UNIT TWO
CHEMICAL BONDING, GASES AND SOLIDS

I. CHEMICAL BONDING

I) TYPES OF BONDS:

A) IONIC BOND.

B) COVALENT BOND.

1) NORMAL COVALENT BOND.

2) COORDINATE COVALENT BOND.

II) LEWIS STRUCTURE (ELECTRON DOT STRUCTURE)FOR COVALENT MOLECULES AND POLYATOMIC IONS

A) EXCEPTIONS TO THE OCTET RULE:

1) ELECTRON DEFICIENT MOLECULES: This is typical of molecules where the central atom belongs to group IIIA.

Example:

2) EXPANDED VALENCE SHELL: This is typical of molecules where the central atom belongs to the third, fourth, fifth, sixth or seventh period.

Example:

3) ODD MOLECULES: This is typical of molecules where the total number of valence electrons is an odd number.

B) <u>RULES FOR DRAWING LEWIS STRUCTURE:</u>

1) Count all the valence electrons for the atoms. (If the species is an ion, add an additional electron for each negative charge or subtract an electron for each positive charge.)

2) Place one pair of electrons for each bond.

3) Complete the octets of the atoms bonded to the central atom. (Remember that the valence shell of any hydrogen atom is complete with only two electrons.)

4) Place any additional electrons on the central atom in pairs.

5) If the central atom still has less than an octet, you must form multiple bonds so that each atom has an octet.

C) <u>PRACTICE</u>: Draw a Lewis structure (Electron-dot structure) for each of the following:

1) SCl_4

2) SO_2

3) NH_4^+

4) ICl_4^-

5) ClF_3

6) NO_3^-

7) CO_3^{2-}

8) CO_2

9) $H\underline{C}N$

10) SO_2

11) SF_4

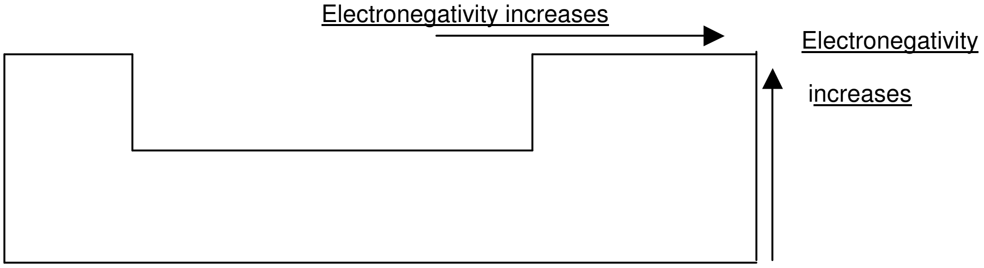
12) BrF_5

13) NH_3

14) H_2O

III) ELECTRONEGATIVITY AND BOND POLARITY

A) **Electronegativity** is the term used to describe an atom’s attraction for the electrons in a bond.



B) BOND POLARITY:

1) POLAR COVALENT BOND:

Within a molecule, equal partial positive and partial negative charges separated by a distance constitute a **dipole** .

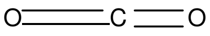
2) NON POLAR COVALENT BOND:

If the difference in electronegativity of the bonded atoms is higher than 1.7, the bond is described as mainly ionic. For example:

IV) POLARITY OF MOLECULES

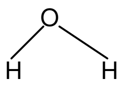
The polarity of a molecule is determined by its molecular shape.

A)



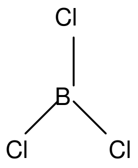
Linear

B)



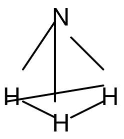
Bent

C)



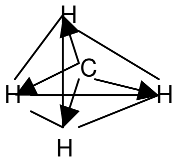
Triangular planar

D)



Pyramidal

E)



Tetrahedral

V) INTERMOLECULAR FORCES

A) HYDROGEN FORCES (HYDROGEN BOND):

Hydrogen bond is the strongest of the intermolecular forces . Still, it is much weaker than a covalent bond within a molecule. The molecule must contain **N——H, O——H** , or **F——H** group. Hydrogen bond takes place between a certain hydrogen atom in one polar covalent molecule and a **F**, **O**, or **N** atom in another polar covalent molecule.

B) DIPOLE-DIPOLE FORCES:

C) LONDON FORCES:

London forces occur as a result of temporary shifts in electron distribution. Electrons are in constant motion, so that for fleeting moments more electrons may be at one side of one atom, ion, or molecule than at the other. These instantaneous unsymmetrical distribution of charge set up a temporary dipole. This dipole in turn induces a similar dipole in a nearby ion, atom, or molecule causing a very weak electrostatic attraction between the positively charged nuclei of the atoms in one atom, ion, or molecule and the negatively charged electrons of another atom.

