

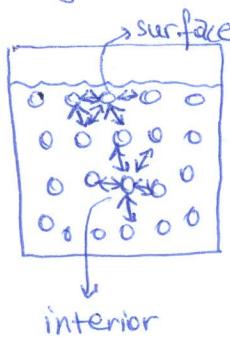
CHAPTER 13

INTER MOLECULAR FORCES: LIQUIDS AND SOLIDS

The forces that exists between molecules are called intermolecular forces. The physical properties of liquids and solids are due to the intermolecular forces.

Some Properties of Liquids:

Surface tension: In a liquid, molecules at the surface are attracted only by other surface molecules or by molecules below the surface.



Molecules in the interior experience forces from neighboring molecules in all direction. This increased attraction by its neighboring molecules places an interior molecule in a lower energy state than a surface molecule. As a consequence, as many as molecules as possible tend to enter inside of liquid.

Thus, there is a tendency for liquids to maintain a minimum surface area.

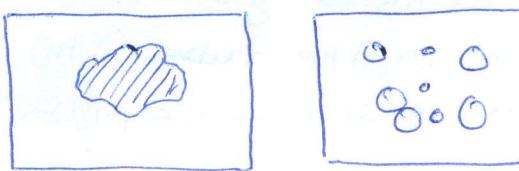
Surface tension is the energy, or work, required to increase the surface area of a liquid.

$$\gamma = \text{J/m}^2$$

* When the temp. increases, the intensity of molecular motions also increases and inter molecular forces become less effective. * Less work is required to extend the surface of a liquid, meaning that surface tension decreases with increased temperature.

Cohesive and Adhesive Forces:

→ When a drop of liquid spreads into a film across the surface we say that the liquid wets the surface.



→ Whether a drop of liquid wets the surface or retains its spherical shape depends on the two types of intermolecular forces.

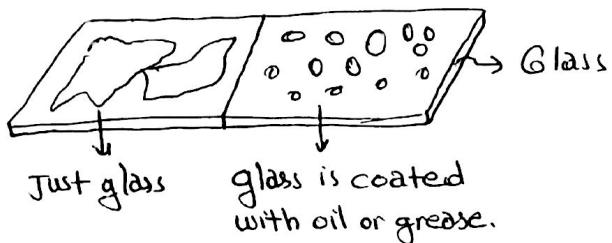
1) The forces exerted between molecules holding them together in the drop are called cohesive forces (CF).

2) Forces between liquid molecules and a surface are adhesive forces (AF).

$CF > AF$ drop maintains its shape

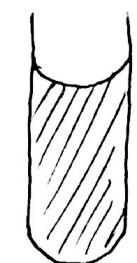
$AF > CF$ drop spreads into a film.

Wetting of a surface



Meniscus formation

Water

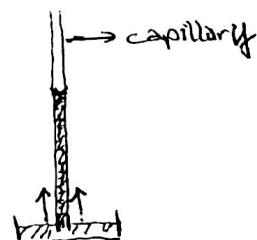


concave

mercury



convex



$AF > CF$

$CF > AF$

* When a small-diameter glass tube, or capillary, is placed in water, water rises in the tube. This action is called capillary action. Hg does not show a capillary rise.

Viscosity

Resistance of a liquid to flow is called viscosity. Some liquids, such as honey and motor oil flow very slowly and they are viscous. Viscosity generally decreases with increasing temp.

Enthalpy of Vaporization :

Escaping of molecules from the surface of a liquid in to the gas phase is called vaporization or evaporation. Evaporation occurs more readily with

1) Increased temp.: More molecules have sufficient kinetic energy to overcome intermolecular forces of attraction in the liquid.

2) Increased surface area of the liquid: A greater proportion of the molecules are at the surface.

3) Decreased strength of intermolecular forces: The kinetic energy needed to overcome intermolecular forces of attraction is less, and more molecules have enough energy to escape.

→ The enthalpy of vaporization is the quantity of heat that must be absorbed when a certain quantity of liquid vaporized at a constant temp.

$$\boxed{\Delta H_{\text{vaporization}} = H_{\text{vapor}} - H_{\text{liquid}}}$$

* Because the vaporization is endothermic process, the sign of ΔH_{vap} must be (+).

→ The conversion of a gas or vapor to a liquid is called condensation. So the condensation is the reverse of vaporization.

Condensation is exothermic process and has a (-) sign.

