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B. Sc. Chemistry Semester-2
C-201 Chapter 1
Basic of Ionic compounds

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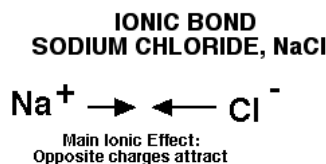
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❖ **Contents**

Sr. No.	Topic	Page No.
1	Introduction	3
2	Born Haber cycle of sodium chloride NaCl, (or any AB-type Mono-valent ionic solid)	4
3	max born equation for calculation for lattice energy	5
4	The limiting radius ratio	6
5	Defects in crystal	7
6	Semiconductors	9
7	Questionary	12

❖ Introduction

Those molecules that consist of charged ions with opposite charges are called IONIC. These ionic compounds are generally solids with high melting points and conduct electrical current. Ionic compounds are generally formed from metal and a non-metal element.

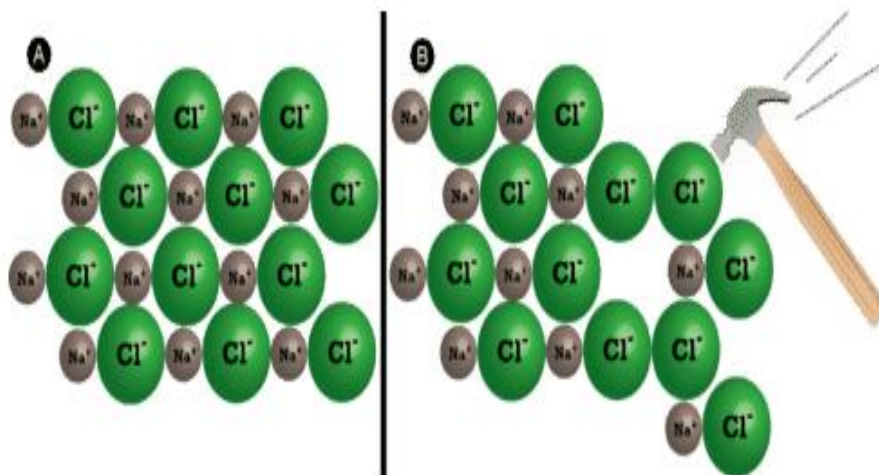


❖ Melting Points

Because of the many simultaneous attractions between cations and anions that occur, ionic crystal lattices are very strong. The process of melting an ionic compound requires the addition of large amounts of energy in order to break all of the ionic bonds in the crystal. For example, sodium chloride has a melting temperature of about 800°C. As a comparison, the molecular compound water melts at 0 °C.

❖ Shattering(Brittleness)

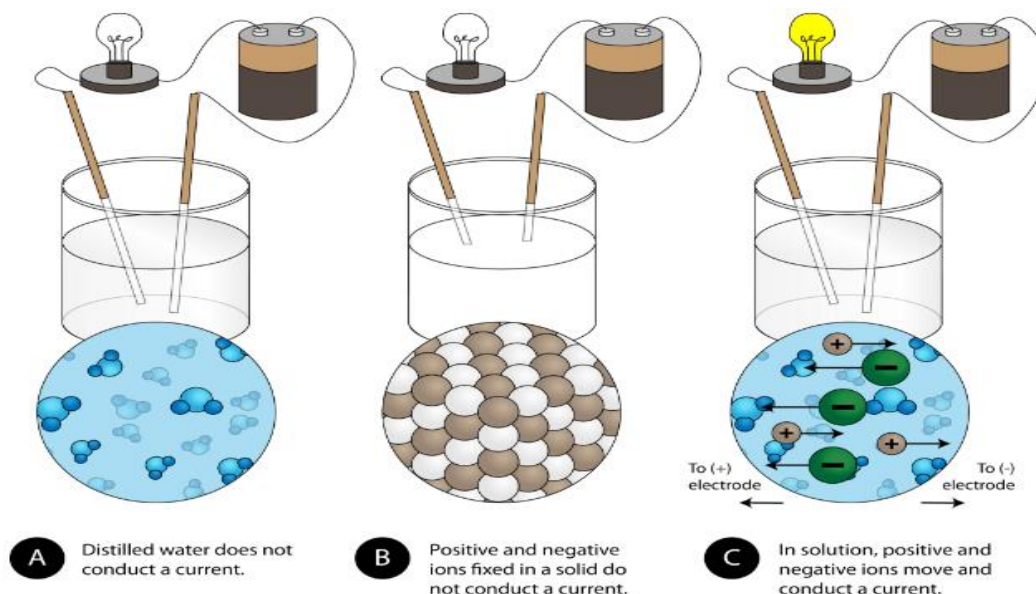
Ionic compounds are generally hard, but brittle. Why? It takes a large amount of mechanical force, such as striking a crystal with a hammer, to force one layer of ions to shift relative to its neighbour. However, when that happens, it brings ions of the same charge next to each other (see below). The repulsive forces between like-charged ions cause the crystal to shatter. When an ionic crystal breaks, it tends to do so along smooth planes because of the regular arrangement of the ions.