London force acts on all atoms and molecules polar or non polar. It is responsible for the liquefaction of even the monatomic noble gases at low enough temperature.

Among molecules of similar shape, London forces increase with an increasing number of electrons, that is, with increasing molecular mass.

EXERCISE:

1) Classify each **molecule** as being polar or non polar .

a) HI _________ b) I_2 ________ c) CO _________

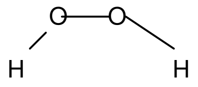
d) CCl_4 (Tetrahedral)________ e) H_2S (Bent) ________

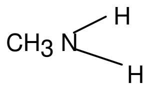
2) Which of the following have **dipole-dipole** forces between their molecules?

a) F_2 b) H_2Se(Bent) c)CS_2 (Linear) d) NO

3) Which of the following have **hydrogen bonds** between their molecules?

a) N_2

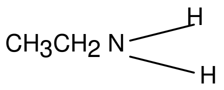
b) 

c) 

d) HBr e) CH_4 (Tetrahedral) f) H_2

4) Are hydrogen bonds, dipole-dipole, or London forces the major type of bonds between the following molecules?

a) CO b) CF_4 (Tetrahedral)

c) 

d) Br_2 e) H_2Te (Bent) f) CH_3 OH

g) CS_2 (Linear)

VI) THE VARIATION OF PROPERTIES

A) ATOMIC SIZE: Atoms are very tiny, they have diameters of about 10^{-10} meter.
1) As we proceed down within a group, the size of atoms, generally, increases and that as we proceed from left to right across a period, a gradual decrease in size is observed.

2) The factors that determine the size of the atoms are:

i) The order of the outer shell.
ii) The amount of nuclear charge that the outer electrons feel.

B) IONIC SIZE: In general positive ions are smaller than the neutral atoms from which they are formed, while negative ions are larger than neutral atoms. The decrease in size that accompanies the creation of a positive ion is often a result of the removal of all electrons from the outer shell of the atom.
Example:

When negative ions are produced from neutral atoms, electrons are added to the outer shell without any change to the nuclear charge. The effective nuclear charge felt by any one electron in the outer shell decreases.

B) IONIZATION POTENTIAL (ENERGY): It is defined as the energy required to remove an electron from an isolated gaseous atom.
First ionization energy:

Second ionization energy:

The variation of the first ionization energy across periods and down groups, parallels the trends in atomic size. Thus as we proceed down within a group, the increase in size that occurs is accompanied by a decrease in ionization energy. As we move across a period, from left to right, the increased effective nuclear charge experienced by the outer shell electrons causes the shell to shrink in size and also makes it more difficult to remove an electron, hence an increase in the ionization potential is observed.

C) ELECTRON AFFINITY: It is the energy that is released or absorbed when an electron is added to a neutral gaseous atom .
Example:

As with the ionization energy, the variations in electron affinity generally parallel the variations in atomic size. Therefore atoms that are very small and have outer shells that experience a high effective nuclear charge have very large electron affinities(elements in the upper right of the periodic table). On the other hand, atoms that are large and whose outer shells feel the effect of a small effective nuclear charge have small electron affinity (elements in the bottom left of the periodic table).

2) GASES

I) TOPICS:

- Properties of gases
- 760 torr= 760 mmHg= 1 atm
- Barometer and manometer
- Boyle's Law
- Charles' Law
- Combined gas law
- Ideal gas Law
- Kinetic molecular theory of gases
- Avogadro's Hypothesis
- Molar volume, 22.4 L/mole at STP
- Stoichiometric calculations dealing with gases
- Graham's Law of diffusion
- Dalton's Law of partial pressures
- Real gases and Ideal gases

II) REVIEW PROBLEMS:

A) GENERAL GAS LAWS PROBLEMS:

1) A sample of CO_2 (g) in a flask at 42°C exerts a pressure of 885 torr. When a 0.260 g N_2 is added to this flask, the pressure rises to 1090 torr. The temperature remains constant and there is no reaction between the CO_2(g) and N_2(g). How many grams of CO_2(g) are in he flask?
Setup:

Answer___________________

2) A steel cylinder with a volume of 855 ml and a pressure of 115 atm at 26.0 $^{\circ}$C was used to supply hydrogen gas for a reaction in another vessel. The pressure in the hydrogen cylinder, after the experiment, was 85 atm (still at 26.0 $^{\circ}$C). How many moles of $H_2(g)$ were taken?