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

Example: A 0.750 L sample of steam was allowed to condense. Estimate the quantity of heat evolved. Whs is the result only an estimation?

$$n_{H_2O(g)} = \frac{PV}{RT} = \frac{1.000 \text{ atm} \times 0.750 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times (273.15 + 100) \text{ K}}$$

\downarrow
Steam obtained
at 100 °C.

$$= 0.245 \text{ mol}$$

$$\Delta H_{\text{cond}} = 0.245 \text{ mol} \times (-44.0 \text{ kJ/mol}) = -1.08 \text{ kJ}$$

* This result is only an estimate

1) ΔH_{cond} is temp. dependent

2) The condensed water was at temp. lower than 373 K. An additional small quantity of heat was liberated on the condensed steam cooled to that lower temp.

Vapor Pressure: The pressure exerted by a vapor in dynamic equilibrium with its liquid is called the vapor pressure.

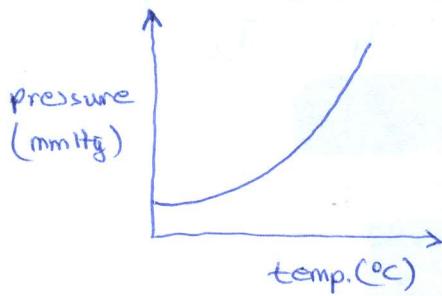


* Liquids with high vapor pressure at room temp. are said to be volatile.

* Liquids with low vapor pressure " " " are nonvolatiles.

* The weaker the intermolecular forces, the more volatile the liquid.

- * A graph of vapor pressure as a function of temp. is known as a vapor pressure curve.



Boiling and The Boiling Point:

A liquid boils when its vapor pressure equals the external pressure. At this point bubbles of vapor form within the liquid. We say that boiling occurs.

The boiling temp. of a liquid at 1 atm pressure is called its normal boiling point.

The Critical Point:

If a liquid is heated in a sealed container, boiling does not occur. Instead, the temp. and vapor pressure rise continuously and following phenomena can be observed.

- The density of liquid decreases and density of the vapor increases.
- The surface tension of the liquid approaches zero. The interface between the liquid and vapor disappears.

→ The critical point is the point that the liquid and vapor become indistinguishable. And the temp. at the critical point is called critical temperature (T_c), and the pressure is called critical pressure(P_c).

- The critical point is the highest point on a vapor-pressure curve and represents the highest temp. at which the liquid can exist.
- A gas can be liquified only at temp.s below its critical temp. (T_c)

Clausius-Clapeyron Equation

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

$$\Delta H_{\text{vap}} = \text{J/mol}$$

$$R = 8.314 \text{ J/molK}$$

Some Properties of Solids:

Melting: As a crystalline solid is heated, the solid loses its definite shape and is converted to a liquid. This process is called melting or fusion.

Melting point: The temp. that the melting occurs is the melting point.

Freezing: The reverse process, the conversion of a liquid to a solid, is called freezing.

Freezing point: The temp. that the freezing occurs is called freezing point.

Sublimation: The direct passage of molecules from the solid to the vapor state is called sublimation.

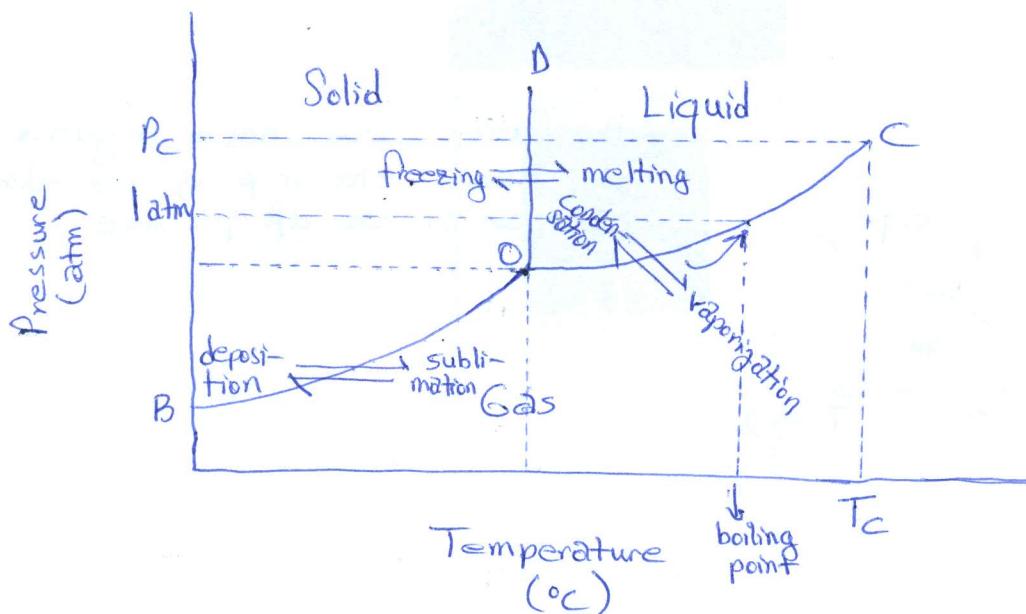
Deposition: The reverse process, the passage of molecules from vapor to solid state is called deposition.

