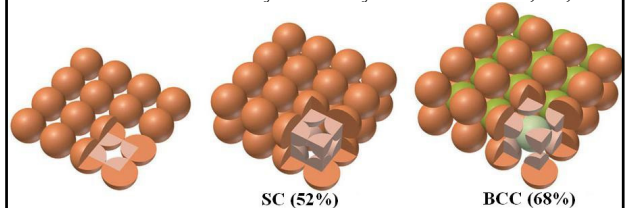


• **Packing efficiency** – part of the total volume of the crystal that is occupied by the particles

- For spherical particles of the same size, the efficiency **increases with the coordination #**

➤ SC & BCC – in each layer, the particles form squares with diamond-shaped holes between them

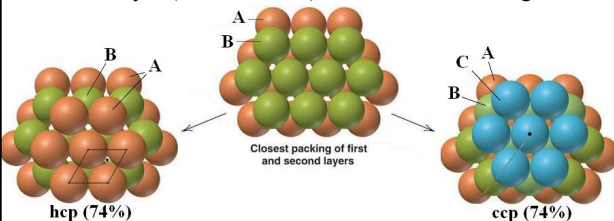
- SC → 2nd, 3rd, ... layers directly on top of 1st layer
- BCC → 2nd layer fits in holes of 1st layer, and 3rd layer fits in holes of 2nd layer directly above 1st → Na, Fe, ...



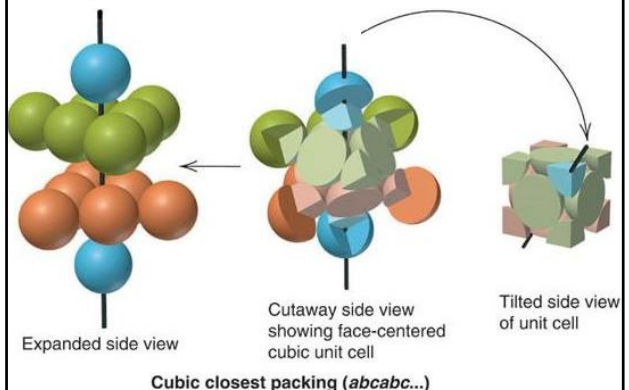
➤ **Closest packing structures** – in each layer, the particles form rhombi with triangular holes between them (more efficient)

➤ **Hexagonal closest packing (hcp)** – 2nd layer fits in holes of 1st layer, and 3rd layer fits in holes of 2nd layer directly above 1st layer (ABAB ...) → Zn, Mg, Ti, ...

➤ **Cubic closest packing (ccp)** – 2nd layer fits in holes of 1st layer; 3rd layer fits in holes of 2nd layer above holes of 1st layer (ABCABC ...) → Al, Ni, Cu, Pb, Ag, ...



- hcp is based on the **hexagonal** unit cell
- ccp is based on the **FCC** unit cell (the same thing)



- **Density of unit cells (d)** – same as that of the crystal
 - $m \rightarrow$ mass of unit cell; $m_p \rightarrow$ mass of 1 particle
 - $V \rightarrow$ volume of unit cell; $V_p \rightarrow$ volume of 1 particle
 - $V_o \rightarrow$ volume of unit cell occupied by particles
 - $n \rightarrow$ # of particles per unit cell
 - $M \rightarrow$ molar mass; $N_a \rightarrow$ Avogadro's number
 - $Eff \rightarrow$ packing efficiency; $r \rightarrow$ radius of a particle

$$V_o = V \times Eff = n \times V_p \Rightarrow V = \frac{n \times V_p}{Eff}$$

$$d = \frac{m}{V} = \frac{n \times m_p}{V} = \frac{n \times (M / N_a)}{V} = \frac{n \times M \times Eff}{n \times V_p \times N_a}$$

$$V_p = \frac{4}{3} \pi r^3 \Rightarrow d = \frac{3}{4} \times \frac{M \times Eff}{\pi r^3 \times N_a}$$

Example: Fe has a density of **7.90 g/cm³** and crystallizes in a **BCC** lattice. Calculate the atomic radius of Fe.

