Lecture 4

Spring 2022

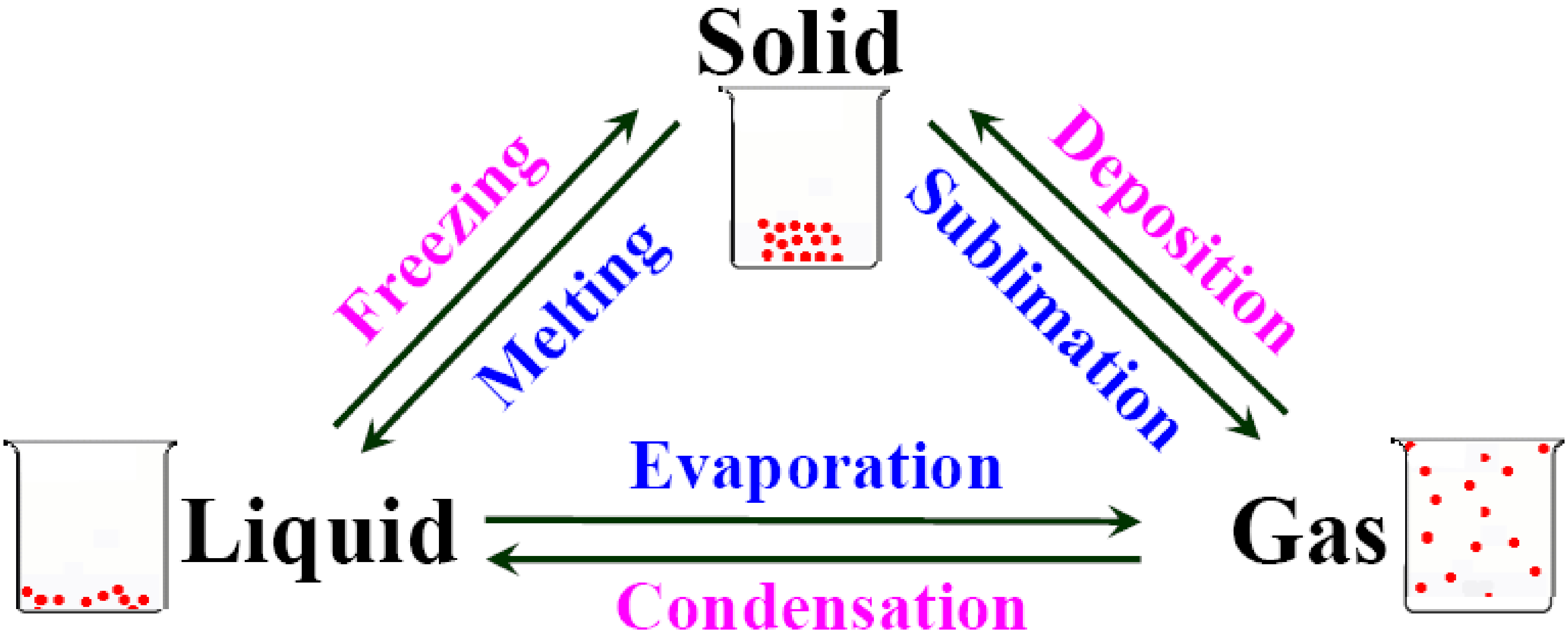
General Chemistry II

Chem 102

Liquids and Solids

Ahmad Alakraa

Recognize



Solid

Freezing

Melting

Deposition

Sublimation

Liquid

Evaporation

Condensation

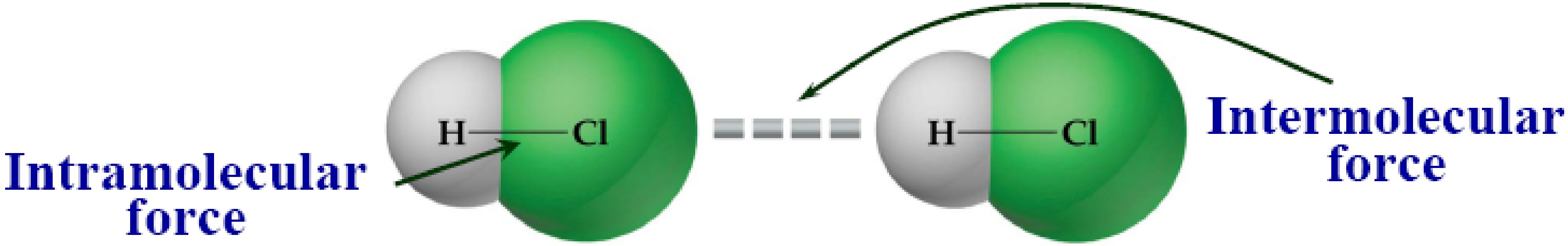
Gas

Properties of liquids are intermediate between those of solids and gases

Intermolecular and intramolecular

- **Intermolecular forces**: are those forces between molecules in the condensed states (liquids or solids).
  - always **physical** in nature.
  - are responsible for bulk properties of materials (melting point, boiling point, etc.)

- **Intramolecular forces**: forces that hold atoms together **within** a molecule.
  - always **chemical** in nature.



Remember

- Intermolecular forces are much weaker than intramolecular forces.

It requires much less energy to evaporate a liquid than to break the bonds in the molecule.

Intramolecular Forces and Chemical Bonding

- Three major types of intramolecular chemical bonding are considered;
  - electrostatic (ionic),
  - covalent, and
  - metallic bonding.

Electrostatic (ionic) bonding

$$F = \frac{q_1 q_2}{4\pi\varepsilon_o r^2} \qquad F = \frac{z_1 z_2 e^2}{4\pi\varepsilon_o r^2}$$

- One atom gives one or more electrons to another atom or atoms (**Octet structure** and **Coulomb attraction** of opposite charges are deriving)

- The above equation represents the Coulomb force F(r) between two static ions if an ion (a point-like body) of charge q_1 is at a center-to-center distance, r, away from another ion of charge, q_2, in a vacuum.

  e_o is the vacuum permittivity = $8.854 \times 10^{-12}\ C^2\ J^{-1} m^{-1}$

- The ionic bonds are long-ranged, non-directional and not so strong (≈ 400 $kJmol^{-1}$)

Non directional

- because charge is uniform in all direction and each ion is surrounded by other ions from all directions.
- In **ionic solids** while stacking atoms, there are **no directional** requirements (bonding can be at any angle) but there are a **size** and **charge** requirements.
- Each ion must have nearest neighbors of appropriate size and of opposite charge.

Long-ranged

- because they **attract** or **repel** other ions beyond the nearest and next-nearest neighbors.

Covalent bonding

☐ Two atoms share one or more pairs of electrons between them to attain a more stable electronic grouping (Octet electronic structure). Examples: H_2 - N_2 - O_2 - Cl_2 – CH_4

☐ Covalent bonds are very short-ranged (operate over very short interatomic separations (0.1–0.2 nm)), highly directional and strong.

☐ Directional means: atoms prefer specific orientations (molecular geometry) in space relative to one another (minimizing repulsion between bonding electrons is driving directionality). As a result, molecules in which atoms are bonded covalently have definite shapes.

- ☐ There are no charge requirements. Each atom does not have to have nearest neighbors of opposite charge.
- ☐ There are no long range requirements. Bonds are only between nearest-neighbor atoms sharing electrons.
- ☐ Typically covalent bond formation energies range from 200 to 1000 $kJmol^{-1}$ at room temperature.
- ☐ Covalent bonding can be single covalent, double covalent, or triple covalent depending on the number of pairs of electrons shared.
- ☐ When both shared electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond

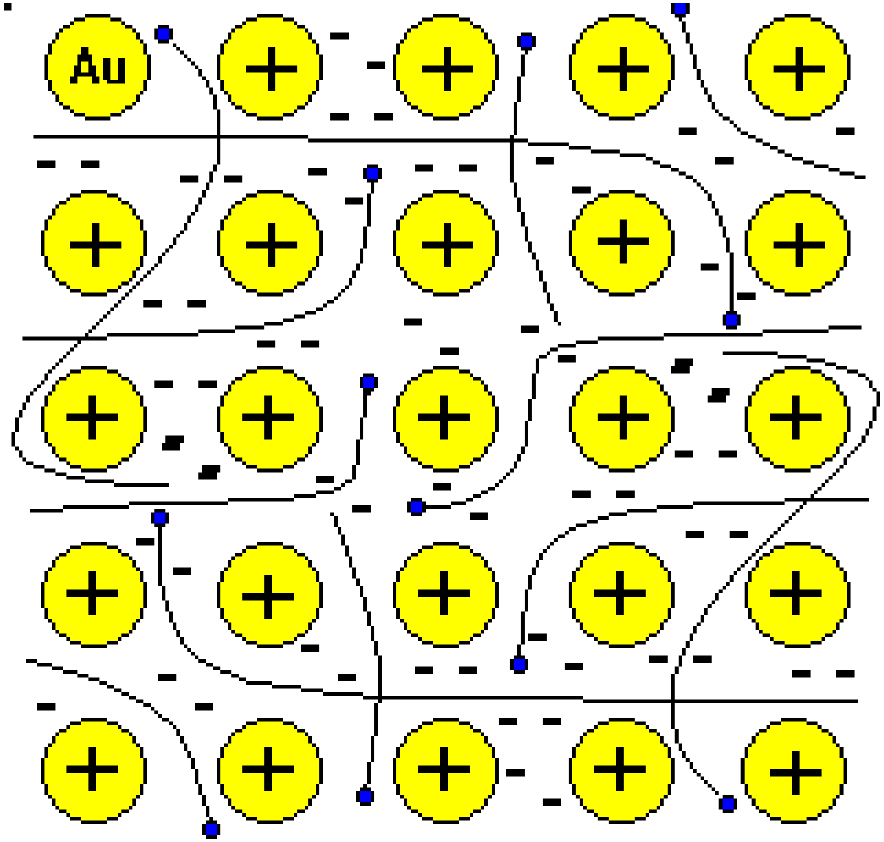
- Covalent bonds can be either **polar** or **nonpolar**. When the shared pair of electrons is not shared equally, one end of the bond is **partially positive**, and the other end is **partially negative**. This produces a bond with two poles called a **polar covalent bond**.

- Molecules having polar covalent bonds are called **dipolar or polar molecules**. Water is an example of a polar molecule.

- When two atoms of the same element share one or more pairs of electrons (such as H or N), the bond is called a **nonpolar covalent bond**. If all the bonds in a molecule are of this kind, the molecule is called a **nonpolar covalent molecule**.

Metallic bonding (Electron sea model)

- The valence electrons are (**delocalized**) not closely associated with individual atoms, **but instead** move around atoms within the crystal.



- The individual atoms can "**slip** تنزلق " over one another yet remain firmly held together by the electrostatic forces exerted by the electrons.

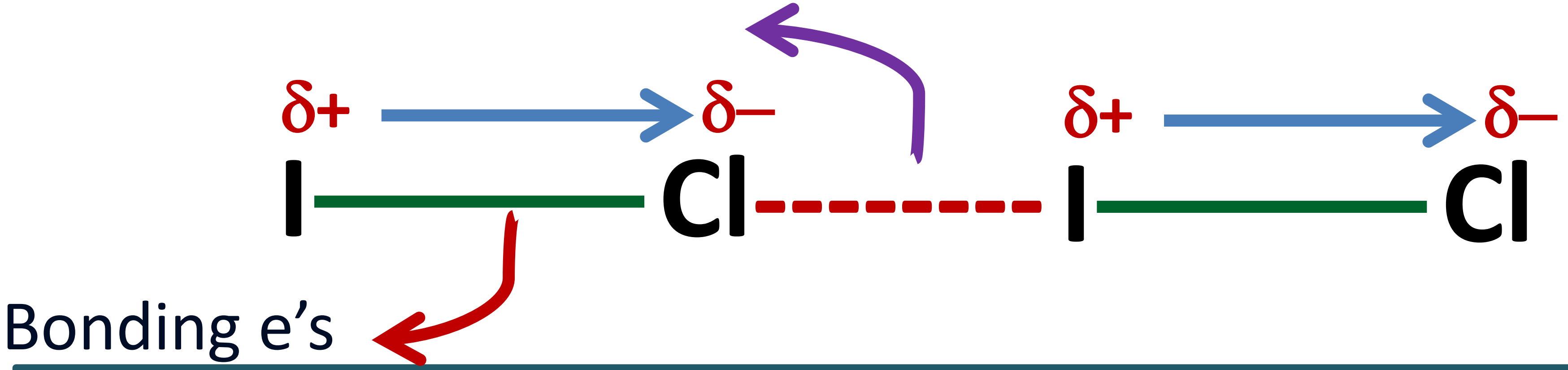
- This is why most metals can be hammered تطرق into thin sheets (malleable قابل للطرق) or drawn into thin wires (ductile قابل للسحب).
- When an electrical potential difference is applied, the electrons move freely between atoms, and current flows.
- Metallic bonds are sometimes as strong as ionic bonds.
- In Metallic bonds there are
  - no charge requirements,
  - no directional requirements, and
  - long range effects.

Intermolecular Forces and Physical Bonding

Major types

- Dipole-Dipole forces.
  - H-bonding
- Charge (ion)-Dipole forces.
- London Dispersion Forces.