→ The enthalpy of sublimation (ΔH_{sub}) is the quantity of heat needed to convert a solid to vapor.

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

PHASE DIAGRAMS

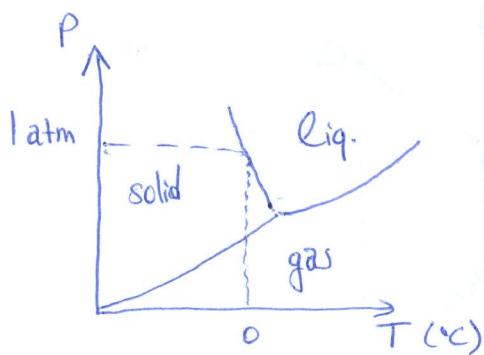
Phase diagrams are graphical representation of the conditions of temperature and pressure at which solids, liquids and gases exist.



- * The different regions correspond to single phases.
- * The line from O to C ($^{\circ}\text{C}$) is the vapor-pressure curve of the liquid. It represents the equilibrium between liquid and vapor.
- * Each curves represent the conditions of temp. and pressure at which the various phases can exist at equilibrium.
- * The vapor-pressure curve ends at the critical point, which is at the critical temp. and the critical pressure of the substance. Beyond the critical point the liquid and the gas phase become indistinguishable from each other. and the state of the substance is supercritical fluid.
- * The line from O to B ($^{\circ}\text{B}$) is the sublimation curve.
- * The line from O to D ($^{\circ}\text{D}$) is the fusion curve. The melting point at 1 atm is the normal melting point. The melting point of a substance is identical to its freezing point. Only their directions are different.

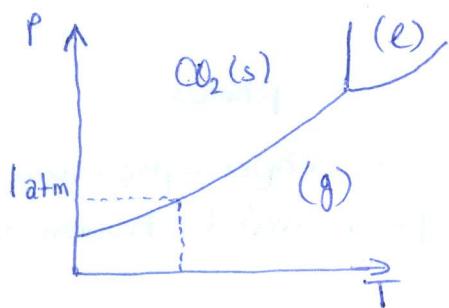
* Point O is known as the triple point. All three states of matter (l,s,g) are in equilibrium at a unique temp. and pressure.

H₂O



* the fusion curve has a negative slope. this means, the m.p. of ice decreases with an increase in pressure.

CO₂



* Solid CO₂ does not melt but sublimes when heated at 1 atm.

→ Crossing of a two-phase curve in a diagram is called phase transition. There are six (6) common phase transitions.

| | | | |
|--------------|---------|--------------|---------|
| melting | (s → l) | freezing | (l → s) |
| vaporization | (l → g) | condensation | (g → l) |
| sublimation | (s → g) | deposition | (g → s) |

VAN DER WAALS FORCES:

Instantaneous and Induced Dipoles: In a normal condition, a nonpolar molecule has a symmetrical charge distribution and does not have a dipole moment. But London recognised that the motion of $\bar{e}s$ in an atom or molecule can create an instantaneous dipole moment with a charge separation (represented as $\delta+$ and $\delta-$).

The instantaneous dipole influence the motion of $\bar{e}s$ on its neighbors, and caused induced dipole.

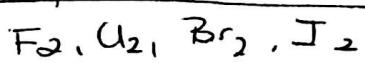
The attractive interactions between instantaneous dipole and induced dipole is called London force or dispersion force.

 Polarizability is the tendency for charge separation to occur in a molecule. Polarizability increases with the increased number of $\bar{e}s$ and number of $\bar{e}s$ increases with increased molecular mass.