Setup:

Answer _______________

3) A large flask, of unknown volume, is filled with air until the pressure reached 3.6 atm. The flask is then attached to a second evacuated flask of 5.21 L volume, and the air from the first flask is allowed to expand into the second flask. The final pressure of the air in both flasks is 2.6 atm. Calculate the volume ,in liters, of the first flask.

Setup:

Answer________________

4) A metallic cylinder contains 0.01765 mole of H_2S gas. The pressure in the cylinder is 725 mmHg and the temperature is 23 °C. An additional 0.00125 mole of $H_2S(g)$ is added into the cylinder. The temperature rises to 35 °C . Calculate the new pressure in atmosphere.
Setup:

Answer________________

5) A sample of $O_2(g)$ in a flask at 35 °C exerts a pressure of 644 torr. When 0.310 g of $CO_2(g)$ are added to this flask, the pressure rises to 870 torr. The temperature remains constant and there is no reaction between $O_2(g)$ and $CO_2(g)$. How many grams of $O_2(g)$ are in the flask?
Setup:

Answer_____________

6) At a particular temperature and pressure , 2.00 x 10^{23} molecules of N_2(g) occupies 5.00 liters. What would be the volume, in liters, occupied by 25.7 g of SO_2(g) at the same temperature and pressure?

Setup:

Answer____________

7) A hydrocarbon gas has a density of 1.22 g/L at 20.0 °C and 1.00 atm pressure. An analysis gives 80.0 % C and 20.0 % H by mass. What is the molecular formula of the hydrocarbon?

Setup:

Answer ___________

8) A mixture of 0.924 g of N_2O(g) and 0.825 g of NO(g) exerts a pressure of 1.32 atm. What is the partial pressure of N_2O (g)? (There is no reaction between the two gases)

Setup:

Answer ___________

9) The complete combustion of 0.430 g of a gaseous compound that contains only C and H, produced 672 ml of CO_2(g) measured at STP and 0.630 g of H2O (l). The 0.430 g sample occupied 156 ml at 50.0 °C and 0.850 atm. What is the molecular formula of the compound?

Setup:

Answer____________

10) An organic compound contains C, H, N, and O. The combustion of 0.1705 g of the compound produced 0.4610 g $CO_2(g)$ and 0.1652 g $H_2O(g)$.
Another sample of the compound was analyzed for nitrogen. A 1.932 g compound produced 110.4 ml of dry $N_2(g)$ at STP. The density of the compound was found to be 5.70 g/L at 130. °C and 367 torr.

a) What is the empirical formula of the compound?

b) What is the molecular formula of the compound?
Setup:

Answer________

11) A 13.0 liter flask contains 0.300 mole N_2(g), 0.200 mole He(g), and 0.400 mole Ar(g) at 30. °C.

a) What is the pressure in atm, inside the flask?

b) What is the partial pressure of Ar(g) in the mixture?

Setup:

Answer____________

12) At 0.522 atm and 63.0 ° C , the density of gas **"X"** is 2.92 g/L. The volume 72.0 ml of gas effuses through an apparatus in 6.22 seconds. The rate of effusion of gas "Y" through the same apparatus and under the same conditions is 14.25 ml/sec. What is the molar mass of gas "Y"?

Answer ____________

13) The Kinetic Molecular Theory of gases is based on few postulates describing an ideal gas behavior.

a) List three postulates.

i)
ii)
iii)

b) How should the temperature and the pressure of a real gas be changed to make it approach an ideal behavior?

Answer: i) The temperature should be (increased, or decreased).
ii) The pressure should be (increased or decreased).

B) **STOICHIOMETRIC CALCULATIONS**

1) Consider the following reaction:

$$4\ NH_3\,(g) + 5\ O_2\,(g) \longrightarrow 4\ NO\ (g) + 6\ H_2O\ (g)$$

How many liters of $H_2O(g)$ measured at 125 °C and 1.00 atm would be formed if 3.00 L of $NH_3(g)$ at 800 °C and 1.30 atm completely react?

Setup:

Answer ______________

2) A piece of sodium is placed in a 3.50 L container with $O_2(g)$. The $O_2(g)$ is at a pressure of 1.80 atm and a temperature of 35.0 °C. Few hours later, the pressure has dropped to 1.20 atm and the temperature has dropped to 28. °C. Calculate the mass of Na_2O (s) produced.