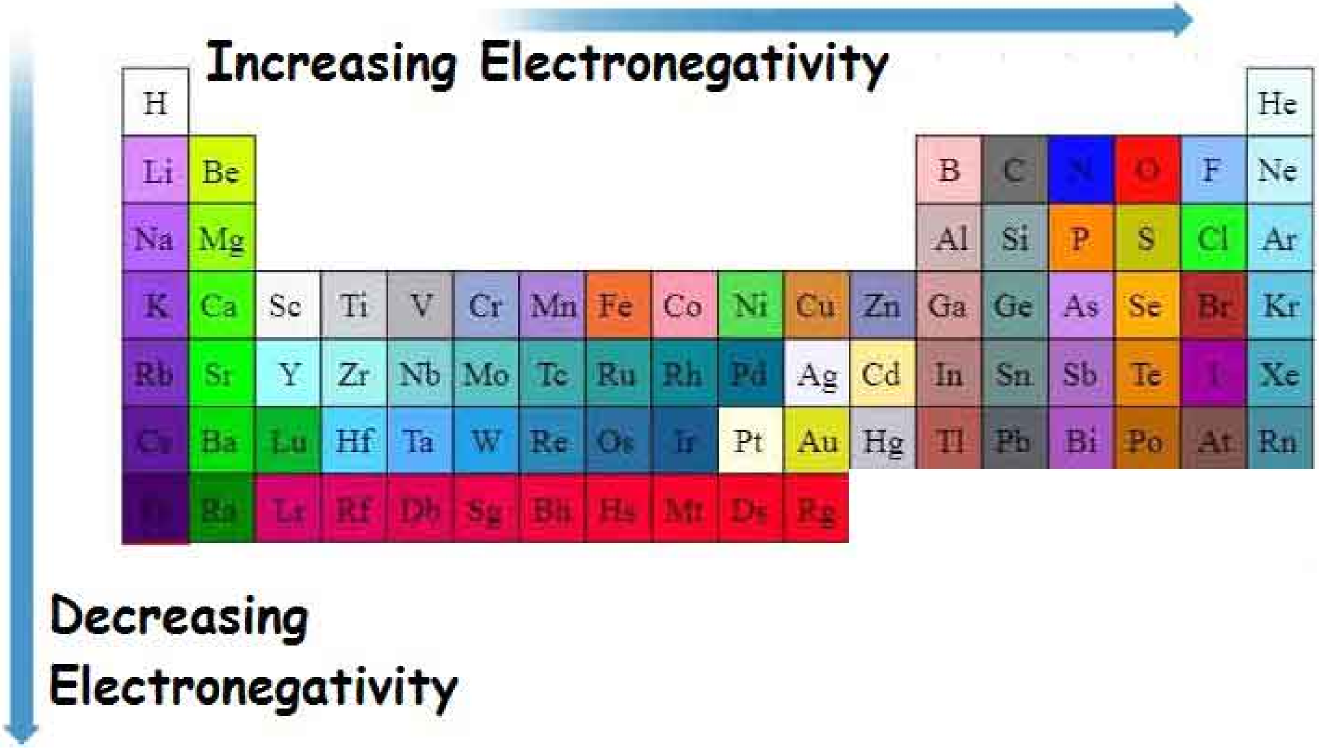
Dipole-dipole Forces



- Forces acting between polar molecules (molecules having **permanent** dipole moments)
- The origin of this force is **electrostatic**. As the **dipole moment** increases, the force increases.
- It is about **100 times** weaker than ionic interactions and falls off quickly with the distance, as a function of **$1/r^3$**.

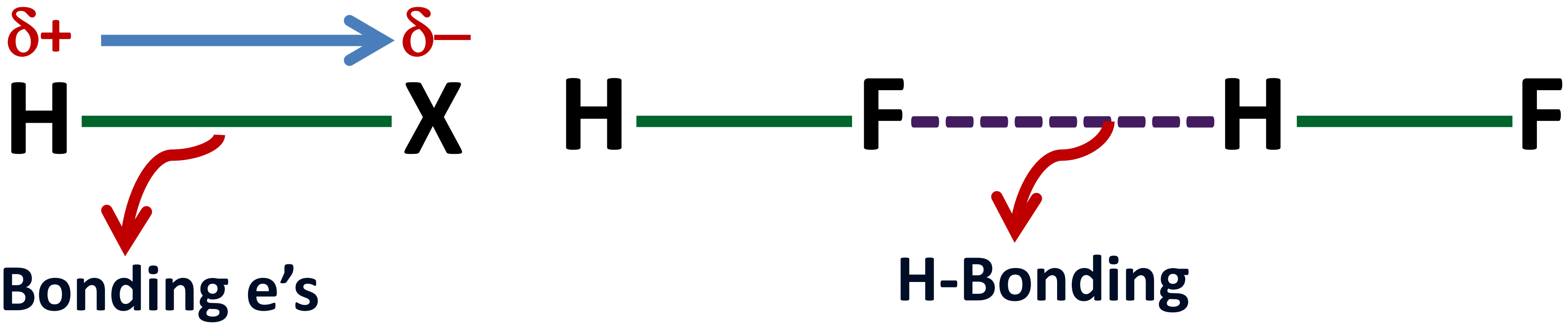
Factors affecting dipole-dipole forces

- Bond polarity
  - The difference in electronegativity predicts this polarity
- Size of ions (how close they may approach each other) .
- The number of **H-bonds** per an atom and per a molecule.



Hydrogen bonding

a special case of polar interactions occurring when hydrogen is bonded to a very electronegative element such as oxygen or fluorine, e.g., O–H---O.



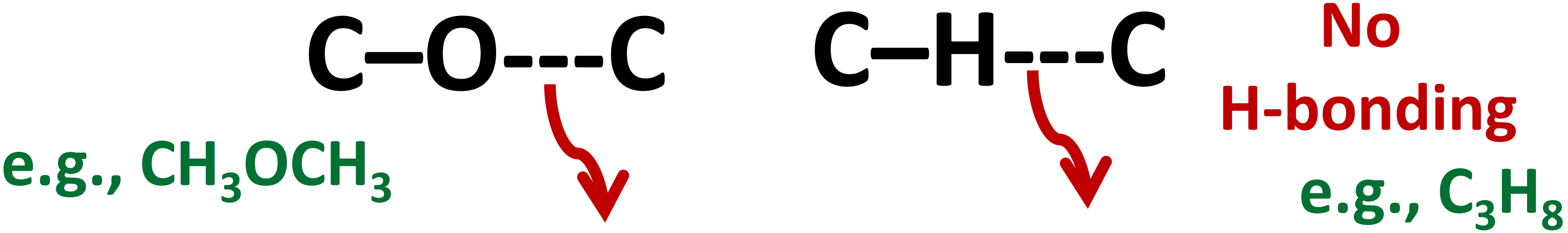
δ+ → δ–

H——X

H——F-------H——F

Bonding e's

H-Bonding



C–O---C

C–H---C

e.g., CH_3OCH_3

No H-bonding

e.g., C_3H_8

The slight difference in electronegativity does not permit H-bonding

Give reasons

The boiling points of hydrogen compounds of gp. 5A, 6A and 7A decreases with the molar mass within a group? Or Why NH_3, H_2O, and HF have the highest BPs?

Answer

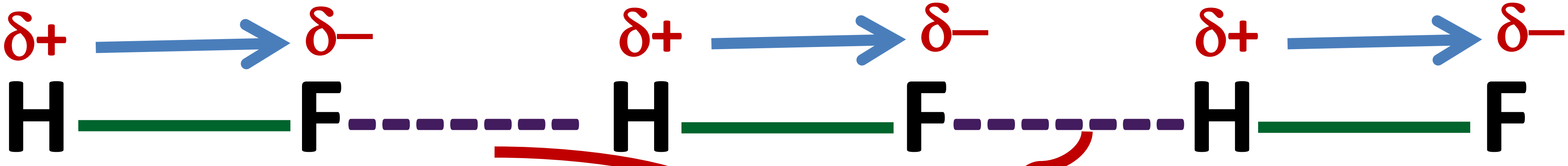
Because as we go down a group, the electronegativity of atoms decreases. Therefore, The strength of H-bonding decreases (lower energy is required for vaporization)

N 3.0	O 3.5	F 4.0
P 2.2	S 2.5	Cl 3.0
As 2.2	Se 2.6	Br 2.8

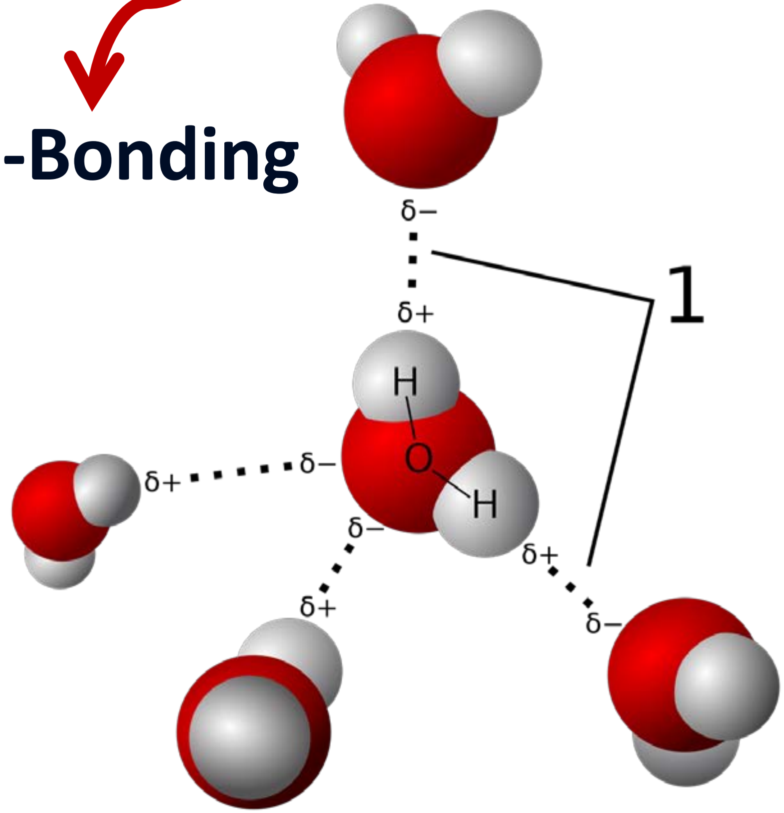
Give reasons

Although fluorine is more electronegative than oxygen, the BP of HF (19.5°C) is lower than that of H_2O (100°C) . Why?

Answer



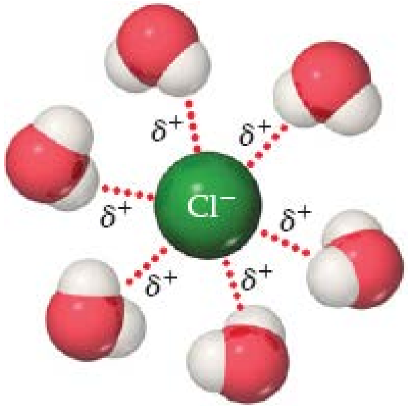
Because each water molecule participate in **4** intermolecular H-bonds but HF has only **2**.

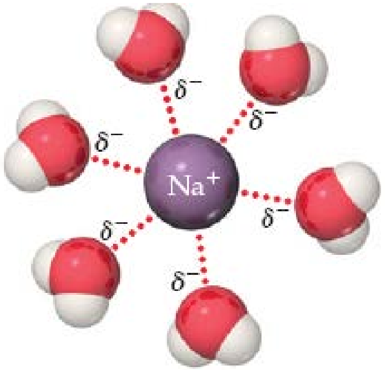


H_2O molecules hold together more tightly.

Charge (ion)-Dipole forces

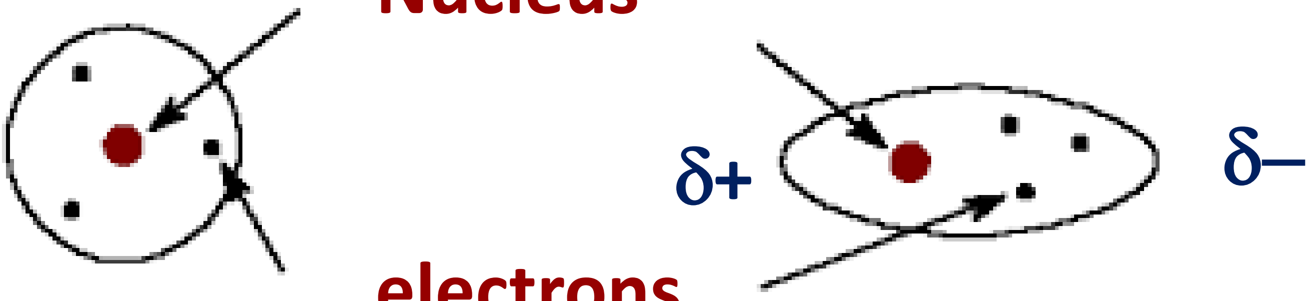
- originated from interaction of a polar molecule to a charged ion (**cation** or **anion**)
- is about **10** to **20** times **weaker** than ion-ion interactions, and decreases with distance as **$1/r^2$**.





For cations ($^{19}\mathrm{K} \rightarrow {}^{18}\mathrm{K}^{+}$) and anions ($^{17}\mathrm{Cl} \rightarrow {}^{18}\mathrm{Cl}^{-}$) of equal charges, cations interact more strongly to dipoles than anions: as cations are usually smaller than anions, their **charge densities** will be higher and therefore interact more strongly.