Mass of molecule \uparrow \bar{e} number \uparrow polarizability \uparrow

The strength of dispersion forces depends on both number of $\bar{e}s$ and molecular shape. $\bar{e}s$ in elongated molecules are more easily displaced; the elongated molecules are more polarizable.

Ex: Compare the melting and boiling points of halogens (F_2, Cl_2, Br_2, I_2)



M.P \uparrow because molecular mass \uparrow
B.P \uparrow

instantaneous
dipole



(a)



(b)



(c)



(d)

dipole-dipole
interactions

a) normal condition

b) instantaneous "

c) induced dipole

d) dipole-dipole attraction

London
force

or dispersion
force.

Dipole-Dipole Interactions:

In a polar substance, the molecule have permanent dipole moment. The polar molecules attract each other when the (+) end of one molecule is near the (-) end of other. This interaction is known as dipole-dipole forces.

| Ex: Compare the boiling points of N_2 , NO and O_2 molecules. | | |
|---|------------------|------------------|
| N_2 (nonpolar) | NO (polar) | O_2 (nonpolar) |
| $M=0$ | $M=0.153D$ | $M=0$ |
| 28 u | 30 u | 32 u |
| $b.p = -77.34^\circ C$ | $121.33^\circ K$ | $90.19^\circ K$ |

There is no electronegativity differences in N_2 and O_2 . Both are nonpolar. In NO , the N has an electronegativity difference and the molecule has dipole moment.

N_2 and O_2 have only London forces.

NO has both London forces and dipole-dipole forces.

We know that, London forces is directly proportional with molecular mass and the boiling point of NO should be between N_2 and O_2 but because of the dipole-dipole forces it has the highest boil. point.

x: Which would you expect to have the higher b.p?

C₄H₁₀ (butane)

58 u

non polar

London forces

$b.p = -0.5^\circ C$

octane (C_8H_{18})

58 u

polar

London + dipole-dipole forces

$b.p = 56.2^\circ C$

acetone.

Summary of Van der Waals forces

- ① Dispersion (London) forces exist between all molecules. They involve motion of all electrons in molecules. The forces depend on the number of electrons and molecular shapes.
 - ② Dipole-dipole forces are found only in substances with resultant dipole moments. Their existence adds to the effect of dispersion forces.
 - ③ When comparing substances of roughly comparable molecular masses, London forces will be equal in two substances. In this case dipole-dipole forces can effect the m.p., b.p. of substances.
 - ④ When comparing substances of widely different molecular masses, dispersion forces are usually more significant than dipole forces.
- Ex:** Within the series HCl, HBr and HI, molecular mass increase sharply and ΔH_{vap} and b-points increase in order to $HCl < HBr < HI$. The more polar nature of HCl and HBr is not sufficient to reverse the trends.
-  "important"

~~Examine the following substances according to their~~

CCl₄, Cl₂, ClNO, N₂ boiling points in increasing order.

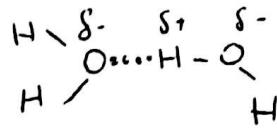
CCl₄, Cl₂ and N₂ are nonpolar and they have only dispersion forces; hence the boiling points should increase with increasing molecular mass $N_2 < Cl_2 < CCl_4$

ClNO is polar and has London-dipole-dipole forces. This suggest a higher boiling point than Cl₂. We should not expect the boiling point of ClNO to be higher than CCl₄ because of the large difference in their molecular masses ~~(*)~~ important.

HYDROGEN BONDING:

Hydrogen bonding is a special type of intermolecular attraction between the H atom in a polar bond and nonbonding e pair of its neighbour electro-negative atom.

For example, a hydrogen bond exists between the H atom in an HF molecule and the F atom of an adjacent HF molecule.



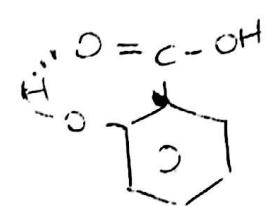
* Hydrogen bonds represented with dotted lines.

* Hydrogen bonds are possible only with certain H-containing compounds such as NH₃, HF, H₂O.

Only F, O and N easily meet the requirements for H-bond formation.

~~(*)~~ H-bonds are stronger than other van der waals forces.

* H-bond between two molecules is called intermolecular H-bond.
H-bonding within a molecule is called intramolecular H-bonding.



salicylic acid



p-hydroxy benzoic acid

NETWORK COVALENT SOLIDS AND IONIC SOLIDS

In a crystalline solid the atoms, ions or molecules are ordered in well-defined 3-dimensional arrangements.