(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.

❖ Conductivity

Another characteristic property of ionic compounds is their electrical **conductivity**. The figure below shows three experiments in which two electrodes that are connected to a light bulb are placed in beakers containing three different substances.



(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.

In the third beaker, the NaCl has been dissolved into the distilled water. Now the crystal lattice has been broken apart and the individual positive and negative ions can move. Cations move to one electrode, while anions move to the other, allowing electricity to flow. Melting an ionic compound also frees the ions to conduct a current.

❖ Born Haber cycle of sodium chloride NaCl, (or any AB-type Mono-valent ionic solid).

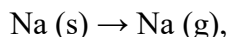
The heat of formation of sodium chloride (ΔH_f^0) from the sodium metal and chlorine gas can be experimentally measured.



The formation of ionic solid sodium chloride from solid sodium metal and gaseous chlorine is not a single step process but goes through several processes. Heat changes of all the processes except the lattice energy can be experimentally measured.

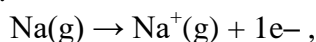
The processes or steps in the formation of sodium chloride are-

Step 1. Solid sodium atom sublimates to gaseous atom by absorbing heat energy (ΔH_{sub}).



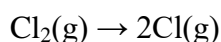
Sublimation energy $\Delta H_{\text{sub}} = +107 \text{ kJ/mol}$

Step 2. Gaseous sodium atom absorbs the ionization energy to release one electron and forms gaseous sodium ion.



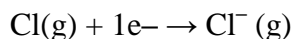
Ionization energy $\Delta H_{\text{IE}} = +502 \text{ kJ/mol}$

Step 3. Diatomic gaseous chlorine breaks into two individual atoms by absorbing bond energy, such that each chlorine atom absorbs half of the bond energy of chlorine molecule.



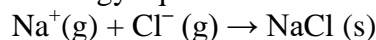
Bond dissociation energy of chlorine = $\frac{1}{2} \Delta H_{\text{diss}} = +121 \text{ kJ/mol}$

Step 4. Chlorine atom accepts an electron to form chloride ion and releases energy equivalent to electron affinity.



Electron affinity = $\Delta H_{EA} = -355 \text{ kJ/mol}$

Step 5. Gaseous sodium ion and gaseous chloride ion combine to form solid sodium chloride molecule and releases energy equivalent to lattice energy.

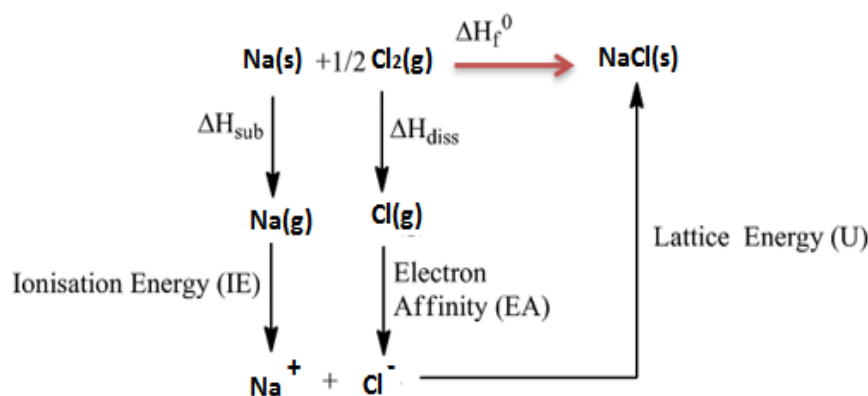


Lattice energy = $\Delta H_{LE} = U = ?$

Summation of enthalpy of all the processes from step 1 to step 5) give the net enthalpy of formation of solid crystalline sodium chloride from sodium and chlorine in their standard conditions of solid and gas respectively. This should be equal to the experimentally measured enthalpy of formation of solid sodium chloride.