Setup:

$$4\ Na(s) + O_2\,(g) \longrightarrow Na_2O(s)$$

3) A 1.34 g of CaC_2 (s) was allowed to react with water. The acetylene,C_2H_2 (g), produced by the reaction was collected over water. If 471 ml of acetylene was collected at a temperature of 23 °C and a pressure of 743 torr, what is the percent yield of the reaction? (The vapor pressure of water at 23 °C is 21.1 torr.)

$$CaC_2\,(s) + 2\ H_2O \longrightarrow C_2H_2\,(g) + Ca(OH)_2\,(s)$$

Setup:

Answer____________

3. SOLIDS

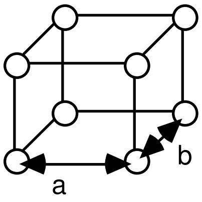
I) Vocabulary

- **Amorphous Solid:** A solid where there is a lack of ordered arrangement of particles.
- **Crystalline solid**: A solid where there is a three-dimensional ordered arrangement of particles.
- **Crystal lattice :** It is the three-dimensional ordered arrangement of particles in space.
- **Unit cell :** it is the basic repeating unit of the arrangement of atoms, ions, or molecules.
- **lattice points:** These are the repeating particles (atoms, ions, or molecules).

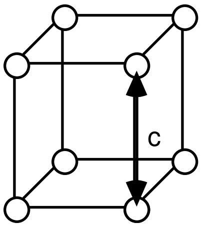
II) THE SEVEN CRYSTAL SYSTEMS (THE SEVEN CLASSES OF UNIT CELLS)

(The seven types of unit cells):

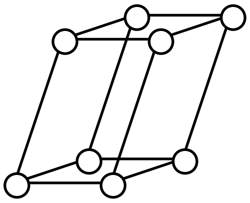
The unit cell may be considered as the fundamental building block of the crystal lattice, because the lattice can be constructed by stacking unit cells. There are seven classes of unit cells that can be used to describe the crystal lattices of all crystalline solids. That is, there are seven ways in which certain liquids can crystallize. (in other words, there are seven ways in which atoms, ions, or molecules can stack and lock in an orderly rigid way.)



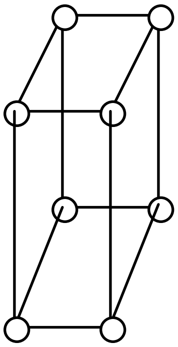
Cubic
$(a = b = c)$
$(\alpha = \beta = \gamma = 90°)$



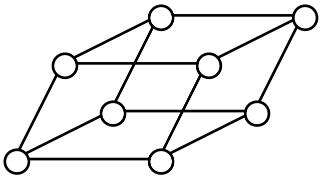
Tetragonal
$(a = b \neq c)$
$(\alpha = \beta = \gamma = 90°)$



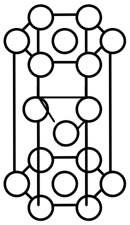
Monoclinic
$(a \neq b \neq c)$
$(\alpha = \beta = 90° \neq \gamma)$



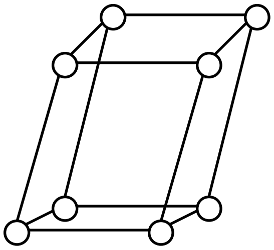
Orthorhombic
$(a \neq b \neq c)$
$(\alpha = \beta = \gamma = 90°)$



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



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



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

III) THE CUBIC SYSTEM

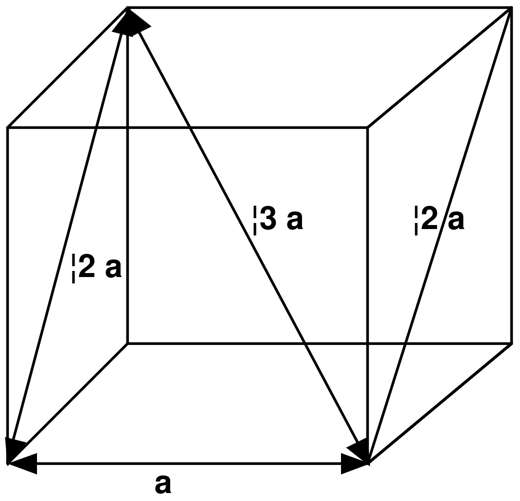


Figure : A CUBE

Body diagonal= √3 a
Face diagonal =√2 a

A) ***PACKING EFFICIENCY OF A CUBIC SYSTEM*** : (Percentage of the cell space occupied by spheres.)

Let us assume that each lattice point is occupied by an atom (a sphere). Depending on the positions of the atoms, we may have a simple cube, a body-centered cube, or a face-centered cube.