In a network covalent solid, covalent bonds extend throughout the crystalline solid. Let's consider two of the allotropes forms of C - diamond and graphite.

- Diamond: In diamond
- Each C atom is bounded to four others.
 - Diamond is the hardest substance known.
 - " does not melt or sublime except at very high temp. (3500°C)
 - " does " conduct electricity.



Graphite:

- Each C atom forms strong covalent bonds with three neighboring C atoms in the same plane giving rise to layers of C atoms.
- Bonding between layers is weak, the layers can glide over one another. As a result, graphite is a good lubricant.
- graphite conducts electricity.
- " is used as electrodes in batteries and in industrial electrolysis.



IONIC SOLIDS:

- The attractive forces between a pair of oppositely charged ions increase \rightarrow increased charge on the ions \rightarrow decreased ionic size



- Lattice energy is the energy given off when gaseous ions (+ and - ions) come together to form one mole of solid ionic compound. L-energy can be useful to predict melting point and water solubilities of ionic compounds.

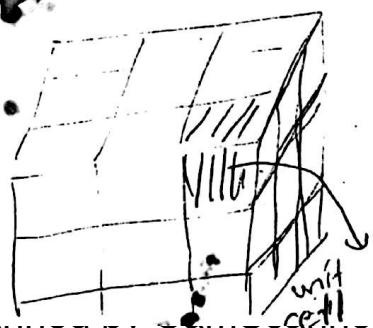
- In general, the higher lattice energy of an ionic compound the higher is its melting point. $L.E \uparrow$ M. Point \uparrow
- The lower the lattice energy, the greater the quantity of an ionic solid that can be dissolved. $L.E \downarrow$; solubility \uparrow

CRYSTAL STRUCTURES

Crystal Lattice: A crystalline solid must be represented by a three dimensional patterns called a crystal lattice.

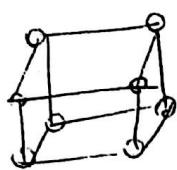
There are 7 basic types of crystal lattice. The crystal-lattice in the chlorine is called

cubic-lattice: In cubic lattice all planes have same distance and mutually perpendicular

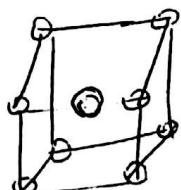


A unit cell is used to generate the entire lattice by replicating it along the three dimensions.

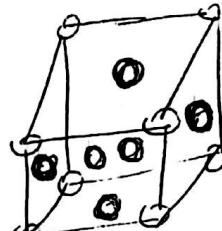
three perpendicular direction. There are 3 different unit cells in the cubic crystal system.



primitive cubic simple cubic cell



body-centered cubic (bcc)



face-centered cubic (fcc)

- If particles (atom, ion or molecule) are at the corners only, the unit cell is called primitive or simple unit cell.
- If particle occur not only at the corner but also in the center of the unit cell, is called body-centered unit cell.
- If the particles are both at the corners and at the center of each face, it is face-centered unit cell.

Closest-Packed Structures:

Unlike boxes, when spheres are stacked together, there must always be some unfilled space. The arrangement of which the spheres come into as close contact as possible to minimize the volume of holes, is called closest packed structure.

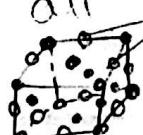
The hole between 3 spheres resembling a triangle is called a trigonal hole.

The hole between 4 spheres is called tetrahedral hole and between 6 spheres is called octahedral holes.

There are two possibility for the third layer. In one arrangement, called hexagonal closest packed (hcp), all the tetrahedral holes are covered. In the other arrangement, called cubic closest packed (ccp), all the Octahedral holes are covered. Each sphere is in contact with 12 others.

\Rightarrow hcp \Rightarrow all tetrahedral holes covered.

$\left\{ \begin{array}{l} \text{hcp} \Rightarrow \text{all tetrahedral holes covered.} \\ \text{ccp} \Rightarrow \text{all octahedral holes covered.} \end{array} \right.$



hexagonal CCP



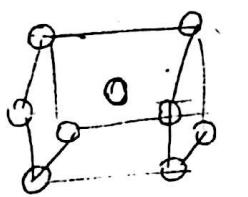
cubic CCP

Coordination number and Number of atoms per Unit cell;
 Coordination number, is the number of particles (atom, ions) immediately surrounding a particle in a crystal structure.