$M \rightarrow 55.85$ g/mol; $Eff \rightarrow 0.68$; $r \rightarrow ???$

$$d = \frac{3}{4} \times \frac{M \times Eff}{\pi r^3 \times N_a} \Rightarrow r = \sqrt[3]{\frac{3}{4} \times \frac{M \times Eff}{\pi \times d \times N_a}}$$

$$r = \sqrt[3]{\frac{3}{4} \times \frac{55.85 \text{ g/mol} \times 0.68}{3.14 \times 7.90 \text{ g/cm}^3 \times 6.022 \times 10^{23} / \text{mol}}}$$

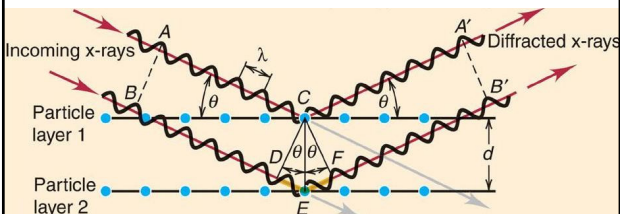
$$r = 1.24 \times 10^{-8} \text{ cm} = 124 \text{ pm}$$

- The structure of the unit cell can be studied by **x-ray diffraction**

- The crystal is irradiated with a narrow beam of x-rays and the resulting diffraction pattern consists of dark and bright spots
- The condition for constructive interference (bright spot in the pattern) is given by the **Bragg Equation**:

$$2d \sin\theta = n\lambda \rightarrow d - \text{distance between layers}$$

$$\rightarrow n - \text{whole number}$$



Types of Crystalline Solids

- **Atomic solids** – consist of atoms
 - The atoms are held together by weak dispersion forces (Examples: **Ne, Ar, Kr, Xe, Rn**)
 - Quite soft; very low T_m ; poor electrical and thermal conductors (T_m increases with increasing molar mass)
- **Molecular solids** – consist of molecules
 - Non-polar molecules are held together by dispersion forces (Examples: **O₂, CH₄, CO₂, ...**)
 - Polar molecules are held together by dispersion, dipole-dipole and in some cases H-bonding forces (Examples: **H₂O, SO₂, sugar, ...**)
 - Soft; low T_m ; poor electrical and thermal conductors

- **Ionic solids** – consist of + and – ions

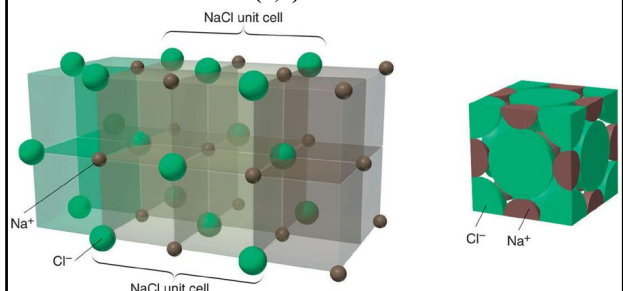
- Ions are held together by very strong ion-ion electrostatic attractions (ionic bonds) \rightarrow Examples: **NaCl, MgO, CaF₂, ...**
- Hard and brittle; high T_m ; conduct electricity and heat when molten
- The unit cell has the same composition (ratio of cations to anions) as the empirical formula
- Typically the smaller cations fit in the gaps between the larger anions

• **Radius ratio** $\rightarrow r_{cat}/r_{an}$

• Depending on the radius ratio and the ion ratio, different structures are possible

\rightarrow Ionic compounds with 1:1 ion ratio

- **Rock salt structures** – FCC arrangement of the anions; the cations fit in the gaps between the anions and also form FCC structure (**NaCl, KBr, MgO, ...**)
 - Typical for compounds with radius ratios of **0.4 - 0.7** (small cations large anions)
 - **Coordination #** \rightarrow **(6,6)** – 6 for cations and 6 for anions



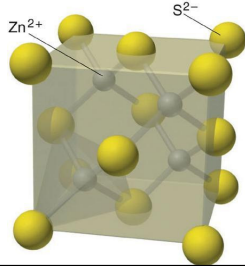
➤ **Cesium chloride structures** – BCC unit cell with eight ions in the corners and one counter-ion in the body center of the cube (CsCl, CsI, ...)

➤ Typical for compounds with radius ratios larger than **0.7** (cations and anions with similar sizes)

➤ **Coordination #** → **(8,8)** – 8 for cations and 8 for anions

➤ **Zinc blende structures** – FCC structure of anions penetrated by FCC structure of cations; each cation is tetrahedrally surrounded by 4 anions and vice versa (ZnS, CdS, AgI, CuCl, ...)

➤ **Coordination #** → **(4,4)** – 4 for cations and 4 for anions



→ Ionic compounds with 1:2 or 2:1 ion ratios

➤ **Fluorite structures** – FCC unit cell of cations, penetrated by 8 anions in the gaps between the cations (CaF₂, SrF₂, BaCl₂, ...)