The enthalpies are represented as a cycle in the figure.

Born Haber Cycle for Sodium Chloride



$$\text{So, } \Delta H_f^0 = \Delta H_{\text{sub}} + \Delta H_{\text{IE}} + \frac{1}{2} \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U$$

or

$$\Delta H_f^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + \frac{1}{2} \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U) = 0$$

$$-411 - (+107 + 502 + 121 - 355 + U) = 0$$

Here, except lattice energy, all other enthalpies can be experimentally measured.

Lattice energy of the sodium chloride solid = $U = \Delta H_f^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + \frac{1}{2} \Delta H_{\text{dis}} + \Delta H_{\text{EA}})$.

$$= -411 - 107 - 502 - 121 + 355$$

$$= -786 \text{ kJ/mol}$$

❖ Max born equation for calculation for lattice energy

- Lattice energy decreases as you go down a group (as atomic radii goes up, lattice energy goes down).
- Going across the periodic table, atomic radii decreases, therefore lattice energy increases.

The Born-Landé equation was derived from these two following equations. The first is the electrostatic potential energy:

$$\Delta U = - \frac{N_A M |Z^+||Z^-| e^2}{4\pi\epsilon_0 r}$$

Here

- M is Avogadro's constant (6.022×10^{23})
- M is the Madelung Constant (a constant that varies for different structures)
- e is the charge of an electron ($1.6022 \times 10^{-19} \text{ C}$).

- Z^+ is the cation charge
- Z^- is the anion charge
- ϵ_0 is the permittivity of free space

The second equation is the repulsive interaction:

$$\Delta U = \frac{NAB}{r^n}$$

Here

- B is the repulsion coefficient and
- n is the Born Exponent (typically ranges between 5-12) that is used to measure how much a solid compresses

These equations combine to form:

$$\Delta U(0K) = \frac{N_A M |Z^+| |Z^-| e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

Here

- r_0 is the closest ion distance

❖ The limiting radius ratio

The limiting radius ratio is the minimum allowable value for the ratio of ionic radii ($\rho = r^+/r^-$) for this structure to be stable. Here, r^+ is the radius of the cation and r^- is the radius of the surrounding anions. Note that the anions are usually larger than cations.

Radius Ratio	Coordination number	Type of void	Example
< 0.155	2	Linear	
0.155 - 0.225	3	Triangular Planar	B_2O_3
0.225 - 0.414	4	Tetrahedral	ZnS, CuCl
0.414 - 0.732	6	Octahedral	NaCl, MgO
0.732 - 1.000	8	Cubic	CsCl, NH_4Br

❖ Defects in crystal

Irregularity in the arrangement of constituent particles in solids is called crystal defect or imperfection in solids. There are two types of crystal defects - Point Defects and Line Defects.

- **Point Defects:** Irregularities or deviation from ideal arrangement of constituent particles around the point or atom in a crystalline solid is known as point defects.
- **Line Defects:** Irregularities or deviation from ideal arrangement of constituent particles in entire row of lattice is known as line defects.

Point Defects: Point Defects are divided into three types:

- 1) Stoichiometric Defects
- 2) Impurities Defects
- 3) Non-stoichiometric Defects

1) Stoichiometric Defects: It is a type of point defects which does not disturb the stoichiometry of solid. This is also known as Intrinsic or Thermodynamic Defects.