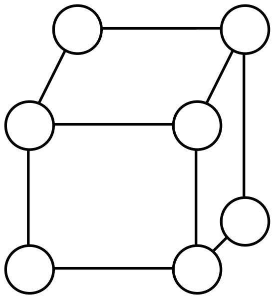


Figure (1)
Simple cube

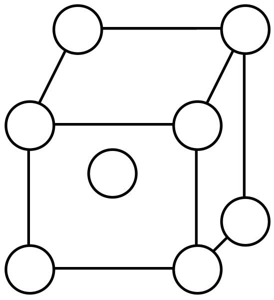


Figure (2)
Body-centered cube

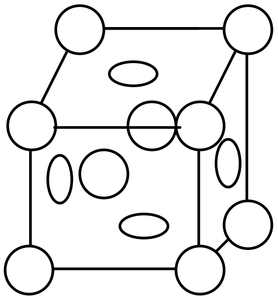


Figure (3)
Face-centered cube

The figures above, show that atoms are confined within small volumes, held together by forces represented by the thin lines. Actually, each atom occupies an appreciable volume in space and is in direct contact with its neighbors.

$$\text{Packing Efficiency} = \frac{\text{Volume of spheres in the unit cell}}{\text{Volume of the unit cell}} \times 100$$

(Let **“r “** be is the radius of the sphere, and **“a “** is the side, edge, of the unit cell.)

1) <u>SIMPLE CUBE:</u>

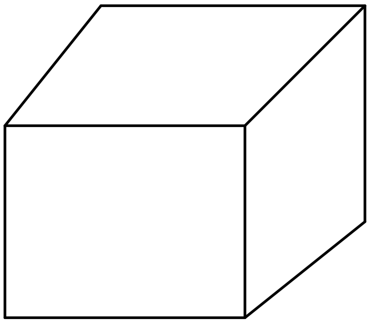
For a simple cubic system:

$a = 2r$

Volume ofone sphere=

Volume of unit cell =

Packing efficiency =



2) <u>BODY-CENTERED CUBE</u> :

Body diagonal =

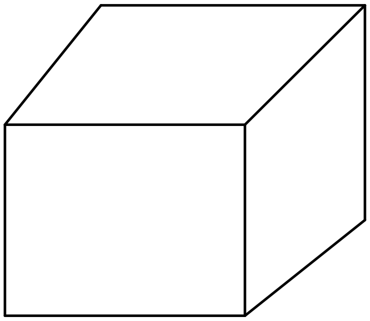
Body diagonal =

for a body centered cube:

Volume of two spheres =

Volume of unit cell =

Packing efficiency=



3) <u>FACE-CENTERED CUBE</u>:

Face diagonal =

Face diagonal =

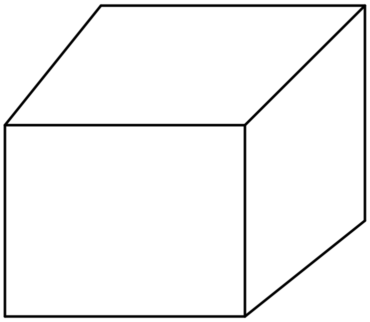
For a face-centered cube:

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

Volume of four spheres=

Volume of unit cell=

Packing efficiency =



B) EXERCISES:

Exercise 1: Chromium crystallizes in a body-centered cubic system. The density of chromium is 7.19 g/ml. What is the volume of **one** chromium atom?

Exercise 2: Nickel has a cubic closest packing structure. Find the density of nickel , in units of, g/ml, if the volume of **one** nickel atom is 9.22×10^{-24} cm^3 .

IV) PACKING ACCORDING TO SIZE OF SPHERES

A) UNEQUAL SIZED-SPHERES

When unequal-sized spheres are placed in lattice, the large particles pack in one of the close-packed arrangements with small particles occupying the holes between the large spheres. For example, in Li_2O the oxide ions pack in a cubic close-packed structure, whereas, the Li^+ ions occupy small cavities that exist between the oxide ions.