London Dispersion Forces (LDF)



Nucleus

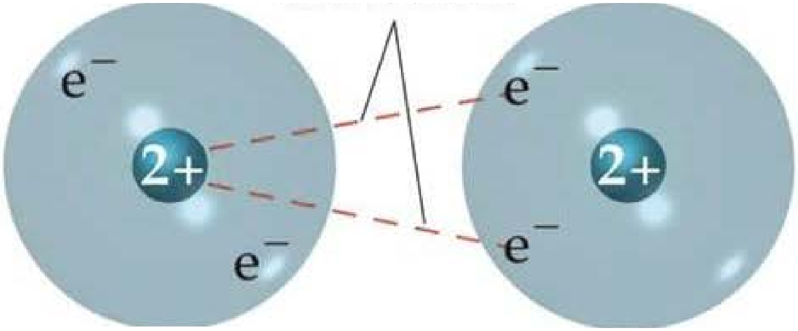
electrons

δ+ δ−

Symmetric distribution

Unsymmetrical distribution

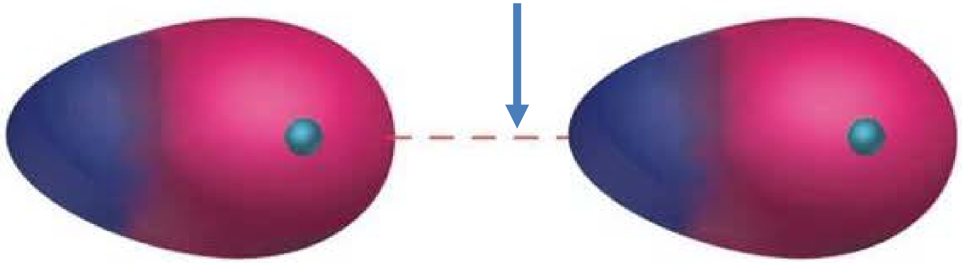
Electrostatic attractions



He atom 1

He atom 2

London Dispersion Forces



δ+ δ− δ+ δ−

London Dispersion Forces

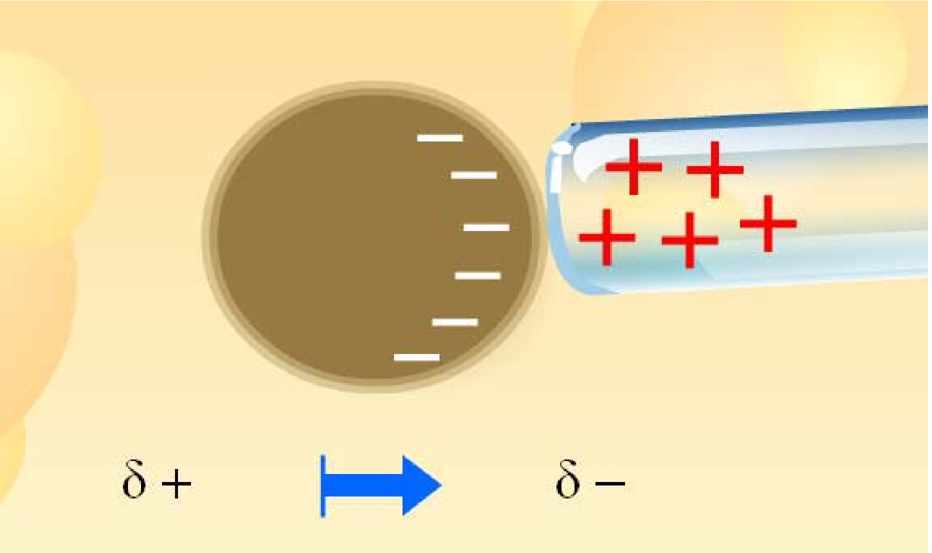
- is a subdivision of van der Waals forces
- is the major force in noble gases and non polar molecules.
- originates from induction الحث in non polar molecules.
  - ✓ The movement of the valence e's creates 'transient dipoles' "momentary non symmetrical electron distribution" and these in turn induce dipole moments in adjacent molecules.
  - ✓ The transient dipole in one molecule can be attracted to the transient dipole in a neighboring molecule, and the result is this weak, short-ranged attractive force.
- drop off rapidly with distance, decreasing as a function of **$1/r^6$**

Factors affecting LDF

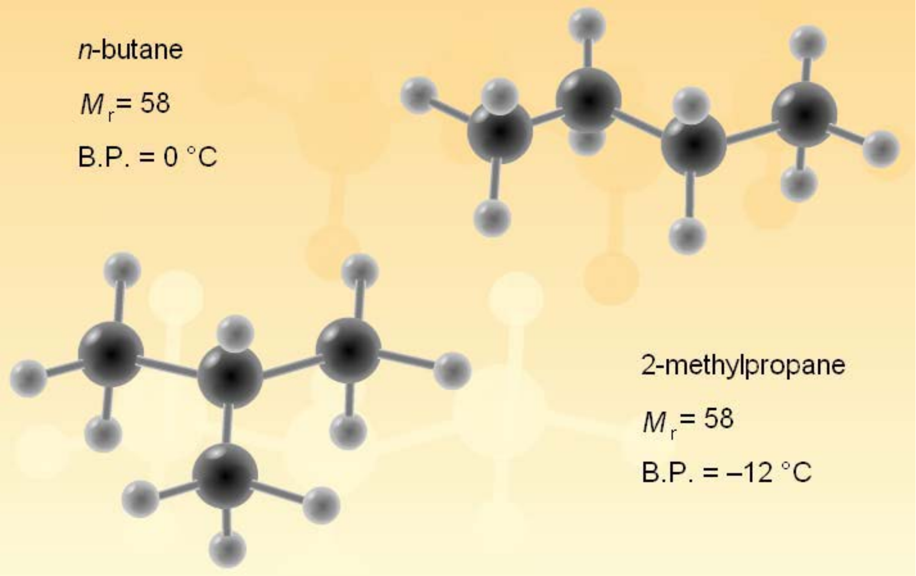
Molecular size

- ☐ The strongest LDF occur between large molecules of large electron clouds that are easily distorted or polarized.

Polarizability,



Molecular shape



n-Butane/2-methyle propane

Why do butane and 2-methylpropane have different boiling points?

- butane and 2-methylpropane have the same molar masses, but 2-methyl propane is more branched and thus the available surface for interaction with other molecules is smaller.
- This makes the intermolecular forces for 3-methylpropane weaker and thus the boiling point lower.

Q Why the noble gas elements have low freezing points?

Because for these weak interaction forces to be strong enough to produce a solid, the motions of the atoms must be greatly slowed down. This occurs at low T

	°C
He	−269.7
Ne	−248.6
Ar	−189.4
Kr	−157.3
Xe	−111.9
Rn	−71

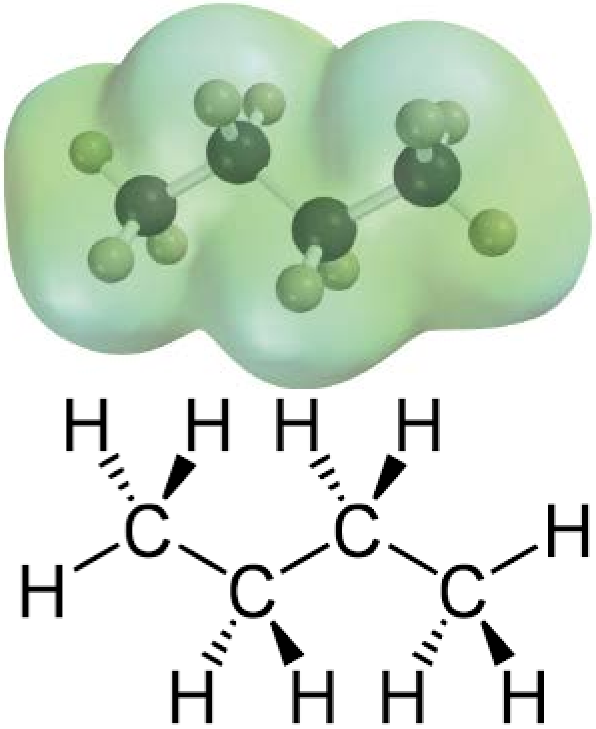
Q The freezing point increases as we go from He to Xe in 8A group elements. Explain why?

Because as we go from He to Xe, the atomic size increases and the polarizability (chance of occurring a momentary dipole moment) increases i.e., London Dispersion Force increases. Therefore, the temperature required for solids to form increases (no need to slow down too much for larger molecules).

	°C
He	−269.7
Ne	−248.6
Ar	−189.4
Kr	−157.3
Xe	−111.9
Rn	−71

Structure affects properties

Why?

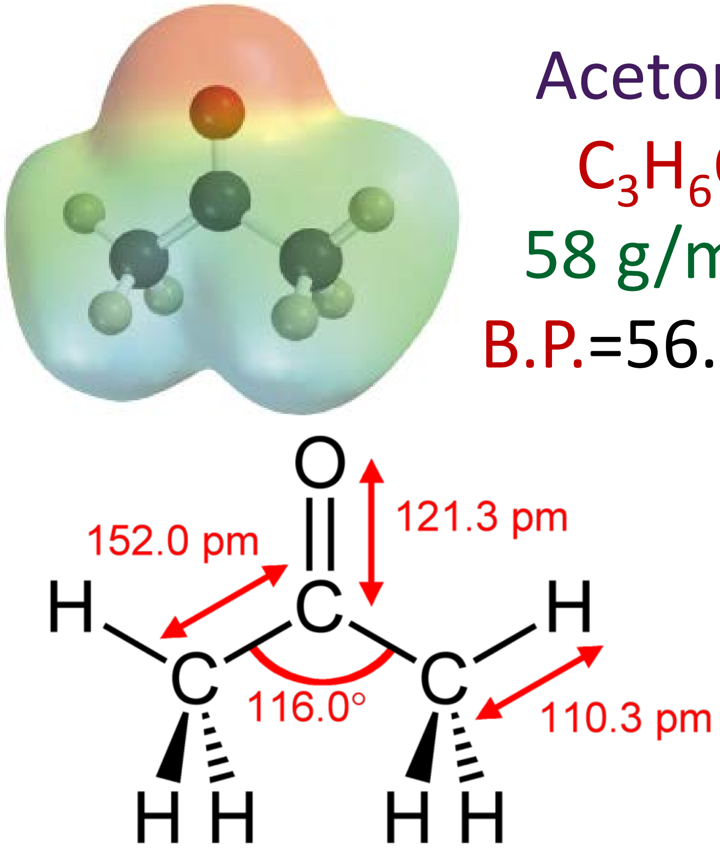


Butane

C_4H_{10}

58 g/mol

B.P.=–0.5°C



Acetone

C_3H_6O

58 g/mol

B.P.=56.2°C

Polarizability / H-bonding

Relative Bond Strength

Increasing Bond Strength

London Dispersion, e.g., CH_4, CCl_4 Br_2, F_2

Dipole-dipole, e.g., CH_3F, HBr

H-Bonding, e.g., NH_3, CH_3OH, HCOOH

Ion-dipole, e.g., NaCl dissolved in H_2O

Ionic bonding, e.g., KBr, NH_4NO_3

Why is I_2 a solid whereas Cl_2 is a gas? Size effects

Compounds may involve several bonding

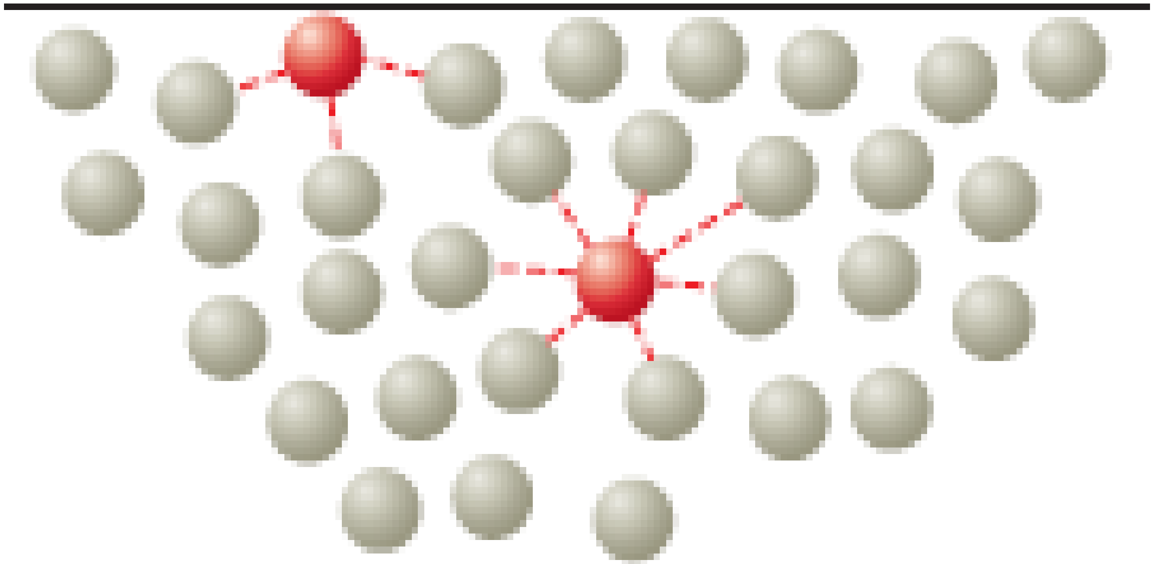
	Dispersion	Dipole-dipole	H-bonding
Non-polar Compounds	🟩		
Polar Compounds	🟩	▨	
Compounds capable to form H-bonding	🟩	▨	🟧

Surface tension, γ Jm^{-2} or Nm^{-1}

- the resistance of a liquid to an increase in its surface area.
- is measured by the amount of energy required to stretch or increase the surface by unit area.

When a liquid is poured onto a solid surface, it tends to bead as droplets!!!!!

Air/liquid interface



- The effect of unequal forces on the surface molecules tends to draw them into the body of the liquid and causes a droplet of liquid to assume the shape that has the minimum surface area—a sphere.

- To increase a liquid’s surface area, molecules must move from the interior of the liquid to the surface. This requires energy, since some intermolecular forces must be overcome.

- Liquids with relatively large intermolecular forces, such as those with polar molecules, tend to have relatively high surface tensions.