Types of stoichiometric defects:

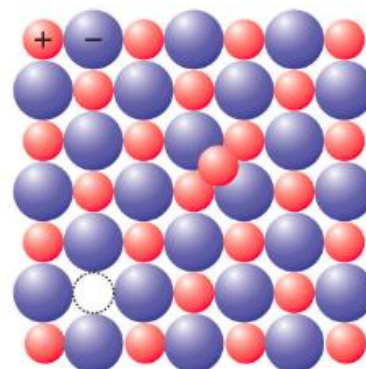
- a) Vacancy Defects
- b) Interstitial defects
- c) Frenkel Defects
- d) Schottky Defects

Vacancy defects and interstitial defects are found in non-ionic compounds while similar defects found in ionic compounds are known as Frenkel Defects and Schottky Defects.

(a) **Vacancy Defects:** When some lattice sites left vacant while the formation of crystal, the defect is called Vacancy Defects. In vacancy defects, an atom is missing from its regular atomic site. Because of missing of atom the density of substance decreases, i.e. because of vacancy defects. The vacancy defect develops on heating of substance.

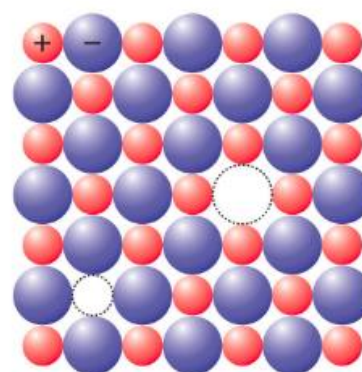
(b) **Interstitial Defects:** Sometime in the formation of lattice structure some of the atoms occupy interstitial site, the defect arising because of this is called Interstitial Defects. In interstitial defect, some atoms occupy sites at which; generally there is no atom in the crystal structure. Because of the interstitial defects, the number of atoms becomes larger than the number of lattice sites. Increase in number of atoms increases the density of substance, i.e. interstitial defects increase the density of substance. The vacancy defects and interstitial defects are found only in non-ionic compounds. Such defects found in ionic compounds are known as Frenkel Defects and Schottky Defects.

(c) **Frenkel Defects:** It is a type of vacancy defect. In ionic compounds, some of the ions (usually smaller in size) get dislocated from their original site and create defect. This defect is known as Frenkel Defects. Since this defect arises because of dislocation of ions, thus it is also known as Dislocation Defects. As there are a number of cations and anions (which remain equal even because of defect); the density of the substance does not increase or decrease. Ionic compounds; having large difference in the size between their cations and anions; show Frenkel Defects, such as ZnS, AgCl, AgBr, AgI, etc. These compounds have smaller size of cations compared to anions.



(b) Frenkel defect

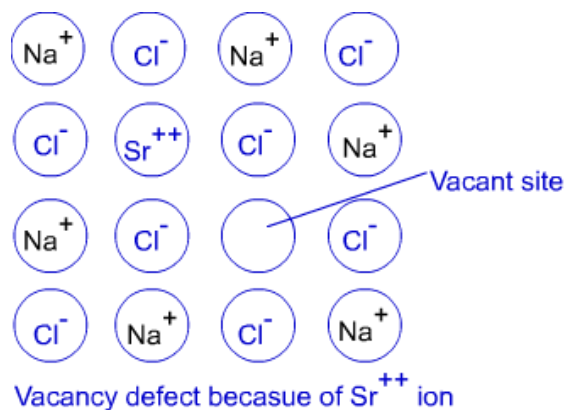
(d) **Schottky Defects:** Schottky Defect is type of simple vacancy defect and shown by ionic solids having cations and anions; almost similar in size, such as NaCl, KCl, CsCl, etc. AgBr shows both types of defects, i.e. Schottky and Frenkel Defects. When cations and anions both are missing from regular sites, the defect is called Schottky Defect. In Schottky Defects, the number of missing cations is equal to the number of missing anions in order to maintain the electrical neutrality of the ionic compound. Since, Schottky Defects arises because of mission of constituent particles, thus it decreases the density of ionic compound.



(a) Schottky defect

2) Impurities Defects: Defects in ionic compounds because of replacement of ions by the ions of other compound is called impurities defects.

In NaCl; during crystallization; a little amount of SrCl₂ is also crystallized. In this process, Sr⁺² ions get the place of Na⁺ ions and create impurities defects in the crystal of NaCl. In this defect, each of the Sr⁺² ion replaces two Na⁺ ions. Sr⁺² ion occupies one site of Na⁺ ion; leaving other site vacant. Hence it creates cationic vacancies equal number of Sr⁺² ions. CaCl₂, AgCl, etc. also shows impurities defects.