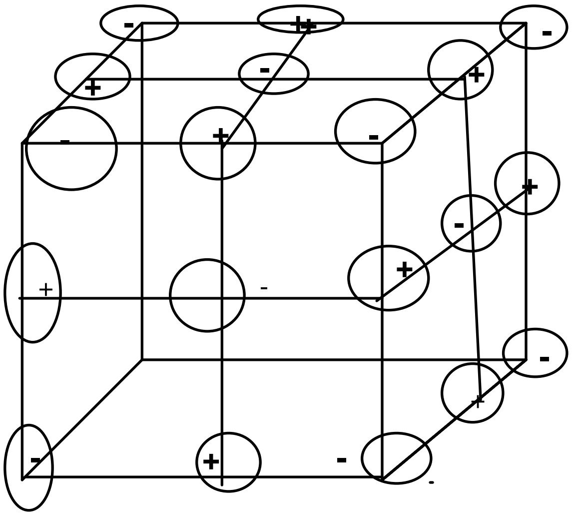
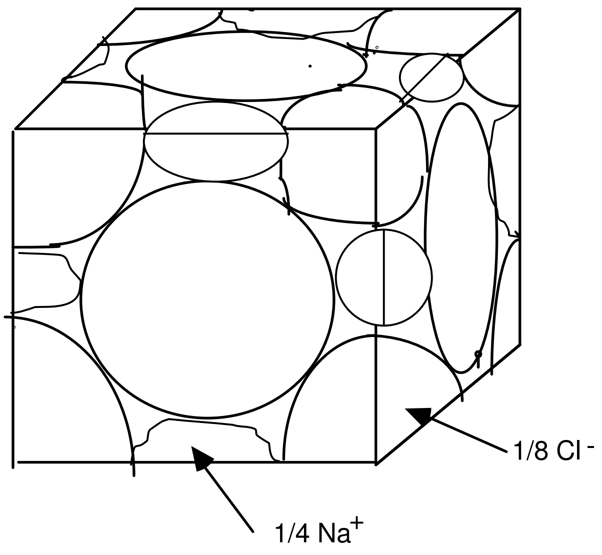


Figure: Unit cell of NaCl

Exercise: Choose the unit cell from the two-dimensional array of particles given in the diagram.

+	-	+	-
-	+	-	+
+	-	+	-
-	+	-	+

Exercise: Consider the figure given below to predict the chemical formula for sodium chloride.

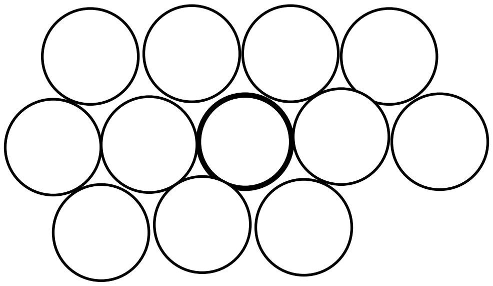


B) EQUAL -SIZED SPHERES

Equal sized spheres can pack most efficiently, that is, with the minimum amount of empty space. Such arrangement is called **closest packing structure**.

CLOSEST PACKING:

1) The most efficient arrangement of a layer of equal sized spheres is one in which each sphere is surrounded by six others in a layer.



Figure(1)

2) The most efficient arrangement of the spheres in a second layer is in the depression of the first layer.

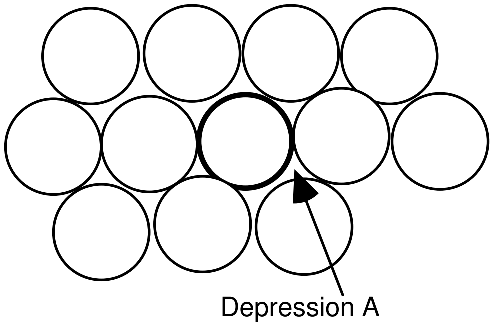


Figure (2)

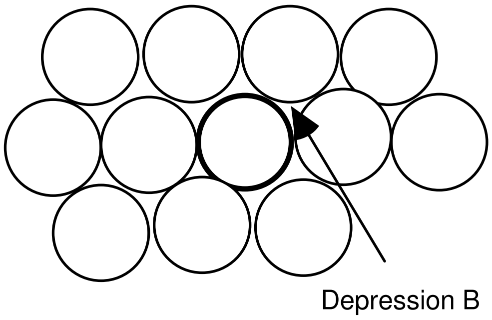


Figure (3)

3) The spheres in the third layer sit in the depressions of the second layer. However, there are two types of depressions (Figures (2) and (3)), and they lead to different structures:

a) The spheres of the third layer are placed immediately above those of the first layer (AB-AB--AB arrangement of layers). The unit cell arising from such arrangement of layers is the **HEXAGONAL CLOSEST PACKING** . The coordination number is twelve and the packing efficiency is 74 %. (Figure (4)).

b) The third layer of spheres is placed in the positions shown in Figure (5) (ABC--ABC--ABC arrangement of layers). The unit cell arising from such arrangement of layers is the **CUBIC CLOSEST PACKING** which is the **face -centered cube**. The coordination number is twelve and the packing efficiency is 74 %.