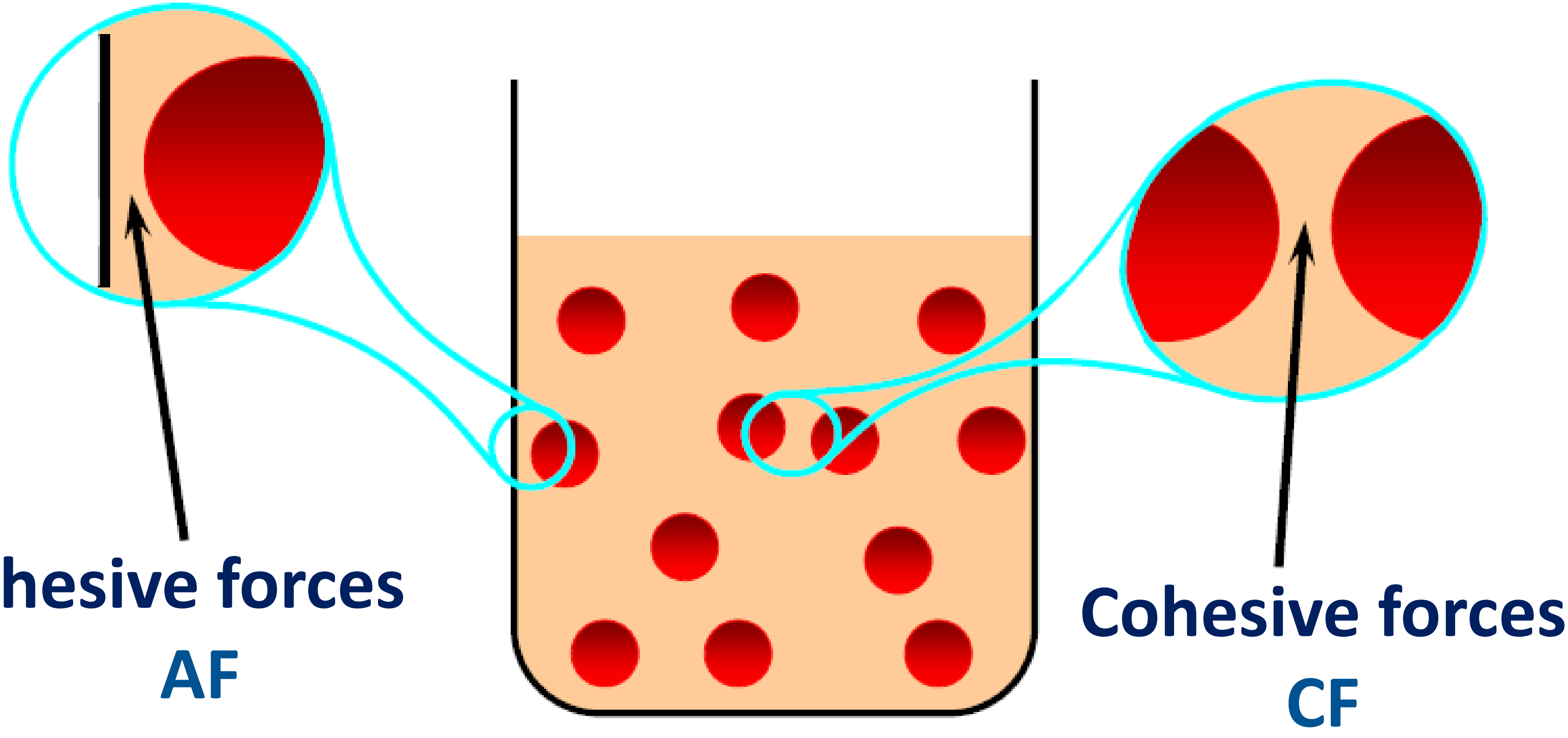
Capillary action

The phenomenon of spontaneous rising or depression of liquids in a narrow capillary tube

Cohesive forces **CF**	intermolecular forces among the molecules of the liquid
Adhesive forces **AF**	forces between the liquid molecules and their container

- A glass surface contains many oxygen atoms with partial negative charges that are attractive to the positive end of a polar molecule such as water.

Cohesive/Adhesion forces

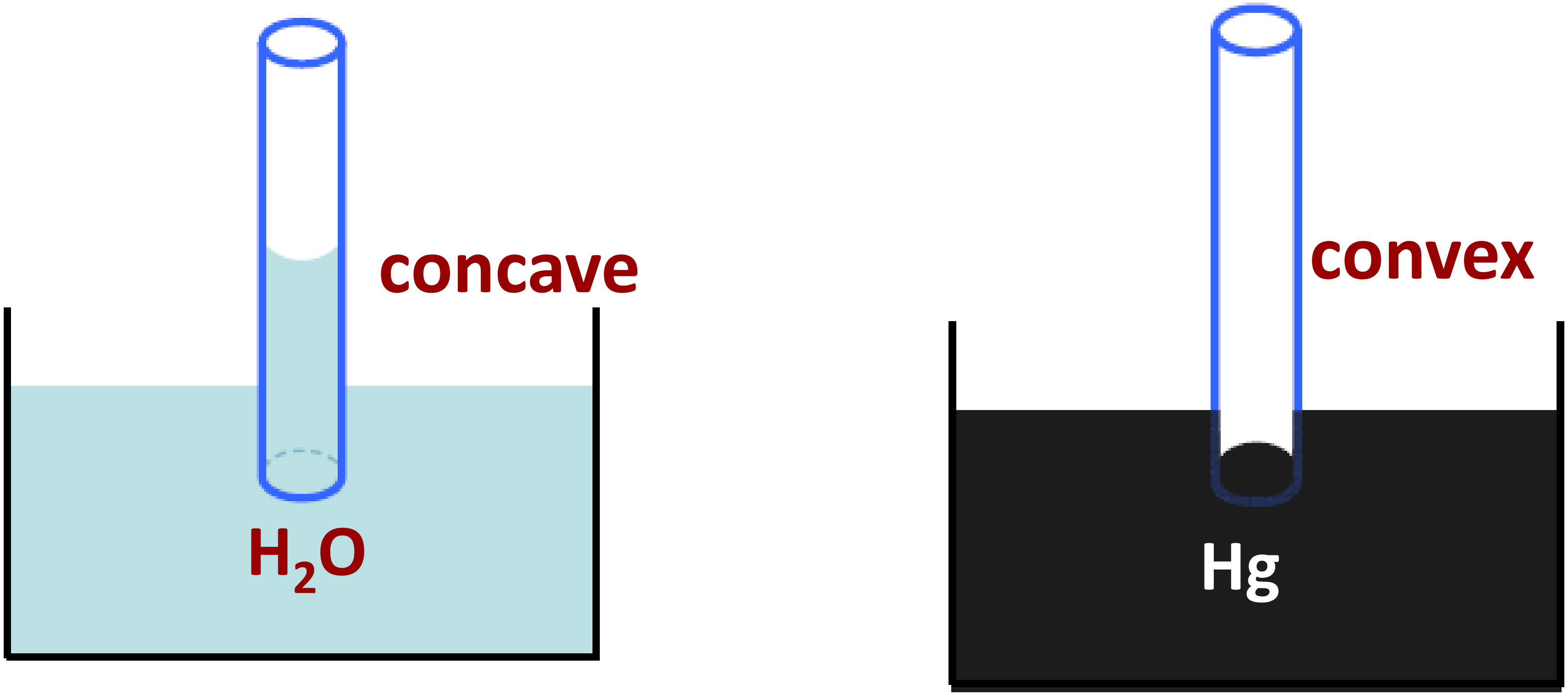


Adhesive forces

AF

Cohesive forces

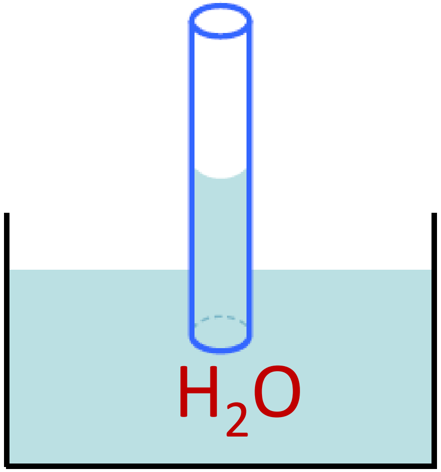
CF

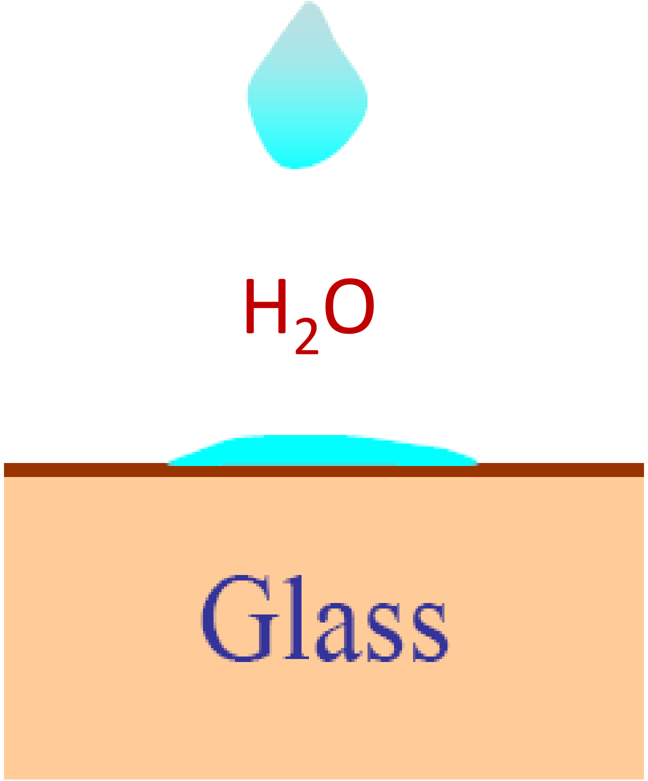


- This ability of water to "wet" glass makes it creep up يرتفع the walls of the tube where water surface touches the glass.
- This tends to increase the surface area of water, which is opposed by CF that try to minimize the surface.

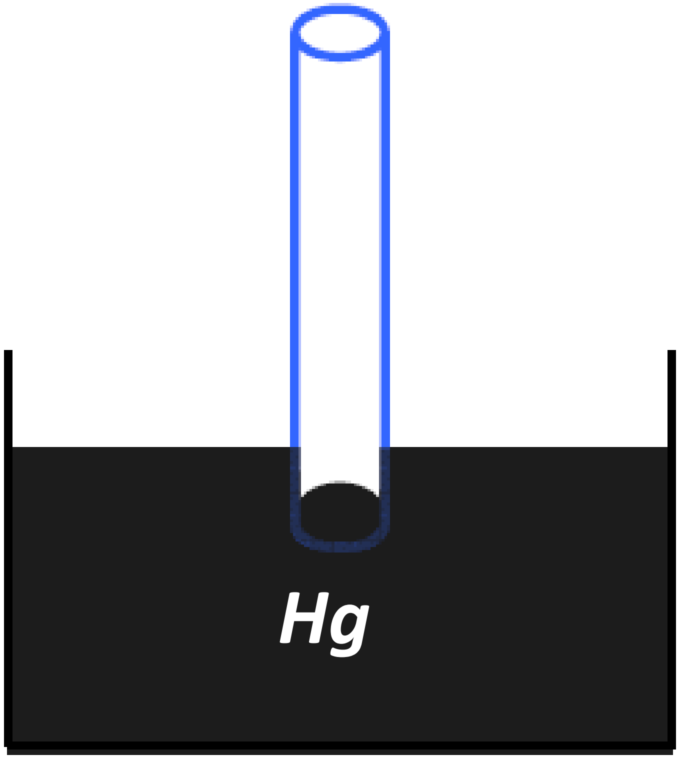
- Because water has both strong (intermolecular) CF and strong AF to glass, it “pulls itself” up a glass capillary tube (a tube with a small diameter) to a height where the weight of the column of water just balances the water’s tendency to be attracted to the glass surface.

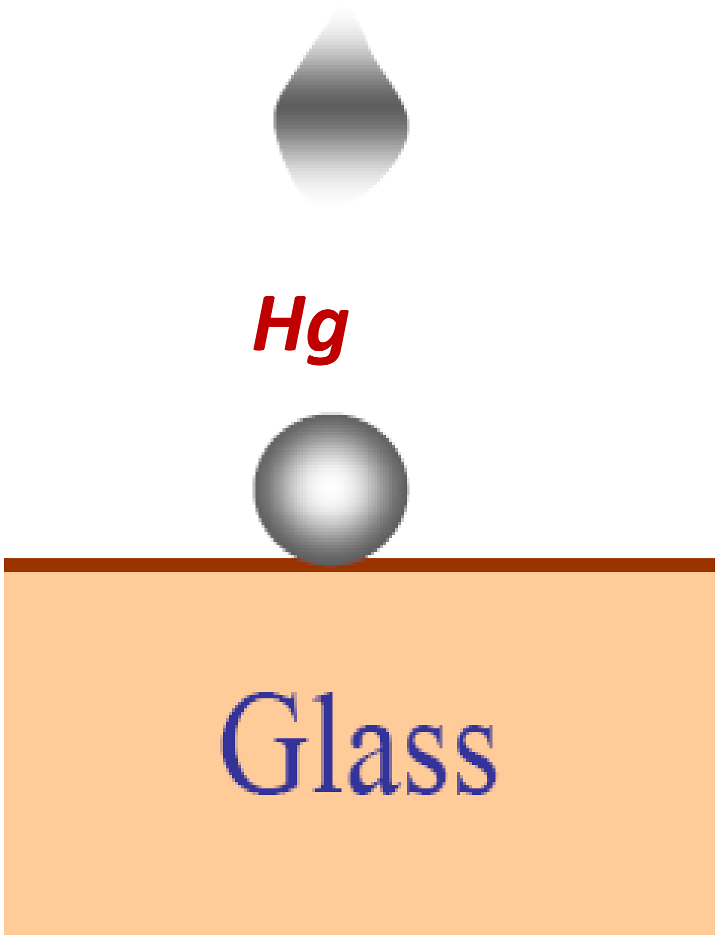
- The concave shape of the meniscus shows that water’s AF toward the glass are stronger than its CF.





- A non polar liquid such as mercury shows a **convex meniscus**. This behavior is characteristic of a liquid in which the CF are stronger than the AF toward glass.





Factors affecting γ

- **Nature of materials** and interfaces (intermolecular forces).

- **Temperature**: As T ↑ , γ ↓

- **Additives**

  - **inorganic salts** affect a little γ

  - **organic additives** as soap, alcohol, acids, and esters lower γ of water

Viscosity, η

a measure of a liquid's resistance to flow. Unit of η is poise (P)

$$1\mathrm{P} = 0.1\ \mathrm{kg\ m^{-1} s^{-1}} = 1\ \mathrm{g\ cm^{-1} s^{-1}} = 1\ \mathrm{dyne\ s\ cm^{-2}}$$

$$10\mathrm{P} = 1\ \mathrm{kg\ m^{-1} s^{-1}} = 1\ \mathrm{N\ s\ m^{-2}} = 1\ \mathrm{Pa\ s}\ (\mathrm{SI\ Unit})$$

Factors affecting viscosity

1- Nature of the fluid: liquids with large intermolecular forces tend to be highly viscous.