3) Non-stoichiometric Defects: There are large numbers of inorganic solids found which contain the constituent particles in non-stoichiometric ratio because of defects in their crystal structure. Thus, defects because of presence of constituent particles in non-stoichiometric ratio in the crystal structure are called Non-stoichiometric Defects.

Non-stoichiometric Defects is mainly of two types – Metal Excess Defects and Metal Deficiency Defects.

(I) Metal Excess Defects:

Metal excess defects are of two types:

a) Metal excess defects due to anionic vacancies:

These types of defects can be seen because of missing of anions from regular site leaving a hole. Which is occupied by an electron to maintain the neutrality of compound. Hole occupied by electron is called F-centre and responsible for showing colour by the compound.

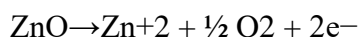
This defect is common in NaCl, KCl, LiCl, etc. Sodium atoms get deposited on the surface of crystal when sodium chloride is heated in an atmosphere of sodium vapour. In this process, the chloride ions get diffused with sodium ion to form sodium chloride. In this process, sodium atom releases electron to form sodium ion. This released electron gets diffused and occupies the anionic sites in the crystal of sodium chloride; creating anionic vacancies and resulting in the excess of sodium metal.

The anionic site occupied by unpaired electron is called F-centre. When visible light falls over the crystal of NaCl, the unpaired electron present gets excited because of absorption of energy and impart yellow colour.

Because of similar defect if present, crystal of LiCl imparts pink colour and KCl imparts violet.

b) Metal excess defect due to presence of extra cations at interstitial sites:

Zinc oxide loses oxygen on heating resulting the number of cations (zinc ion) become more than anions present in zinc oxide.



On heating the formula of zinc oxide becomes Zn⁺²

The excess cations (Zn⁺² ions) move to interstitial site and electrons move to neighbouring interstitial sites. Because of this zinc oxide imparts yellow colour when heated. Such defects are called metal excess defects.

(II) Metal Deficiency Defects:

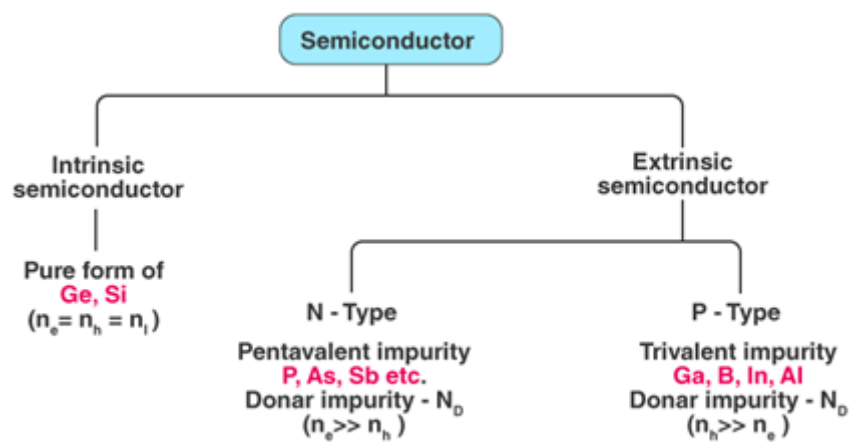
Many solids show metal deficiency defects as they have less metals compare to ideal stoichiometric proportion. The less proportion of metal is compensated by same metals having higher valence. Such defects are shown generally by transition elements. Thus, when metal present less than ideal stoichiometric proportion in a solid, it is called metal deficiency defect.

