# THE SOLID STATE

# **IMPERFECTIONS IN SOLIDS**

# **CRYSTALLISATION: -**

Crystallization occurs in two major steps. The first one is nucleation, which gives the looks of a crystalline phase from either a supercooled liquid or a supersaturated solvent. The second step is understood as crystal growth, which is the increase within the size of particles and results in a crystal state. A crucial feature of this step is that loose particles form layers at the crystal's surface and lodge themselves into open inconsistencies like pores, cracks, etc.

# Process of Crystallization: -

The crystallization process consists of two major events. One is nucleation and the other is crystal growth which both are driven by thermodynamic properties also as chemical properties. Nucleation is the primary step where the solute molecules or atoms dispersed within the solvent start to collect into clusters, that become stable under the present operating conditions. These stable clusters constitute the nuclei. Therefore, the clusters got to reach a critical size so as to become stable nuclei. It's at the stage of nucleation that the atoms or molecules arrange during a defined and periodic manner that defines the crystal structure.

Crystal growth refers to the increase in the size of the nuclei which is able to achieve the critical cluster size. Many compounds have the power to crystallize with some having different crystal structures, a phenomenon called polymorphism. Certain polymorphs can be metastable, meaning that although it's not in thermodynamic equilibrium, it's kinetically stable and requires some input of energy to initiate a change to the equilibrium phase.

# Methods of Crystallization: -

Crystal formation methods are primarily of two types. The first sort of crystals is composed of a cation and anion, also referred to as salt, like sodium acetate. The second sort of crystals is composed of uncharged species, for instance, menthol.

Crystal formation takes place through various methods, such as cooling, evaporation, the addition of a second solvent to scale back the solubility of the solute, sublimation, solvent layering, changing the cation or anion, also as other methods. An old laboratory technique for crystal formation is to dissolve the solid during a solution during which it's partially soluble, usually at high temperatures to get supersaturation.

The most common equipment for maximum industrial manufacturing of crystallization is Tank crystallization. It's an old method still utilized in some specialized cases. Saturated solutions, intank crystallization, are allowed to chill in open tanks. After a period of your time, the main liquid is drained and therefore the crystals are taken out.

# In Nature - Formation: -

There are many samples of natural action that involve crystallization. Geologic time scale process examples include: Natural (mineral) crystal formation (see also gemstone); Stalactite/stalagmite, rings formation; Human duration process examples include: Snowflakes formation. Snowflakes are a really well-known example, where subtle differences in crystal growth conditions end in different geometries. Honey crystallization (nearly all kinds of honey crystallize).

## Thermodynamic View: -

Now, maximum processes that yields more perfect results have been achieved by applying heat, where crystals usually form at lower temperatures—especially by supercooling. This process somehow primarily appears to violate the second principle of thermodynamics. However, thanks to the discharge of the heat of fusion during crystallization, the entropy of the universe increases. Thus, this principle remains unaltered.

When the molecules of a pure, perfect crystal, is heated by an external source, the crystal becomes liquid. In liquid form, the complicated architecture of the crystal collapses. When the liquid crystal cools down, the molecules again return to their crystalline form. It happens once the temperature falls beyond the turning point. This is often because the thermal randomization of the environment compensates for the loss of entropy that results from the reordering of molecules within the system. The character of a crystallization process is governed by both thermodynamic and kinetic factors, which may make it highly variable and difficult to regulate.

## **Dynamics**

#### Nucleation:

Nucleation is that the initiation of a phase transition during a small region, like the formation of a solid crystal from a liquid solution. Total nucleation is the sum effect of two categories of nucleation – primary and secondary.

## Primary nucleation: -

This is the step, where the initial formation of a crystal occurs. Here, there may not be any other crystals present or if there are crystals present within the system, they don't have any influence on the method. This will occur in two conditions. the primary is homogeneous nucleation, which is nucleation that's not influenced in any way by solids. The second category, then, is heterogeneous nucleation. Homogeneous nucleation rarely occurs in practice.

Secondary nucleation is said when a crystal growth is initiated with contact with other existing crystals or "seeds". Contact nucleation has been found to be the foremost effective and customary method for nucleation.

## <u>Growth: -</u>

Once the first basic small crystal forms, it acts as a convergence point for molecules of solute touching – or adjacent to – the crystal in order that it increases its own dimension in successive layers. There are certain physical factors that influence the rate of growth like, the physical phenomenon of the solution, pressure, temperature, relative crystal velocity within the solution, Reynolds number, then forth.

## Size Distribution: -

It is extremely important in crystallization. Large crystals with uniform size are important for laundry, filtering, transportation, and storage because large crystals are easier to filter of an answer than small crystals. Large crystals have higher purity.

#### Main Crystallization Processes: -

There are two main families of crystallization processes:

# Cooling crystallization: -

The cooling crystallizers are usually tanks in which a mixer is given for internal circulation, where temperature decrease is obtained by heat exchange with an intermediate fluid circulating during a jacket. These simple machines are utilized in batch processes, as in the processing of pharmaceuticals and are susceptible to scaling.