For the bcc structure \rightarrow C-number is 8

For the fcc and hcp structures \rightarrow C-no is 12

We used 9 atoms to draw body-centred cubic cell but the cell consists of Only two atoms.



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

↓
center atom
corner atoms

* fcc - structure

$$\text{Number of atoms} = \underbrace{\left(8 \times \frac{1}{8}\right)}_{\text{atoms at corners}} + \underbrace{\left(6 \times \frac{1}{2}\right)}_{\text{atoms at center of faces}} = 4$$

* for simple cubic unit cell;

$$N. \text{ of atoms} = \frac{1}{8} \times 8 = 1$$

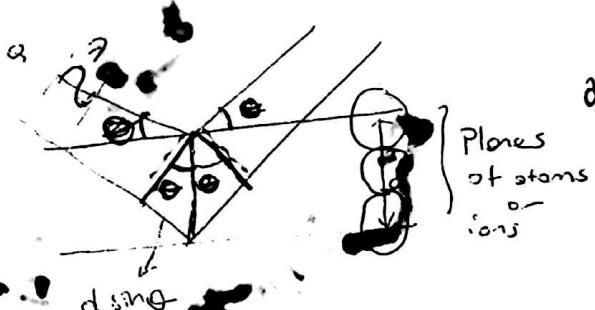
* Only the center atom belongs totally to the bcc unit cell.

The other atoms (at the corner) are shared with 8 unit cells. Only one-eighth of each corner atom belongs to a given unit cell.

The atoms on the face are shared by two unit cell. Only half of atoms belong to a given unit cell.

X-RAY DIFFRACTION:

When a beam of x-rays encounters atom, the x-rays interact with it and the original beam is scattered in all directions. The pattern of this scattered radiation is related to the distribution of electronic charge in the atoms. The scattered x-ray can produce a visible pattern on a photographic film and give us idea about the microscopic structure of atom.



$$d \sin \theta = 2 \lambda$$

any integer λ : the wavelength of x-ray

$$r_{Fe} = ?$$

$$d_{Fe} = ?$$

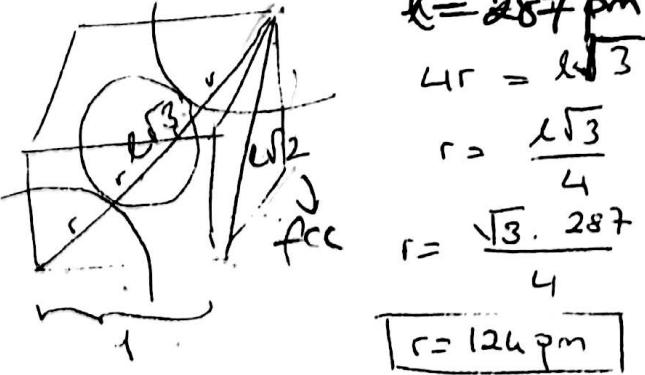


$$d = \sqrt{l^2 + l^2} = l\sqrt{3}$$

atom number in cube:

At room temperature, iron crystallized in a body-centered cubic structure. By x-ray diffraction, the edge of the cubic cell found to be 287 pm. What is the radius of the iron atom and calculate the density of iron? $287 \text{ pm} = 2.87 \times 10^{-8} \text{ cm}$

buane nuance



The volume of unit cell is:

$$V = l^3 = (2.87 \cdot 10^{-8} \text{ cm})^3 = 2.36 \cdot 10^{-23} \text{ cm}^3$$

There are 2 iron atoms in FCC structure. We need the mass of these 2 atoms.

$$1 \text{ mol Fe} = 6.02 \cdot 10^{23} \text{ Fe atoms} = 55.85 \text{ g}$$

$$\begin{array}{rcl} 6.02 \cdot 10^{23} \text{ Fe atom} & & 55.85 \text{ g} \\ 2 \text{ Fe atoms} & & \times \end{array}$$

$$m = 2 \text{ Fe atoms} \cdot \frac{55.85 \text{ g}}{6.02 \cdot 10^{23} \text{ Fe atoms}}$$

$$m = 1.855 \cdot 10^{22} \text{ g}$$

IONIC CRYSTAL STRUCTURES:

If we try to apply this packing model to an ionic crystal, we come across two complications:

- (1) Some of the ions are positively charged and some are negatively charged.
- (2) The cations and anions are of different size.