- H_2O is highly viscous because of H-bonding.
- Glycerol (has 3 – OH gps) has an unusually high viscosity due mainly to its high capacity to form hydrogen bonds

2- Molecular mass and complexity:

leads to higher viscosity because very large molecules can become entangled with each other.

- Gasoline, a non-viscous liquid, contains hydrocarbon molecules of the type $CH_3-(CH_2)_n-CH_3$, n varies from about 3 to 8.

- Grease, which is very viscous, contains much larger hydrocarbon molecules in which n varies from 20 to 25.

3- Temperature: Viscosity decreases ↓ rapidly with temperature ↑.

4- Additives: Addition of highly ionized salts decreases viscosity

Addition of suspended matters increases viscosity

Solids

Solids

Ionic	Molecular	Macromolecular	Metallic
		Giant	
Ionic	Dipole-Dipole London dispersion	Covalent	Delocalized covalent
NaCl MgO $CaCO_3$	Sucrose I_2 water	Diamond, C SiO_2	Cu Na Mg

Ionic solids

- High mp, conductors in molten state or water solution.
- Usually solids at 25°C and soluble in water, insoluble in organic solvents
- Simple solids as NaCl and MgO melt without change in chemical composition.
- Polyatomic ionic solids as $CaCO_3$ decompose before melting

Hydroxides $\xrightarrow{\Delta}$ Metal oxide H_2O gas

Carbonates $\xrightarrow{\Delta}$ Metal oxide CO_2 gas

Hydrated Salts $\xrightarrow{\Delta}$ Loss some water of crystallization

Molecular solids

- They are solids at room temperature.
- Have strong intermolecular forces.
- They include non-polar substances of high molecular mass as:

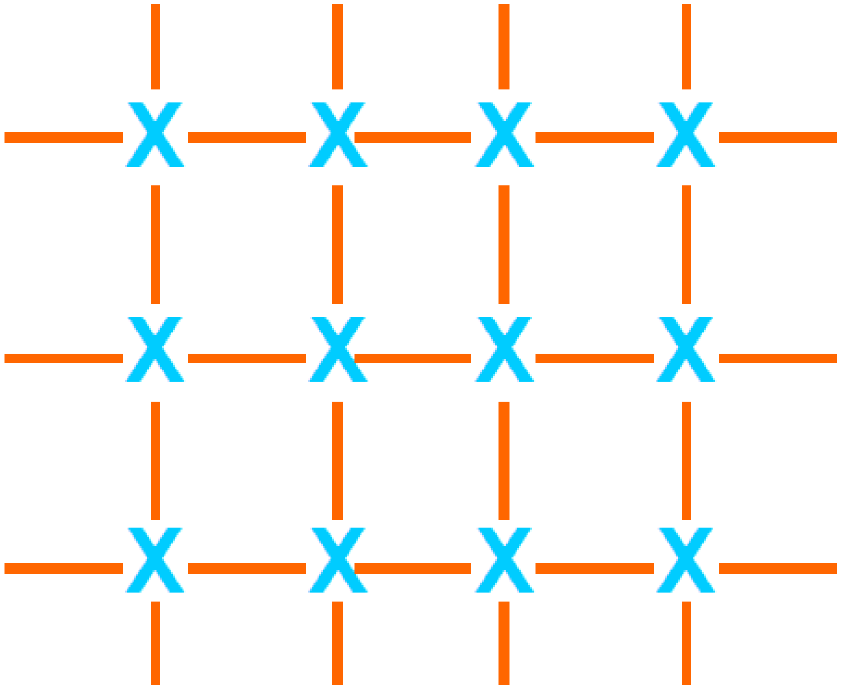
I_2	M.wt. = 254
naphthalene	M.wt. = 128

Others contain hydrogen bonds as:

Ice Urea

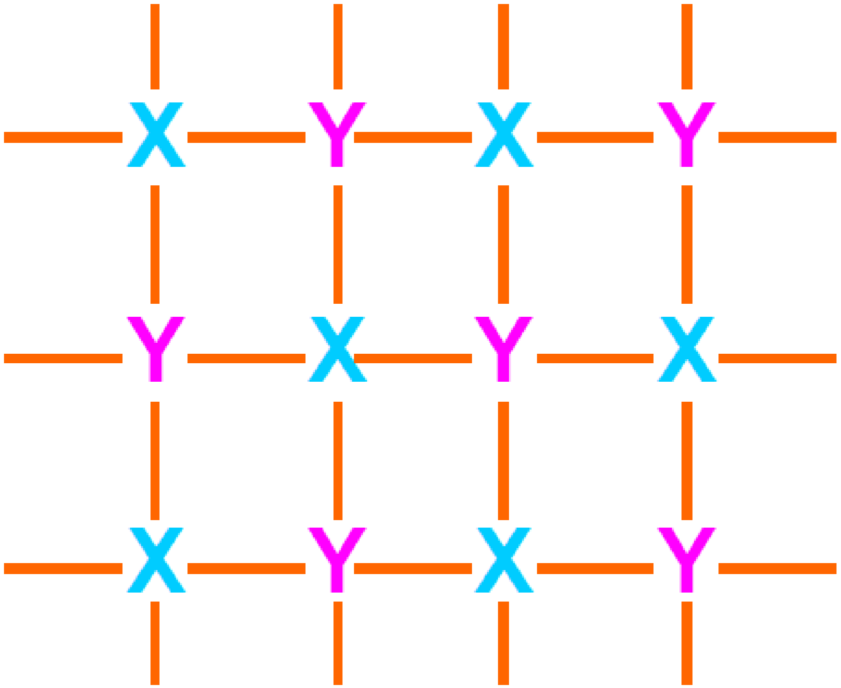
Macromolecular solids

- atoms are held together by a two dimensional network of electron-pair bonds, such as:



Element

Diamond, C

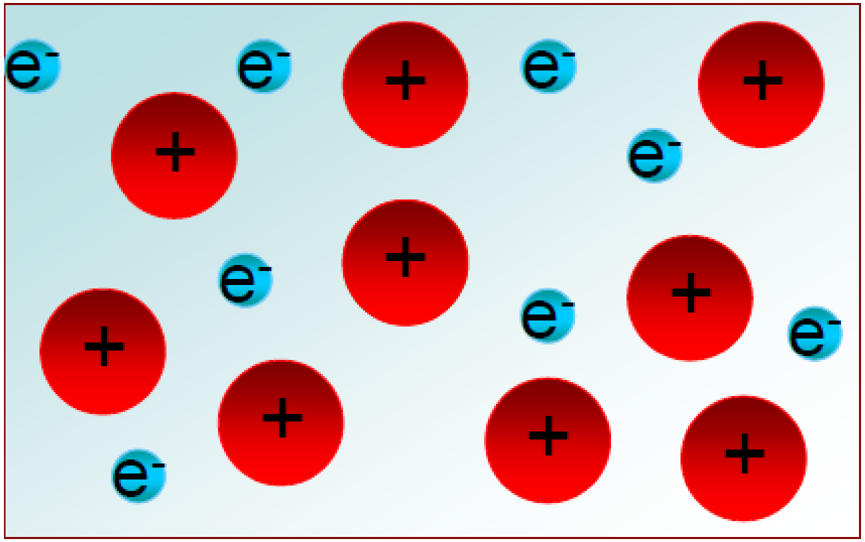


Compound

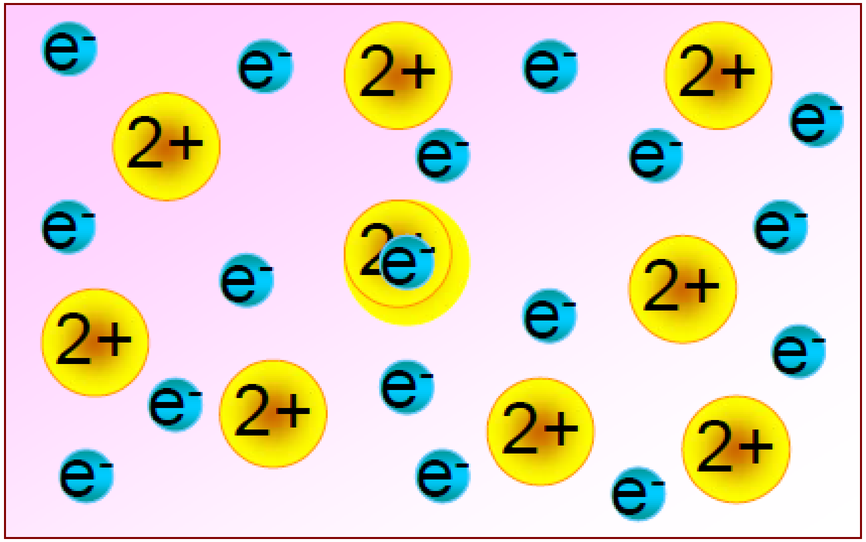
SiO_2

Metallic solids

- good conductors of electricity (electron sea model) and heat.
- ductile and malleable.
- their surfaces are good reflectors of light.



Na metal



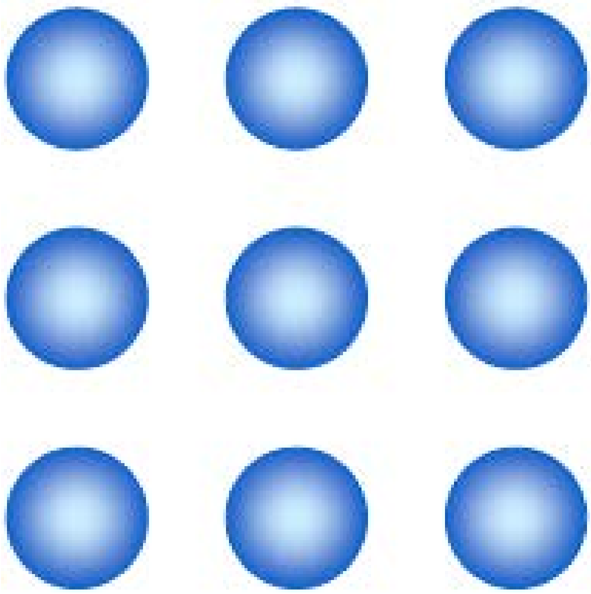
Mg metal

The lattice energy of Mg is greater than that of Na.

Structure and Bonding in Metals

- Metals are characterized by high thermal and electrical conductivity, malleability قابلية الطرق (hammered into thin sheets), and ductility قابلية السحب (drawn into thin wires) because of the non-directional covalent bonding in metallic crystals.

- A metallic crystal can be pictured as containing spherical atoms packed together uniformly and most efficiently using the available space and bonded to each other equally in all directions. Closest Packing



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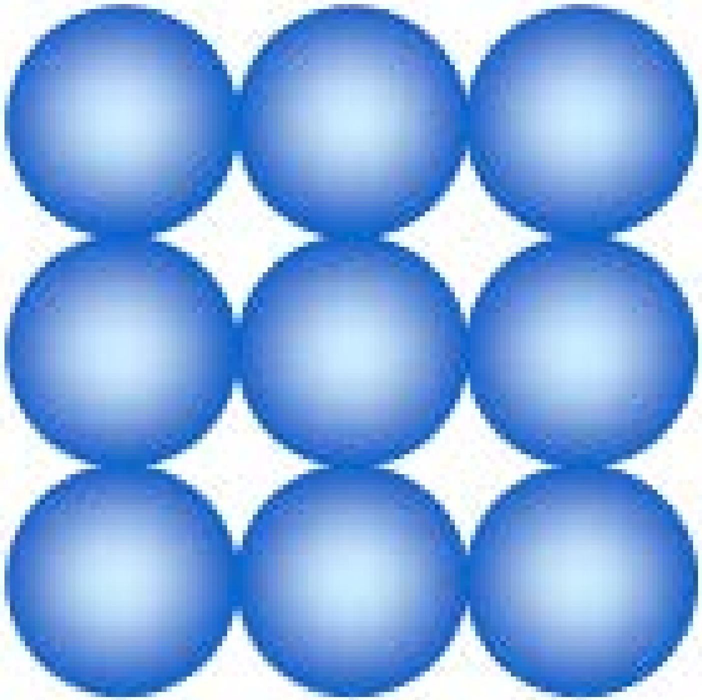
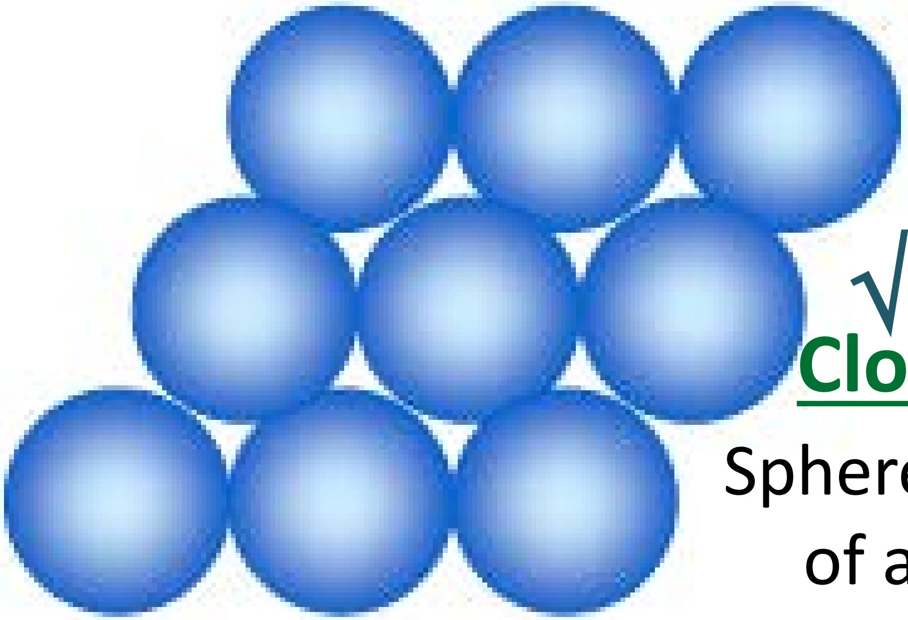