#### Evaporative crystallization: -

Most industrial crystallizers are of the evaporative type, like the very large common salt and sucrose units, whose production accounts for quite 50% of the entire world production of crystals. The foremost common type is that the forced circulation (FC) model.

## Chemistry

# <u>TYPES OF DEFECTS</u>: -DEFECTS OR IMPERFECTIONS IN SOLIDS IDEAL CRYSTAL

The crystal in which all the lattice points are occupied by the component particles or groups of particles is called an ideal crystal. Solid state is characterised by vibratory motion about the mean position of constituent particles. At absolute zero, all the types of motions cease, and therefore crystals tend to have a perfectly ordered arrangement. As the temperature increases, molecular motions (vibratory amplitudes) increase and therefore the ions may lose their usual sites and either get missed or occupy interstitial positions in the crystal, i.e., deviations from ordered arrangement take place. Any deviation from the perfectly ordered arrangement gives rise to a defect or imperfection in the crystal. Defect in crystals is produced either due to thermal effects or by adding certain impurities in the pure crystals (doping). Defects in crystals may be discussed under two titles:

- A. Stoichiometric defects
- B. Non-stoichiometric defects

# [A] Defects in stoichiometric compounds:

Stoichiometric compounds are those in which the number of positive and negative ions are exactly in the ratio as shown by their chemical formulae. Two types of defects are observed in these compounds.

- (i) Schottky defect,
- (ii) Frenkel defect

# (i) Schottky defect:

This type of defect is produced when one cation and anion are missing from their respective positions leaving behind a pair of holes. The crystal as a whole remains neutral because the number of missing positive ions (cations) and negative ions (anions) is the same

- Schottky defect appears generally in ionic compounds in which radius ratio [r<sup>+</sup>/r<sup>-</sup>] is not far below unity. For this defect, the cations and anion should not differ much in size.
- For Schottky defect, co-ordination numbers of the ions should be high, Examples of ionic solids showing this defect are NaCl, CsCl, KCI, KBr etc. Consequences of Schottky defect:
- Density of the crystal decreases
- > The crystal begins to conduct electricity to small extent by ionic mechanism.
- > The presence of too many 'voids' lowers lattice energy or the stability of the crystal.



Schottky defect

# (ii) Frenkel defect:

This type of defect is created when an ion leaves its appropriate site in the lattice and occupies an interstitial site. A hole or vacancy is thus produced in the lattice.



Frenkel defect

The electroneutrality of the crystal is maintained since the number of positive and negative ions is the same. Since positive ions are small, in size, they usually leave their positions in the lattice and occupy interstitial positions.

#### Chemistry

Frenkel defect is exhibited in ionic compounds in which the radius ratio  $[r^+/r^-]$  is low. The cations and anions differ much in their sizes and the ions have low co-ordination numbers. Examples are ZnS, AgBr, AgI, AgCl.

#### **CONSEQUENCES OF FRENKEL DEFECT: -**

- > The closeness of like charges tends to increase the dielectric constant of the crystal.
- The crystal showing a Frenkel defect conducts electricity to a small extent by ionic mechanism.
- > The density of the crystal remains the same

## [B] Non-stoichiometric defect:

These types of defects are observed in the compounds of transitional elements. These defects arise either due to the presence of excess metal ions or excess non-metal ions.

#### (i) Metal excess defect due to anion vacancies:

A compound may have excess metal ion if an anion (negative ion) is absent from its appropriate lattice site creating a 'void' which is occupied by an electron. Ionic crystal which are likely to possess Schottky defect, may also develop this type of metal excess defect. When alkali metal halides are heated in a atmosphere of vapours of the alkali metal, anion vacancies are created. The anions (halide ions) diffuse to the surface of the crystal from their appropriate lattice sites to combine with the newly generated metal cations. The elost by the metal atom diffuse through the crystal are known as F-centres. The main consequence of metal excess defect is the development of colour in the crystal. For example, when NaCl crystal is heated in an atmosphere of Na vapours, it becomes yellow. Similarly, KCI crystal when heated in an atmosphere of potassium vapours, it appears violet.

## (ii) Metal excess defect due to interstitial cations:

This type of defect is shown by crystals which are likely to exhibit Frenkel defect. An excess positive ion is located in the interstitial site. To maintain electrical neutrality, an electron is present in the interstitial site. An example showing this type of defect is ZnO. When ZnO is heated, it loses oxygen reversibly. The excess Zn++ ions are accommodated in the interstitial sites, the, electrons are enclosed in the neighbouring interstitials. The yellow colour of ZnO when hot is due to these trapped electrons. These electrons also explain electrical conductivity of the ZnO crystal.

# Chemistry

# Doping: -

The addition of small amount of foreign impurity in the host crystal is called as doping. It results in an increase in the electrical conductivity of the crystal. Doping of group 14 elements (such as Si, Ge, etc.) with elements of group 15 (such as as) produces an excess of electrons in the crystals, thus giving n-types semiconductors. Doping of groups 14 elements with group 13 elements (such as Indium) produces holes (electron deficiency) in the crystals. Thus p-type semiconductors are produced. Then symbol 'p' indicates flow of positive charge