A common arrangement in ionic solid is the cubic closest packed arrangement. One of the ions usually anion adopting the cubic closest packed arrangement. While the cation fits in the holes. The radius of cation r_{cation} is given by the equation $(2R_{anion} + 2r)^2 = (2R_{cation} + 2r)^2 \Rightarrow 2(2R_{anion}) = 2(2r) \Rightarrow R_{cation} = 2r$.

$$r = 0.414 R \text{ (for octahedral hole)}$$

$$r = 0.225 R \text{ (for tetrahedral hole)}$$

$$r = 0.155 R \text{ (for trigonal hole)}$$



$$R: \text{The radius of anion. } (\sqrt{2}-1) R = r$$

$$r = 0.414 R$$

Cubic closest packed - simple cubic arrangement

Another arrangement in ionic solid, is the simple cubic arrangement. The simple cubic structure has a cubic hole in the center of the unit cell. The size of the cubic hole is $r = 0.732 R$. This is the largest hole.

Which hole does the cation occupy in a close packed structure of anions? That is, in FCC structure, cations fit in octahedral holes.

$$0.225 R_{anion} < \frac{r_{cation}}{R_{anion}} < 0.414 R_{anion}$$

In CCP (f.c.c) structures, cations fit in tetrahedral holes.

If the radius ratio

$$0.414 < \frac{r_c}{R_A} < 0.732$$

Oh

in fcc

" cubic structure, cations fit in octahedral holes.

(7)

If the radius ratio is:

$0.732 < \frac{r_c}{R_A}$ Simple Cubic hole

In CCP (fcc) structure, cations fit in octahedral holes.

In the simple cubic arrangement, cations fit in the hole of unit cell. (cubic hole, bcc)

NaCl:

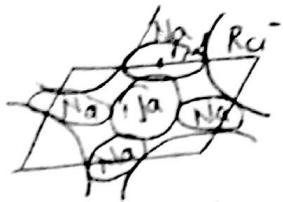
The radius ratio of NaCl is $\frac{r_{Na^+}}{r_{Cl^-}} = \frac{98 \text{ pm}}{181 \text{ pm}} = 0.55$

We expect, Na^+ ions to occupy the octahedral holes of the cubic closest packed arrays of Cl^- ions.

$$\text{The number of } Cl^- \text{ ions} = (8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$$

$$Na^+ \text{ ions} = (12 \times \frac{1}{4}) + (1 \times 1) = 4$$

(corner
number) in the
middle



$$l = 2r^+ + 2r^-$$

for fcc structure

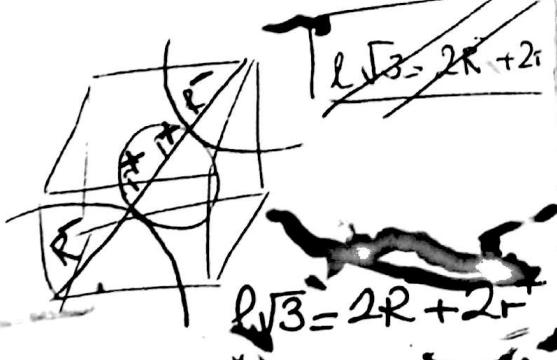
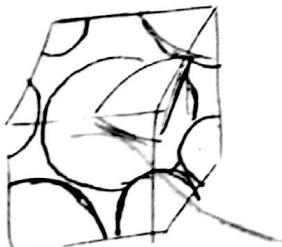
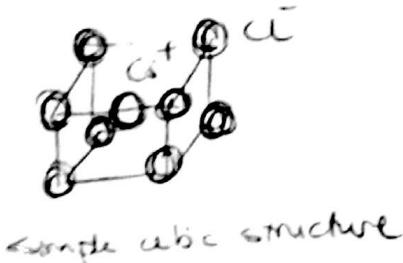


CsCl Body centered

The radius ratio of CsCl is

$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{168 \text{ pm}}{181 \text{ pm}} = 0.934$$

We expect the cubic hole of simple cubic array of Cl^- ions occupied by the Cs^+ .