❖ Semiconductors

Types of Semiconductors

Semiconductors can be classified as:

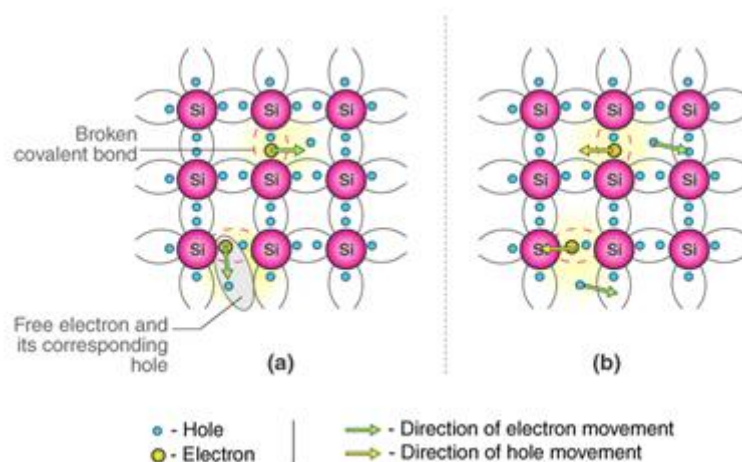
- a) **Intrinsic Semiconductor**
- b) **Extrinsic Semiconductor**



Classification of Semiconductors

(I) Intrinsic Semiconductor

An **intrinsic type of semiconductor material** is made to be very pure chemically. It is made up of only a single type of element.



Conduction Mechanism in Case of Intrinsic Semiconductors (a) In absence of electric field (b) In presence of electric Field

Germanium (Ge) and Silicon (Si) are the most common type of intrinsic semiconductor elements. They have four valence electrons (tetravalent). They are bound to the atom by covalent bond at absolute zero temperature.

When the temperature rises, due to collisions, few electrons are unbound and become free to move through the lattice, thus creating an absence in its original position (hole). These free electrons and holes contribute to the conduction of electricity in the semiconductor. The negative and positive charge carriers are equal in number.

The thermal energy is capable of ionizing a few atoms in the lattice, and hence their conductivity is less.

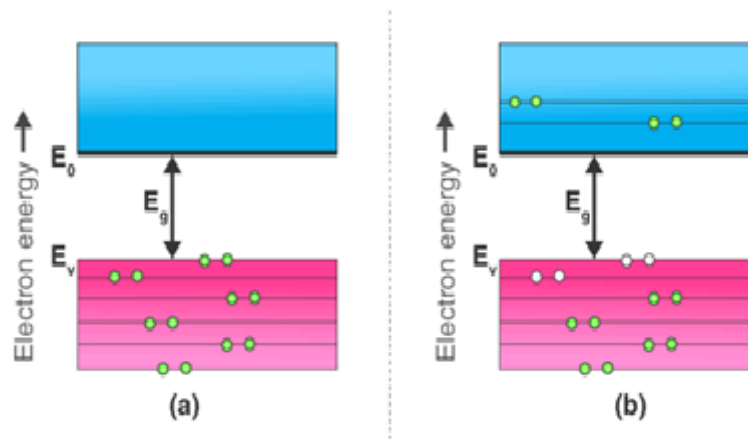
The Lattice of Pure Silicon Semiconductor at Different Temperatures

At absolute zero Kelvin temperature: At this temperature, the **covalent bonds** are very strong and there are no free electrons and the semiconductor behaves as a perfect insulator.

Above absolute temperature: With the increase in temperature few valence electrons jump into the conduction band and hence it behaves like a poor conductor.

Energy Band Diagram of Intrinsic Semiconductor

The energy band diagram of an intrinsic semiconductor is shown below:



(a) Intrinsic Semiconductor at $T = 0$ Kelvin, behaves like an insulator (b) At $t > 0$, four thermally generated electron pairs

In intrinsic semiconductors, current flows due to the motion of free electrons as well as holes. The total current is the sum of the electron current I_e due to thermally generated electrons and the hole current I_h

$$\text{Total Current (I)} = I_e + I_h$$

For an intrinsic semiconductor, at finite temperature, the probability of electrons to exist in conduction band decreases exponentially with increasing band gap (E_g)

