INDIAN SCHOOL AL WADI AL KABIR		
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HANDOUT	TOPIC: SOLID STATE	NOTE: A4 FILE FORMAT
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## **Imperfections in solids**

- Defects in solids are basically irregularities in the arrangement of constituent particles.
- > Defects are of two types; *Point defects and line defects*.
- Point defects are the irregularities from ideal arrangement around a point or an atom in a crystalline substance.
- Line defects are the irregularities from ideal arrangement in entire rows of lattice points.

#### **Types of point defects**

#### (a) Stoichiometric defects

- > They are also called intrinsic or thermodynamic defects.
- > These defects that do not disturb the stoichiometry of the solid.
- For non-ionic solids, stoichiometric defects are of two types, vacancy defects and interstitial defects

#### i) Vacancy defect

- Vacancy defect is developed when some of the lattice sites are vacant. This results in decrease in density of the substance.
- This defect can also be developed when a substance is heated.



### ii) Interstitial defect

Interstitial defect is developed when some constituent particles occupy an interstitial site. This defect increases the density of the substance.



### **Stoichiometric defects in ionic solids**

- > Ionic solids must always maintain electrical neutrality.
- > They exhibit defects as Frenkel and Schottky defects.

### Frenkel defect

- This defect is shown by ionic solids in which there is large difference in the size of anion and cation. Usually cation is smaller.
- The smaller ion is dislocated from its normal site to an interstitial site. It creates a vacancy defect at its original site and an interstitial defect at its new location.
- Frenkel defect is also called dislocation defect. It does not change the density of the solid.
- > Eg:- ZnS, AgCl, AgBr and AgI due to small size of  $Zn^{2+}$  and  $Ag^+$  ions.



# Schottky defect

- This defect is shown by ionic substances in which the cation and anion are of almost similar sizes.
- It is basically a vacancy defect in ionic solids. The number of missing cations and anions are equal so that electrical neutrality is maintained.
- Density of the substance decreases due to Schottky defect.

Eg:- NaCl, KCl, CsCl and AgBr.

\* AgBr shows both Frenkel as well as Schottky defects.



### (b) Impurity defects

- If molten NaCl containing a little amount of SrCl<sub>2</sub> is crystallised, some of the sites of Na<sup>+</sup> ions are occupied by Sr<sup>2+</sup>.
- Each Sr<sup>2+</sup> replaces two Na<sup>+</sup> ions. It occupies the site of one ion and the other site remains vacant.
- The cationic vacancies thus produced are equal in number to that of Sr<sup>2+</sup> ions.



\* Another similar example is the solid solution of  $CdCl_2$  and AgCl.

## (c) Non-stoichiometric defects

- > Due to these defects, stoichiometry of the substance is disturbed.
- Non-Stoichiometric defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

# (i) Metal excess defect

#### a) Metal excess defect due to anionic vacancies

- When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal.
- The Cl<sup>-</sup> ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by the loss of electrons by sodium atoms to form Na<sup>+</sup> ions.
- The released electrons diffuse into the crystal and occupy anionic sites. As a result, the crystal now has an excess of sodium.



- The anionic sites occupied by unpaired electrons are called F- centres (German word Farbenzenter for colour centre).
- > They impart **yellow** colour to the crystals of NaCl.

- The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals.
- Excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

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

- > Zinc oxide is white in colour at room temperature.
- > On heating it loses oxygen and turns **yellow**.

$$ZnO \xrightarrow{heating} Zn^{2+} + \frac{1}{2}O_2 + 2e^{-}$$

- Now there is excess of zinc in the crystal and its formula becomes Zn<sub>1+x</sub>O.
- The excess Zn<sup>2+</sup> ions move to interstitial sites and the electrons to neighbouring interstitial sites.

### (ii) Metal deficiency defect

- This defect arises when metal ions are present in different valency. A typical example of this type is FeO which is mostly found with a composition of Fe<sub>0.95</sub>O.
- In crystals of FeO some Fe<sup>2+</sup> cations are missing and the loss of positive charge is made up by the presence of required number of Fe<sup>3+</sup> ions.

## **QUESTION**

Analysis shows that nickel oxide has the formula  $Ni_{0.98}O_{1.00}$ . What fractions of nickel exist as  $Ni^{2+}$  and  $Ni^{3+}$  ions?

## ANSWER

Let Ni<sup>2+</sup> be x so that Ni<sup>3+</sup> will be 0.98-x. The compound is electrically neutral. Therefore, 2x + 3(0.98-x) - 2 = 0x = 0.94% of Ni<sup>2+</sup>  $= \frac{0.94}{0.98} \times 100$ = 95.9 %% of Ni<sup>3+</sup> = 100 - 95.9= 4.1 %

Prepared by Mr. Anoop Stephen

Checked by :HOD – Science