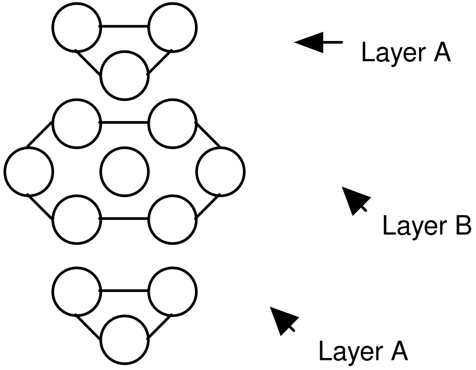


Figure (4)
Hexagonal closest packing
(AB--AB--AB arrangement of layers)

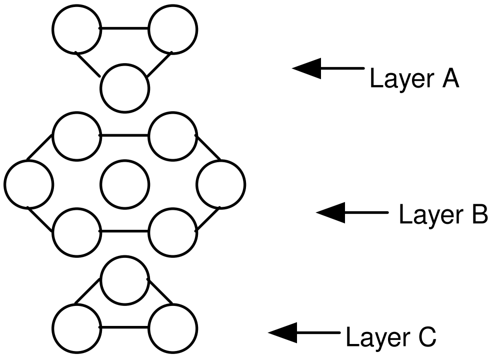


Figure (5)
Cubic-closest Packing
(ABC--ABC--ABC arrangement of layers)

* SEE FOR YOURSELF IN THE LAB THAT THE FACE-CENTERED CUBE HAS THE ABC--ABC--ABC ARRANGEMENT OF LAYERS.

V) TYPES OF CRYSTALLINE SOLIDS

	IONIC	**MOLECULAR**	**COVALENT NETWORK**	**METALLIC**
Basic units (lattice particles)	Positive and negative ions.	Polar or nonpolar covalent molecules.	Atoms	Metal ions (Cations).
Bonding between units (Attractive forces)	Ionic (Electrostatic attraction)	Intermolecular forces as: Dipole-dipole,Hydrogen bond, and London forces.	Covalent bonding. Sharing of electrons.	The crystal is held together by the attraction between the positive metallic ions and its highly mobile "sea" of electrons.
Properties	• High melting point and boiling point. NaCl melts at 801 C. • Poor conductors (insulators). • Hard, Brittle.	• Moderate to low melting point and boiling point. • Electrical and thermal insulators. • Soft.	• High melting point and boiling point. • Semi conductors or insulators. • Hard.	• Variable melting point and boiling point. Example: Hg is liquid,while Fe is solid. Na is soft while Ti is hard. • Good conductors of heat and electricity.
Types of Elements or compounds that are most likely to exhibit this type of crystalline solid.	Ionic crystals are found to be formed from metallic and nonmetallic elements.	Compounds made of nonmetal elements.	Covalent network crystals may be formed from atoms of nonmetal elements that belong to group IIIA,IVA, or VA.	Metallic elements.

VI. BORN HABER CYCLE

A) INTRODUCTION

Ionization energy: It is the energy required to remove an electron from an isolated **gaseous** atom in its ground state (most stable state.)

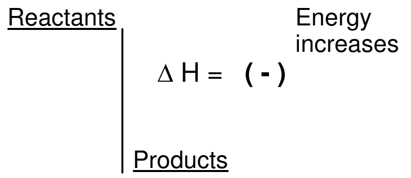
$Li\ (g) \longrightarrow Li^{+}\ (g) + e^{-}$ First ionization energy

$Li^{+}\ (g) \longrightarrow Li^{2+} + e^{-}$ Second ionization energy

Electron affinity: It is the energy that is released or absorbed when an electron is added to a neutral **gaseous** atom in its ground state.

$X\ (g) + e^{-} \longrightarrow X^{-}\ (g)$

HESS LAW OF CONSTANT HEAT SUMMATION :



Figure(a): Potential energy profile for an exothermic reaction.

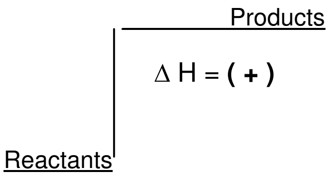


Figure (b): Potential energy profile for an endothermic reaction.

$$\boxed{\Delta H = \underset{\text{Heat content of the products}}{H} - \underset{\text{Heat content of the reactants}}{H}}$$

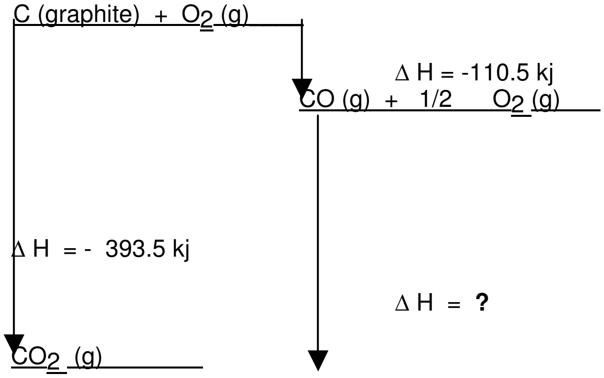
Hess Law: The overall enthalpy change, Δ H overall, of a reaction, is equal to the sum of the enthalpy changes for the individual steps.