Square close Packing

Spheres occupy 52.48 % of available space

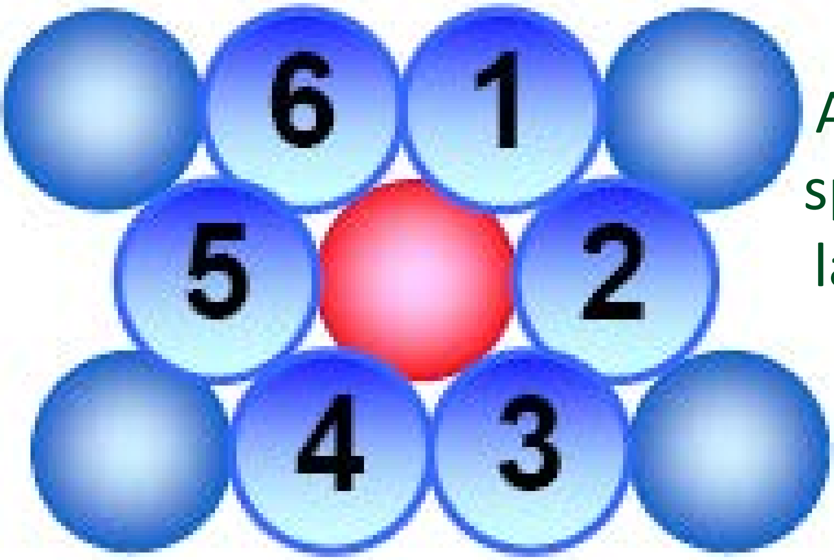


√

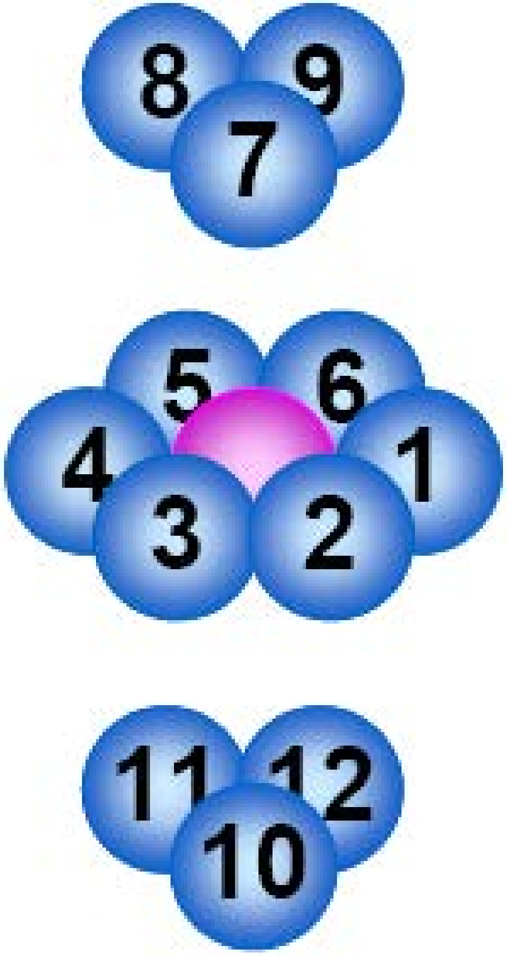
Closest Packing

Spheres occupy 60.4 % of available space

- The spheres are packed in layers, in which each sphere is surrounded by six others.
- In the second layer the spheres do not lie directly over those in the first layer. Instead, each one occupies an indentation (or dimple) formed by three spheres in the first layer.

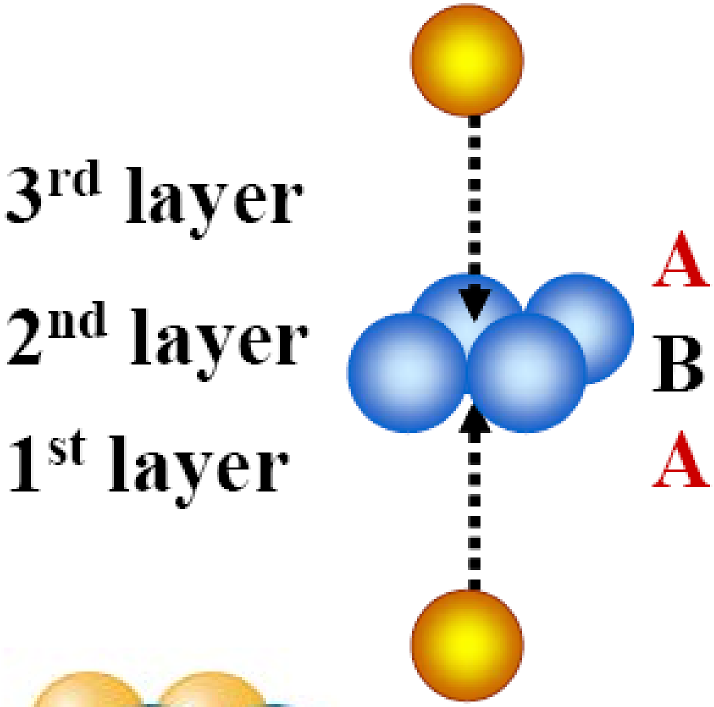


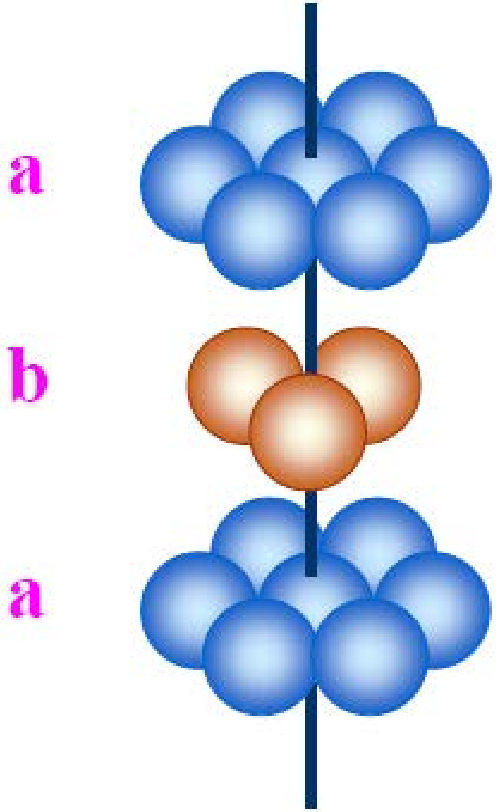
A sphere touches 6 spheres in the same layer + 3 above + 3 below = 12



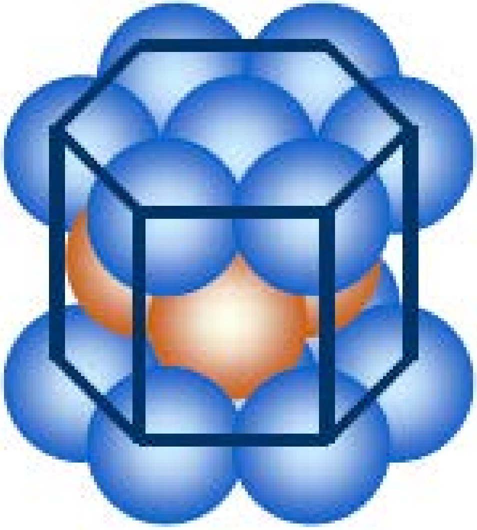
12 equivalent nearest neighbors

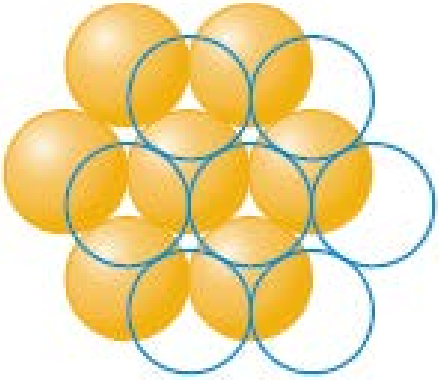
- In the third layer the spheres can occupy the dimples of the second layer in two possible ways:
    - Occupying positions so that each sphere in the third layer lies directly over a sphere in the first layer [the aba arrangement]



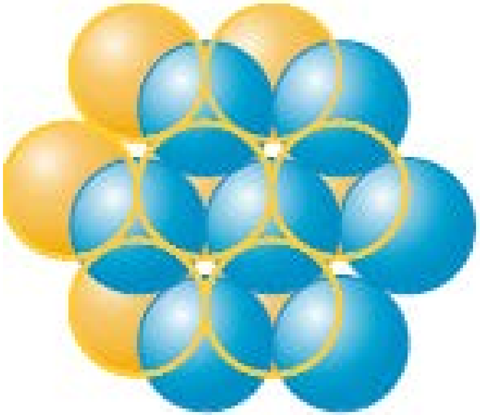


Hexagonal unit cell

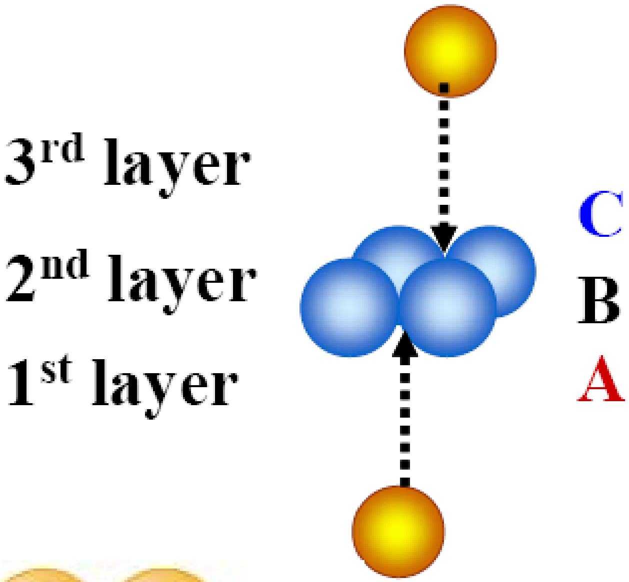


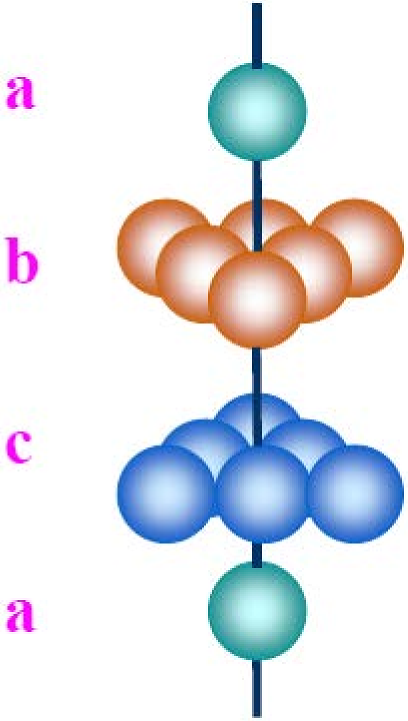


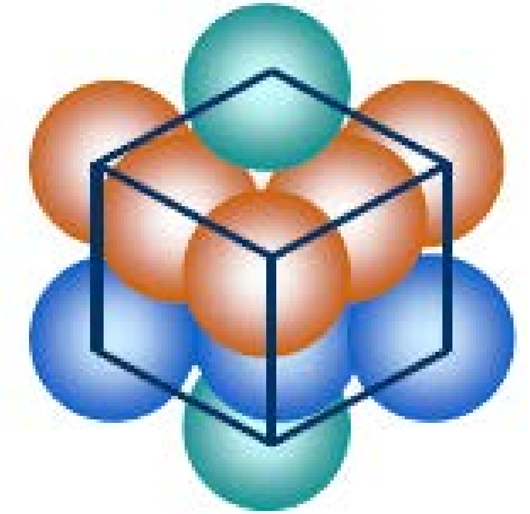
Hexagonal closest packed (hcp) structure

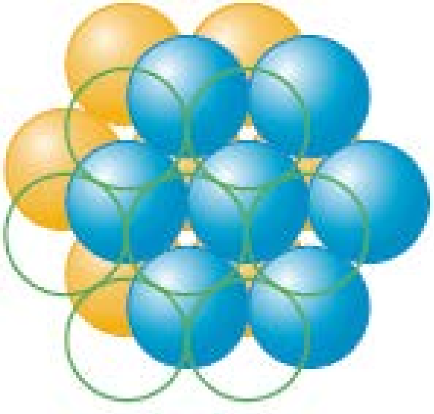


- Occupying positions so that no sphere in the third layer lies over one in the first layer [the abc arrangement].