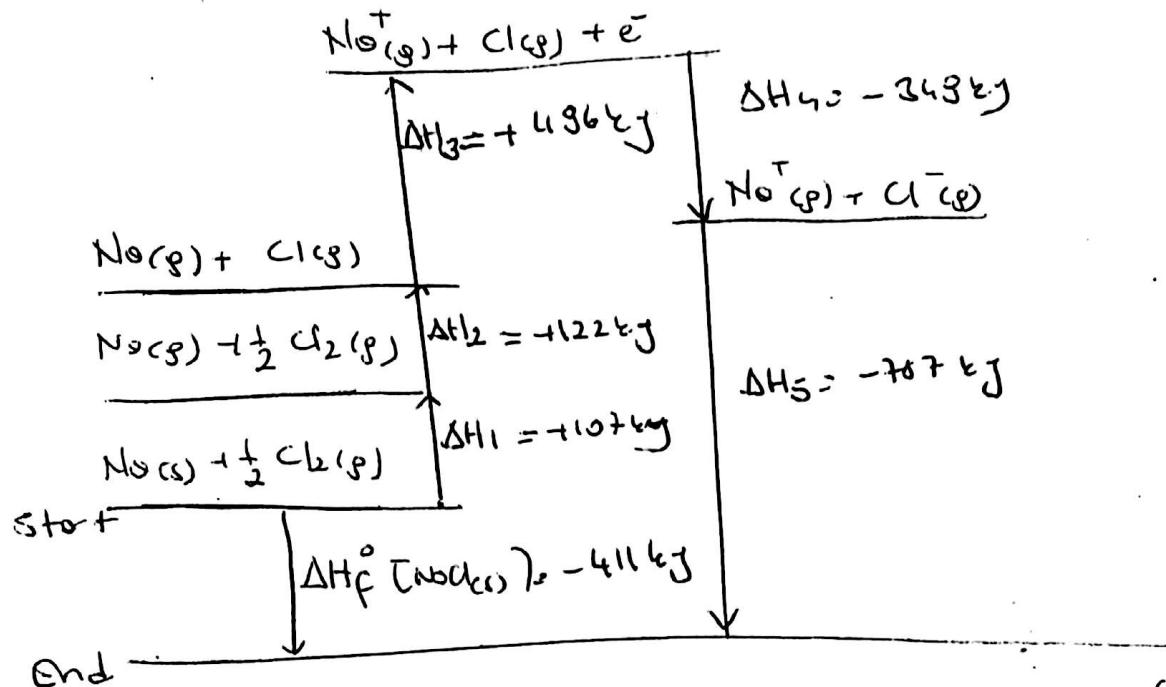


There is one Cs^+ in the center of the unit cell and

$$(8 \times \frac{1}{8}) = 1 \quad \text{one } Cl^- \text{ ions at the corner}$$



Energy changes in the formation of ionic crystals



Step 1) $\text{Na(s)} \rightarrow \text{Na(g)}$ $\Delta H_1 = \Delta H_{\text{sublimation}} = +107 \text{ kJ}$ (Sublimation of 1 mole solid Na)

Step 2) $\frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$ $\Delta H_2 = \frac{1}{2} \text{Cl-Cl bond energy} = +122 \text{ kJ}$ (Dissociation of Cl-Cl bond into one mole of Cl(g))

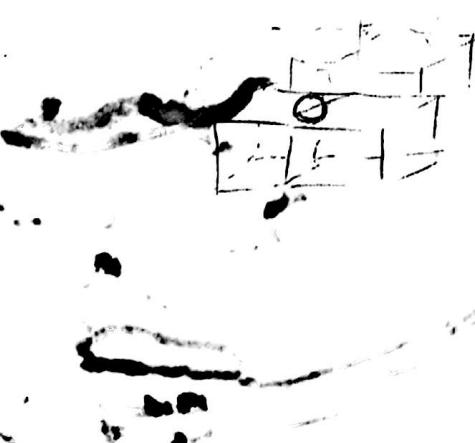
Step 3) $\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + e^-$ $\Delta H_3 = 1^{\text{st}} \text{ ionization energy} = +486 \text{ kJ}$

Step 4) $\text{Cl(g)} + e^- \rightarrow \text{Cl}^-(\text{g})$ $\Delta H_4 = \text{electron affinity of Cl} = -343 \text{ kJ}$

Step 5) $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl(s)}$ $\Delta H_5 = \text{lattice energy of NaCl} (-787 \text{ kJ})$

* The overall changes in these 5 steps is the same in which NaCl(s) is formed from its elements ($\Delta H_f^\circ \text{ NaCl}$)

$$\Delta H_f^\circ (\text{NaCl(s)}) = \Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$



12 edges
and only



Other Name Gul Hamida salt (Gulcayen)