Example

$< \text{———} \Delta H = 20\ kj \text{———} >$

$A + B \xrightarrow[\Delta H = 5\ kj]{} C+D \xrightarrow[\Delta H = 3\ kj]{} E + F \xrightarrow[\Delta H = \ ?]{} G$

Example



Born Haber cycle uses Hess' Law for the determination of the **lattice energies** of ionic compounds.

Lattice energy : It is the energy released when the ions in the **gaseous** state combine to form the ionic crystals.

Li^{+} **(g)** + F^{-} **(g)** → LiF **(s)** ΔH **(lattice energy)** = **?**

Heat of formation : It is the enegy released on forming one mole of an ionic compound from the elements in their standard states .

$Li\ \mathbf{(s)} + 1/2\ F_2\ \mathbf{(g)} \longrightarrow LiF(s)$ = - 594.1 kj $\Delta H_{\textbf{formation}}$ = + 155.2 kj/mole

The previous reaction can be broken into the following five steps:

1) Conversion of Li (s) to Li (g) (Sublimation of lithium) $Li(s) \longrightarrow Li(g)$
ΔH_{Sub} = + 155.2 kj/mole

2) Ionization of a mole of gaseous Li atoms $Li(g) \longrightarrow Li^+ (g) + e^-$

ΔH_{Ioniz} = = + 520 kj/mole

3) Bond energy $1/2\ F_2\ (g) \longrightarrow F(g)$
(Dissociation energy of 1 mole of F_2 molcules)

ΔH_{diss} = **1 /2 (+ 150.6)** kj/mole

4) Electron affinity of F (g) $F(g) + e^- \longrightarrow F^-$ (g
$\Delta H_{Elect.Aff.}$ = - 333 kj/mole

5) Combination of gaseous Li^+ (g) and F^- (g) ions to form a mole of solid LiF (s). $Li^+ (g) + F^- (g) \longrightarrow LiF(s)$

$\Delta H_{\textbf{Lattice}}$ = **?**

$Li(s) \longrightarrow Li(g)$ ΔH = + 155.2 kj/mole of Li atoms

$Li(g) \longrightarrow Li^+ (g) + e^-$ ΔH = = + 520 kj/mole of Li atoms

$1/2\ F_2 (g) \longrightarrow F(g)$ ΔH = **1 /2 (+150.6 kj)= + 75.3 kj/mole of F atoms**

$F(g) + e^- \longrightarrow F^- (g)$ ΔH = - 333 kj/mole of F atoms

$Li^+ (g) + F^- (g) \longrightarrow LiF(s)$ ΔH = **?**

Add the five equations given above:

$Li(s) + Li(g) + 1/2\ F_2 (g) + F(g) + e^- + Li^+ (g) + F^- (g) \longrightarrow Li(g) + Li^+ (g) + e^- + F(g) + F^- (g) + LiF(s)$

$Li(s) + 1/2\ F_2 (g) + \longrightarrow LiF(s)$ ΔH **(overall)** = - 594.1 kj
(Formation)

$\Delta H_{\textbf{(overall) (formation)}} = \Delta H_{\textbf{Sublimation}} + \Delta H_{\textbf{Ionization}} + \mathbf{1/2}\,\Delta H_{\textbf{Dissociation}} + \Delta H_{\textbf{Elect. Aff.}} + \Delta H_{\textbf{(Lattice energy)}}$

-594 kj = 155.2 kj + 520 kj + **75.3** kj + (-333) kj + $\Delta H_{\textbf{(Lattice energy)}}$

$\Delta H_{\textbf{(Lattice energy)}}$ = **-** 1010 kj

Exercise: a) Sketch a diagram for **Born Haber cycle** for the formation of $MgCl_2$ using the data given below.

b) Calculate the lattice energy of $MgCl_2$ (s) (in units of kj/mole) using the above cycle .

The enthalpy of formation of magnesium chloride is - 698 kj/mole.
The enthalpy of sublimation of magnesium is +120. kj/mole.
The first and second ionization energies of Mg(g) are 756 kj/mole and 1490 kj/mole, respectively.
The bond energy for Cl_2 (g) is 248 kj/mole.
The electron affinity of Cl is - 368 kj/mole.

Setup: **Answer: - 2576 kj**