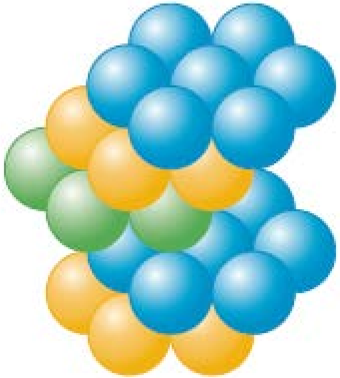






face-centered cubic (fcc) unit cell

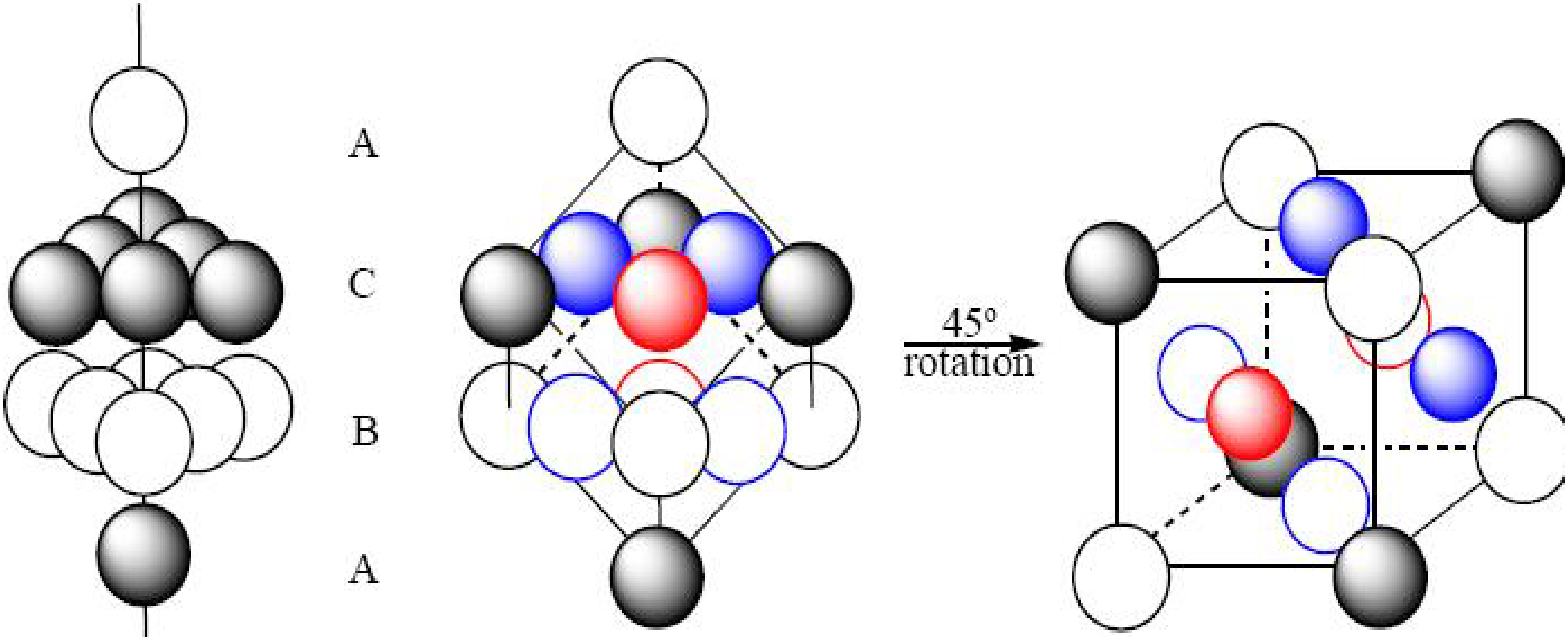
cubic closest packed (ccp) structure



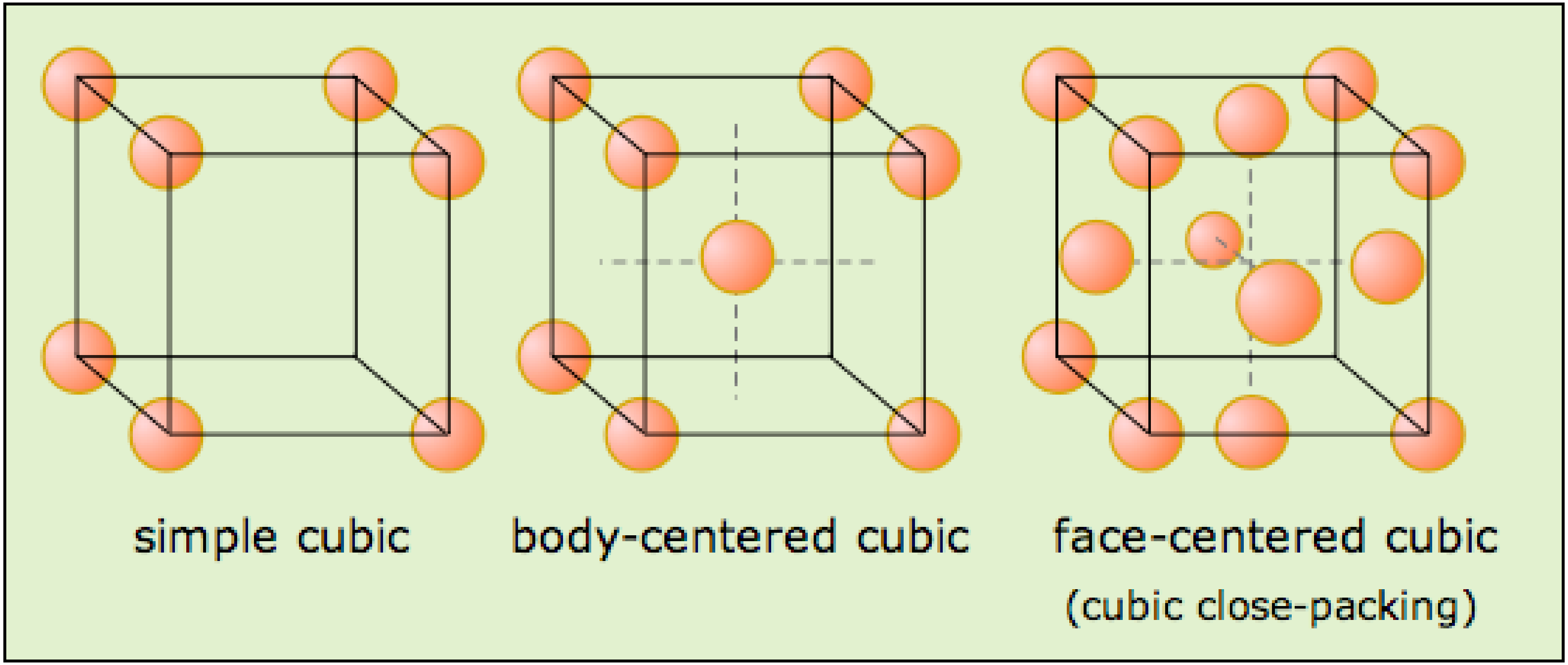
Unit Cell, UC

- the smallest group of atoms which has the overall symmetry of a crystal, and from which the entire lattice can be built up by repetition in three dimensions.

- If the cubic close packed structure is rotated by 45° the face centered cube (fcc) unit cell can be viewed



3 types of cubic lattices



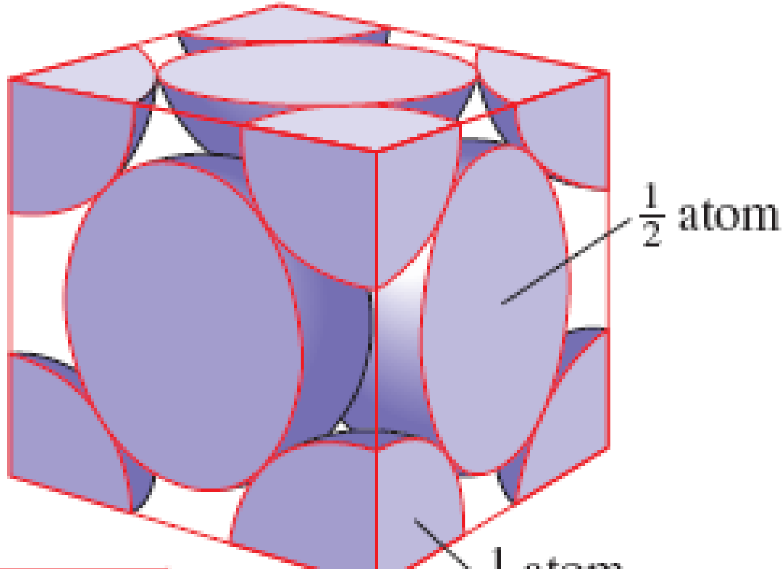
simple cubic

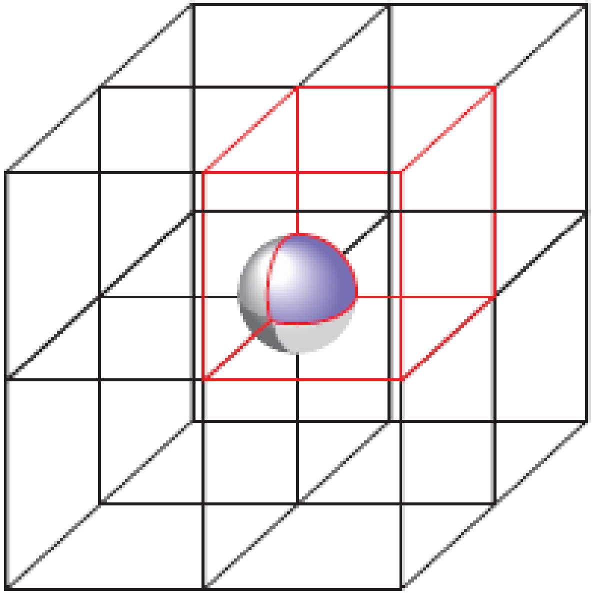
body-centered cubic

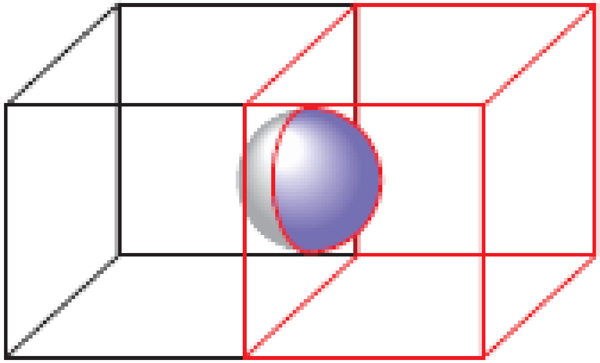
face-centered cubic
(cubic close-packing)

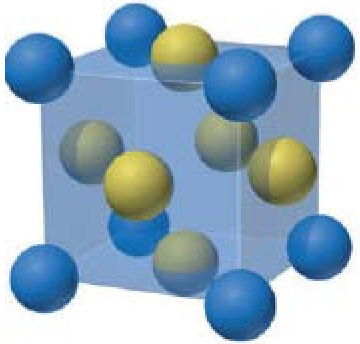
Net number of spheres (atoms) in fcc unit cells

- centers of the spheres on the cube's corners + spheres at the center of each face.









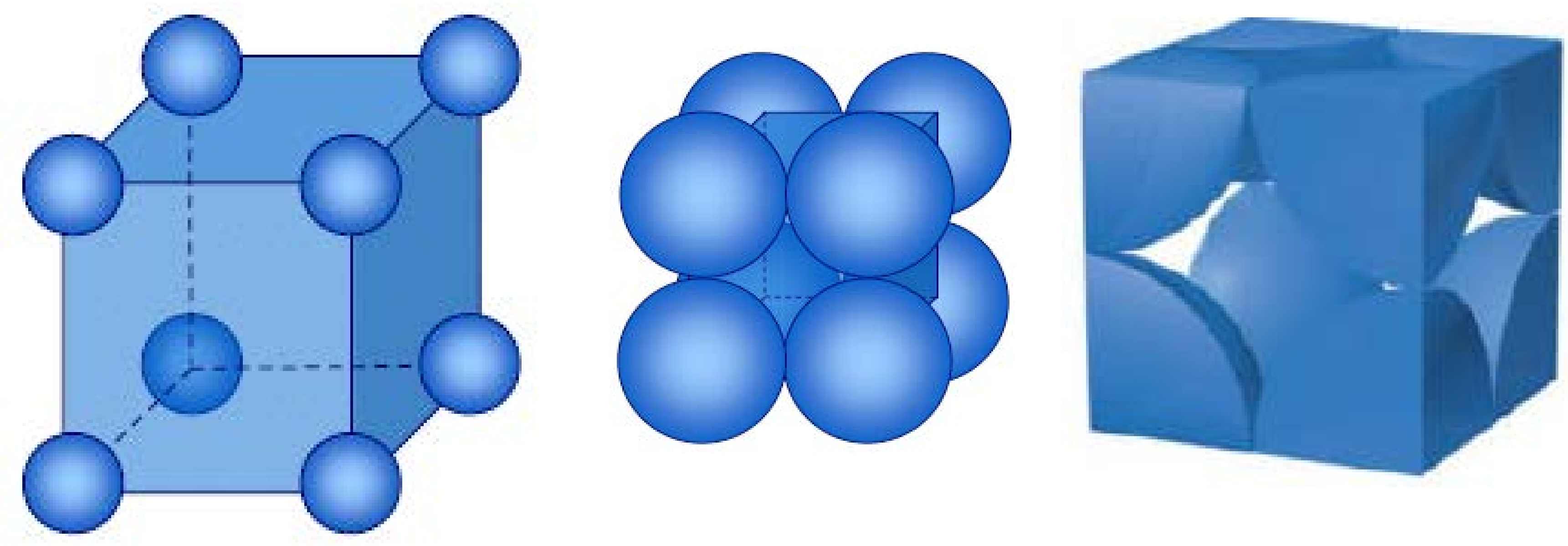
$$\textbf{Total spheres} = \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$

Position of atoms and fraction in a single UC

Position of Atom in the Unit Cell	# of adjacent cells sharing atom	Fraction contained within a single unit cell
Cube Corner	8	1/8
Edge	4	1/4
Face	2	1/2
Internal (bulk)	1	1

Net number of spheres in simple cubic unit cell

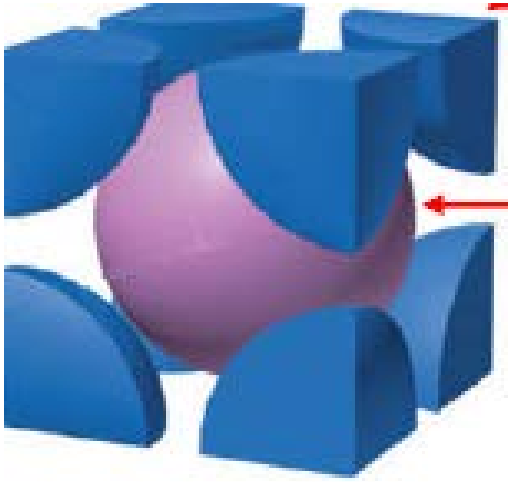
centers of the spheres on the cube’s corners