$$n = n_0 e^{-E_g/2 \cdot K_b \cdot T}$$

Where,

E_g = Energy band gap

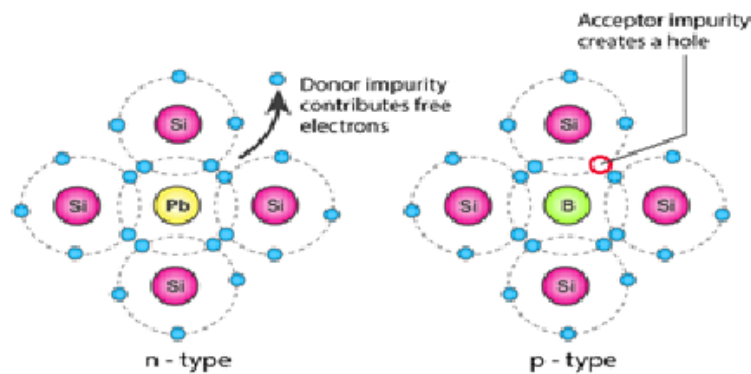
K_b = Boltzmann's constants

(II) Extrinsic Semiconductor

The conductivity of semiconductors can be greatly improved by introducing a small number of suitable replacement atoms called **impurities**. The process of adding impurity atoms to the pure semiconductor is called **doping**. Usually, only 1 atom in 10^7 is replaced by a dopant atom in the doped semiconductor. An extrinsic semiconductor can be further classified into:

- **N-type Semiconductor**
- **P-type Semiconductor**

EXTRINSIC SEMICONDUCTORS



Classification of Extrinsic Semiconductor

a) N-Type Semiconductor

Mainly due to electrons

Entirely neutral

$$I = I_e \text{ and } n_e \gg n_h$$

Majority – Electrons and Minority – Holes

If a pure semiconductor (Silicon or Germanium) was doped by pentavalent impurity (P, As, Sb, Bi). Then four electrons out of five valence electrons bonds with the four electrons of Ge or Si.

The fifth electron of the dopant is set free. Thus, the impurity atom donates a free electron for conduction in the lattice and is called “**Donor**”.

Since the number of free electron increases by the addition of an impurity, the negative charge carriers increase. Hence, it is called **n-type semiconductor**.

Crystal as a whole is neutral, but the donor atom becomes an immobile positive ion. As conduction is due to a large number of free electrons, the electrons in the n-type semiconductor are the **majority carriers** and holes are the **minority carriers**.

b) P-Type Semiconductor

It is mainly due to the presence of holes, entirely neutral in nature.

$$I = I_h \text{ and } n_h \gg n_e$$

Majority – Holes and Minority – Electrons

When a pure semiconductor is doped with a trivalent impurity (B, Al, In, Ga) then, the three valence electrons of the impurity bonds with three of the four valence electrons of the semiconductor.

This leaves an absence of electron (hole) in the impurity. These impurity atoms which are ready to accept bonded electrons are called “**Acceptors**”.

With the increase in the number of impurities, holes (the positive charge carriers) are increased. Hence, it is called **p-type semiconductor**.

Crystal as a whole is neutral, but the acceptors become an immobile negative ion. As conduction is due to a large number of holes, the holes in the p-type semiconductor are **majority carriers** and electrons are **minority carriers**.

Difference between Intrinsic and Extrinsic Semiconductors

Intrinsic Semiconductor	Extrinsic Semiconductor
Pure semiconductor	Impure semiconductor
Density of electrons is equal to the density of holes	Density of electrons is not equal to the density of holes
Electrical conductivity is low	Electrical conductivity is high
Dependence on temperature only	Dependence on temperature as well as on the amount of impurity
No impurities	Trivalent impurity, pentavalent impurity

❖ Questionary

Sort answer the following question

1. What is lattice energy?
2. What is coordination number?
3. Give the max born equation for lattice energy.
4. What is radius ratio?
5. What is geometry of coordination number 6?
6. Give the types of lattice defect.
7. What is point defect?
8. What is stoichiometric defect?
9. What is Non-stoichiometric defect?
10. What is Frenkle defect?
11. What is semiconductor?
12. What is p-type conductor?
13. Define Shottky defect

Brief answer the following question

14. Explain Shottky defect.
15. Explain structure of fluorite.
16. Derive the radius ratio for the triangular planner.
17. What is limiting radius ratio? Give usefulness of limiting radius ratio.
18. Write note on n-type semi-conductor.
19. Explain metal excess defect briefly.
20. Explain extrinsic semi-conductor.
21. Explain characteristics of Ionic Solid.
22. Explain Born Haber cycle briefly.