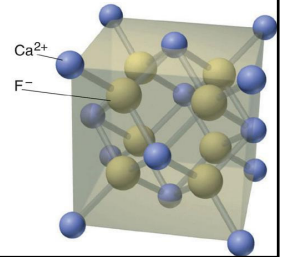
➤ Typical for 1:2 compounds with large radius ratios

Coordination # → **(8,4)** – 8 for cations and 4 for anions

➤ **Antifluorite structures** – FCC unit cell of anions, penetrated by 8 cations in the gaps between the anions (K₂S, ...)

➤ Typical for 2:1 compounds with small radius ratios

➤ **Coordination #** → **(4,8)** – 4 for cations and 8 for anions



• **Metallic solids** – consist of metal atoms

– The atoms are held together by strong metallic bonding forces (Examples: **Fe, Cu, Ti, Na, ...**)

– Wide range of hardness; luster; malleable and ductile; wide range of T_m ; excellent electrical and thermal conductors

• **Network solids** – consist of atoms

– The atoms are held together by strong covalent bonds [Examples: **C(diamond), SiO₂(quartz), ...**]

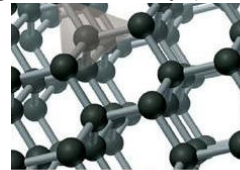
– Most are very hard; very high T_m ; usually poor electrical and thermal conductors

– Hardness and conductivity vary with the way atoms are bonded together

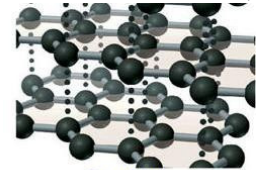
Example: Carbon has two common allotropic forms:

➤ **Diamond** → tetrahedral network of covalently σ -bonded C atoms in sp^3 hybridization → extremely hard; poor conductivity (insulator)

➤ **Graphite** → flat sheets of covalently bonded C atoms in sp^2 hybridization (can be viewed as condensed benzene rings with delocalized π -bonding) → soft and slippery (weak *IFs* between the sheets allow sliding); good conductivity (delocalization of the π -electrons)



Diamond



Graphite

The Band Theory of Solids

• Application of the **MO** theory to solids

– A metallic crystal can be viewed as one enormous molecule made of many atoms

– The valence **AOs** of these atoms merge to form delocalized **MOs** (N AOs produce N MOs)

– The large number of **MOs** form “**bands**” of closely spaced energy levels

– The different types of **AOs** (s, p, d, ...) form different bands (s-band, p-band, ...)

– Some bands are separated by **band gaps** where energies are not allowed

– Bands can be empty, partly filled, or filled with e^-

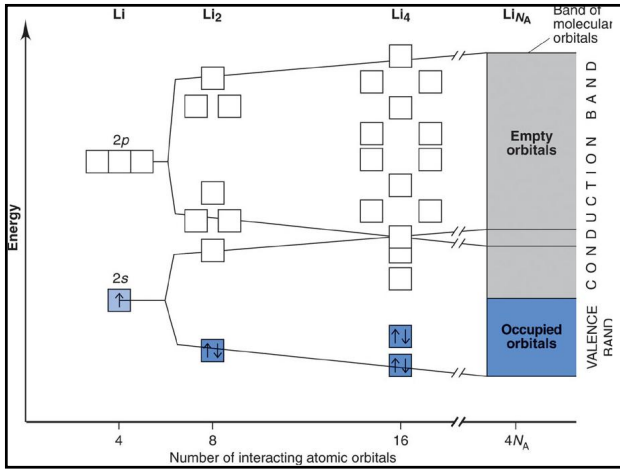
➤ The band occupied by the valence electrons is called **valence band**

➤ The band of empty orbitals directly above the valence band is called **conduction band**

➤ Electrons from the valence band can be excited to the conduction band and become mobile → provide conductivity

Example:

In **Li**, each atom contributes **1** s-electron to the s-band. N Li atoms contribute N electrons. N Li atoms have N s-orbitals and produce N MOs. N MOs can hold $2N$ electrons ⇒ The s-band is half-full.



➤ **Metal conductors** – the valence and conduction bands overlap (no band gap) ⇒ the electrons need an extremely small amount of energy to jump in the conduction band

➤ Conductivity decreases with increasing T since the random motion of the atoms hinders the directional motion of electrons

➤ **Semiconductors** – the valence and conduction bands are separated by a small band gap ⇒ the electrons need a fairly small amount of energy to jump in the conduction band

➤ Conductivity increases with increasing T since the electrons are thermally excited to the conduction band

➤ **Insulators** – the valence and conduction bands are separated by a large band gap ⇒ the electrons can not be excited to the conduction band → no conductivity

➤ **Superconductivity** – conduction with no energy loss (extremely low resistance)

➤ Metals can super conduct at very low T (<4K)

➤ New materials can super conduct at higher T s