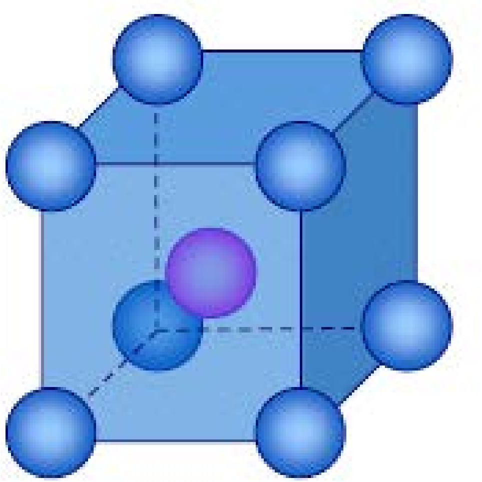


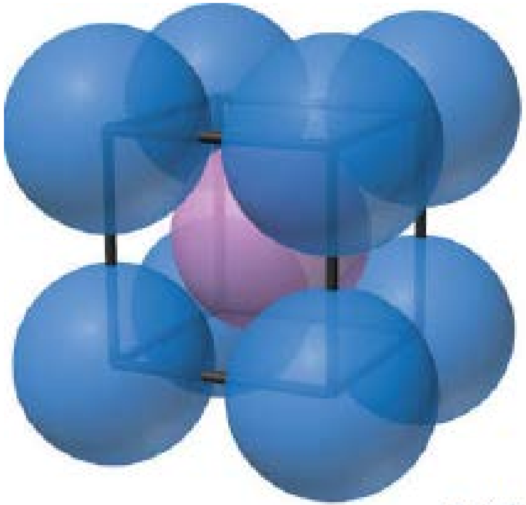
$$\textbf{Total spheres} = \left(8 \times \frac{1}{8}\right) = 1$$

Net number of spheres in bcc unit cell

centers of the spheres on the cube’s corners + 1 sphere in the center







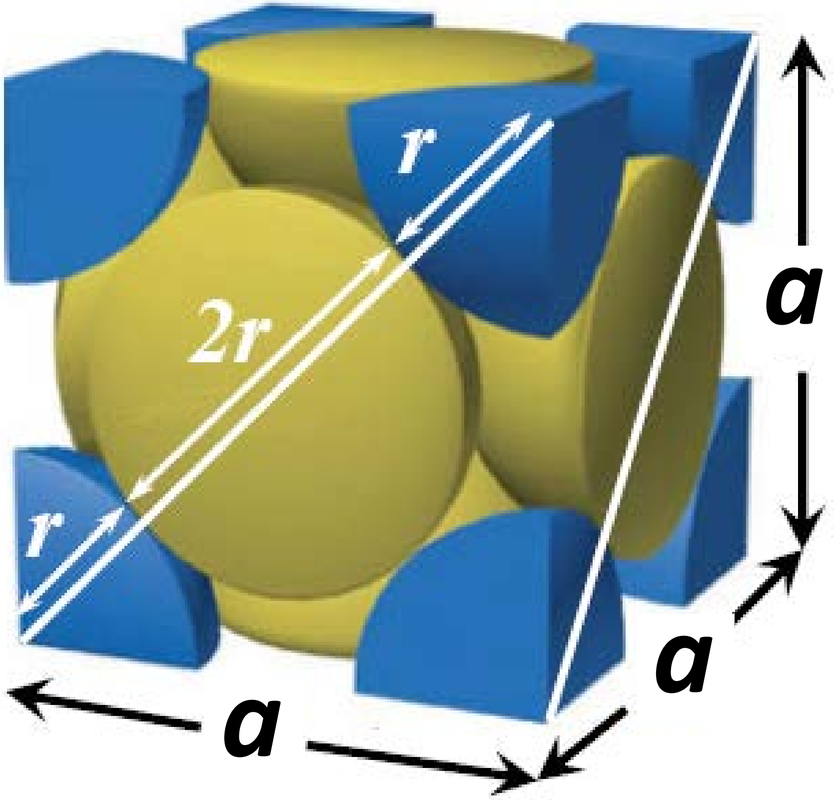
$$\textbf{Total spheres} = \left(8 \times \frac{1}{8}\right) + (1 \times 1) = 2$$

Density of a Closest Packed Solid

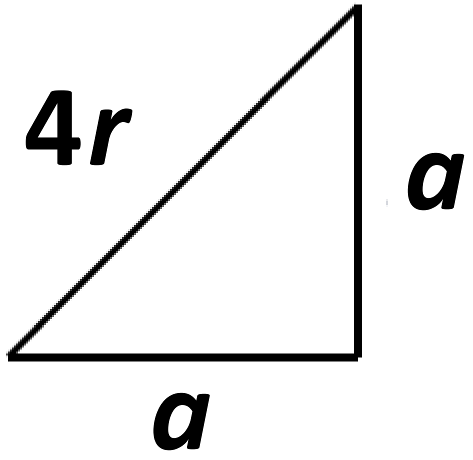
Silver crystallizes in a cubic closest packed structure. The radius of a silver atom is 1.44 Å (1 Å = 10^{-8} cm). Calculate the density of solid silver.

- The structure is cubic closest packed, which means the unit cell is face-centered cubic.
- Find the volume of this unit cell for silver and the net number of atoms it contains.
- Atoms touch along the diagonals for each face and not along the edges of the cube.

Diagonal length = r+2r+r = 4r



❑ Find the length of the edge of the cube by the Pythagorean theorem



$$(4r)^2 = a^2 + a^2 = 2a^2$$

$$a^2 = 8r^2$$

$$a = r\sqrt{8}$$

radius of a silver atom is 1.44 Å.

$$a = r\sqrt{8} = 1.44\,\overset{o}{A}\sqrt{8} = 4.07\ \overset{o}{A}$$

V (unit cell) = $a^3 = 67.4\left(\overset{o}{A}\right)^3 = 6.74 \times 10^{-23}\,cm^3$

$$4\ \ Ag\,atoms\ \ occupy\ \ 6.74\times 10^{-23}\,cm^3$$

$$\text{Atomic}\ mass\ \text{of Ag} = \frac{107.9\,g}{mol} = \frac{107.9\,g}{6.022\times 10^{23}\,atoms}$$

- ☐ Calculate the mass of 4 atoms existing in the fcc unit cell

$$mass\ \text{of Ag unit cell} = \frac{107.9\,g}{6.022\times 10^{23}\,atoms}\times 4\,atoms = 71.7\times 10^{-23}\,g$$

$$density\ \text{of Ag} = \frac{mass}{volume} = \frac{71.7\times 10^{-23}\,g}{6.74\times 10^{-23}\,cm^3} = 10.6\,g\,cm^{-3}$$

Generally

$$\textbf{density (d)} = \frac{Z \times M}{a^3 \times N_A}$$

d = Density (g/cm^3)

Z = number of atoms per unit cell

M = Molar mass in g/mol

a = Edge length in cm

N_A = Avogadro number $= 6.022 \times 10^{23}$ atoms/mol

Value of Z
- simple cubic = 1
- bcc = 2
- ccp or fcc = 4

Relationship between atomic radius and edge length

Simple cubic

$$r = \frac{a}{2}$$

BCC

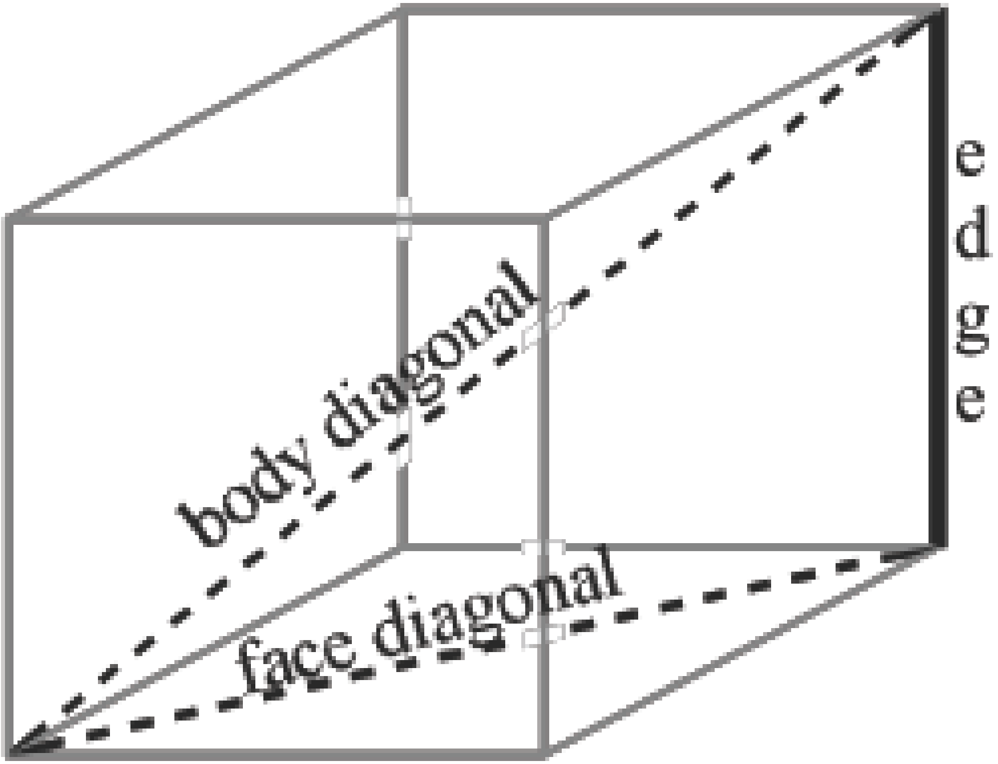
$$r = \frac{a\sqrt{3}}{4}$$

FCC

$$r = \frac{a\sqrt{2}}{4}$$

$$a = r\sqrt{8}$$

Usually



$fd^2 = a^2 + a^2 = 2\ a^2$

$bd^2 = fd^2 + a^2$

$= a^2 + a^2 + a^2 = 3\ a^2$

- The length of the cell edge is represented by a.
- The direction from a corner of a cube to the farthest corner is called body diagonal (bd).
- The face diagonal (fd) is a line drawn from one vertex to the opposite corner of the same face.
- If the edge is a, then we have

- ☐ If atoms touch each other along the body diagonal (bd), thus, the body diagonal has a length that is four times the radius of the atom, r. bd = 4 r

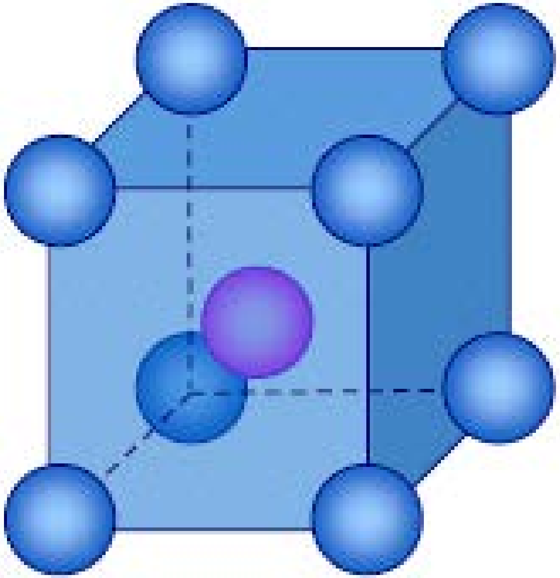
$$\boxed{(4r)^2 = 2a^2 + a^2 = 3a^2}$$

$$4r = a\sqrt{3}$$

$$\boxed{a = \frac{4r}{\sqrt{3}}}$$

$$\boxed{r = \frac{a\sqrt{3}}{4}}$$

Packing fraction for a bcc packed structure



$$r = \frac{a\sqrt{3}}{4} \Rightarrow a = \frac{4r}{\sqrt{3}}$$

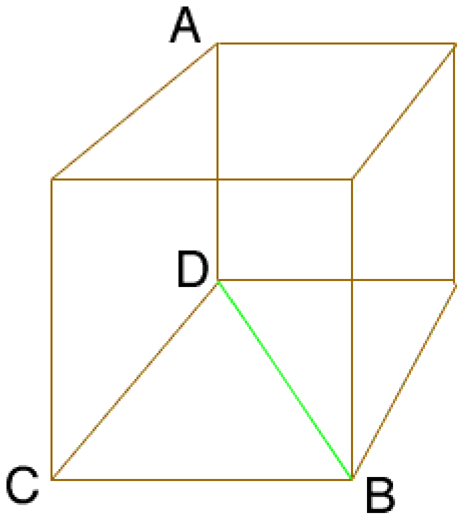
$$\textit{Packing fraction} = \frac{V_{sphere}}{V_{unit\ cell}} = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\,\pi}{8} = 0.6802$$

The packing fractions are

fcc and hcp	**bcc**	**simple cubic**
74.05 %	68.02 %	52%

Packing fraction of fcc lattice = 0.74

- Atoms are touched along the face diagonal (fd).
- For spheres of radius r, the diagonal of the cube face is equal to 4r, and is also equal to √2 a, where a is the dimension of the unit cell.



$$|DB|^2 = |DC|^2 + |CB|^2$$

$$r = \frac{a\sqrt{2}}{4}$$

As there are 6 atoms in the faces and half of each is in the unit cell:

$$6 \times \frac{1}{2} \times \frac{4}{3}\pi r^3 = 4\pi\left(\frac{a\sqrt{2}}{4}\right)^3 = 0.55536\,a^3$$

There are also 8 atoms in the corners of the unit cell, and 1/8 of each is in the cell:

$$\boxed{8\times\frac{1}{8}\times\frac{4}{3}\pi r^3=\frac{4}{3}\pi\left(\frac{a\sqrt{2}}{4}\right)^3=0.18512\,a^3}$$

The volume of the unit cell is a^3 and the total volume of the spheres in the unit cell is

$$V(spheres)=(0.5536+0.18512)=0.74048\,a^3$$

$$\boxed{Packing\ fraction=\frac{0.74048\,a^3}{a^3}=0.74048}$$