## IMPERFECTIONS IN SOLIDS

### Crystallisation

Crystallization involves two primary stages. The first is nucleation, where a crystalline phase emerges from either a supercooled liquid or a supersaturated solvent. The second step is known as crystal growth, characterized by the enlargement of particles, leading to the formation of a crystal state. A significant aspect of this stage is the arrangement of loose particles into layers on the crystal's surface, securing themselves into open irregularities such as pores, cracks, etc.

### Process of Crystallization

The process of crystallization involves two primary phases influenced by both thermodynamic and chemical properties: nucleation and crystal growth. Nucleation, the initial step, sees solute molecules or atoms in a solvent forming clusters that stabilize under prevailing conditions, constituting nuclei. To achieve stability, these clusters must attain a critical size. During nucleation, atoms or molecules align in a defined and periodic manner, shaping the crystal structure.

Crystal growth follows nucleation, involving the enlargement of nuclei that have reached the critical cluster size. Many compounds exhibit the ability to crystallize, with some displaying different crystal structures, a phenomenon known as polymorphism. Certain polymorphs may be metastable, meaning they are not in thermodynamic equilibrium but are kinetically stable, requiring an input of energy to initiate a change to the equilibrium phase.

### Methods of Crystallization

Methods for crystal formation primarily fall into two categories. The first involves crystals composed of a cation and anion, commonly known as salts, such as sodium acetate. The second category comprises crystals formed from uncharged species, exemplified by menthol.

Crystal formation employs various techniques, including cooling, evaporation, the addition of a second solvent to decrease solute solubility, sublimation, solvent layering, altering the cation or anion, and other approaches. A traditional laboratory method for crystal formation involves dissolving a solid in a solution where it is partially soluble, typically at elevated temperatures to achieve supersaturation.

One widely used technique for large-scale industrial crystallization is tank crystallization, an established method still employed in specific cases. In this process, saturated solutions are allowed to cool in open tanks. After a designated period, the primary liquid is drained, and the crystals are extracted.

### In Nature – Formation

Numerous instances of natural processes involving crystallization exist. Examples from geological timescales include the natural formation of mineral crystals (see also gemstones), stalactite/stalagmite formations, and ring formations.

On a human timescale, examples encompass the formation of snowflakes, where slight variations in crystal growth conditions lead to distinct geometries. Another example is honey crystallization, a phenomenon observed in nearly all types of honey.

### Thermodynamic View

Presently, optimal processes yielding more precise outcomes often involve the application of heat, with crystals typically forming at lower temperatures, particularly through supercooling. Although this process initially seems to contradict the second law of thermodynamics, the release of fusion heat during crystallization leads to an increase in the entropy of the universe, preserving this fundamental principle.

When a pure, flawless crystal is heated by an external source, it transitions into a liquid state, causing the intricate structure of the crystal to collapse. Upon cooling, the liquid crystal reverts to its crystalline form, occurring once the temperature drops below a critical point. This phenomenon is a result of the thermal randomization of the environment compensating for the entropy loss caused by the reordering of molecules within the system. The nature of a crystallization process is influenced by both thermodynamic and kinetic factors, rendering it highly variable and challenging to control

## Dynamics

### Nucleation

Nucleation is the initiation of a phase transition within a confined region, such as the development of a solid crystal from a liquid solution. Total nucleation comprises the combined effects of two types of nucleation: primary and secondary.

### Primary nucleation

This is the phase where the initial formation of a crystal takes place. During this stage, there may be an absence of other crystals, or if crystals are present within the system, they do not exert any influence on the process. This can happen under two conditions. The first is homogeneous nucleation, which is nucleation unaffected by solids. The second category is heterogeneous nucleation. Homogeneous nucleation is rarely observed in practical situations.

Secondary nucleation is termed when crystal growth is triggered by contact with other existing crystals or "seeds." Contact nucleation has proven to be the most effective and prevalent method for nucleation.

### Growth

Upon the formation of the initial small crystal, it serves as a focal point for solute molecules to adhere to, either directly or in close proximity, allowing it to expand in successive layers. Several physical factors influence the growth rate, including the viscosity of the solution, pressure, temperature, the relative velocity of crystals within the solution, Reynolds number, and so forth.

### Size Distribution

Crucial in the process of crystallization, the significance lies in the production of large crystals with uniform size. This quality is paramount for activities such as washing, filtering, transportation, and storage, as the filtration of a solution containing large crystals is more efficient than that of one with small crystals. Additionally, large crystals tend to exhibit higher purity.

## Main Crystallization Processes

There are two principal categories of crystallization methods:

### Cooling crystallization

The Cooling crystallizers typically consist of tanks equipped with internal circulation mixers, where temperature reduction is achieved through heat exchange with an intermediate fluid circulating in a jacket. These straightforward machines find application in batch processes, such as in pharmaceutical processing, but may be prone to scaling.

### Evaporative crystallization

The majority of industrial crystallizers belong to the evaporative category, exemplified by large-scale units producing common salt and sucrose, contributing to over 50% of global crystal production. The forced circulation (FC) model is the most prevalent type in this category.

## Types of Defects

## Defects Or Imperfections in Solids

### Ideal Crystal

An ideal crystal is one in which all lattice points are filled by the constituent particles or groups of particles. The solid state is characterized by vibratory motion around the mean position of these constituent particles. At absolute zero, all types of motion come to a halt, leading to a perfectly ordered arrangement in crystals. However, as temperature rises, molecular motions, or vibratory amplitudes, increase. Consequently, ions may deviate from their usual sites, either becoming displaced or occupying interstitial positions within the crystal. Such deviations result in imperfections or defects in the crystal structure. These defects can arise due to thermal effects or the introduction of specific impurities into 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 characterized by a precise balance between the numbers of positive and negative ions, aligning with their chemical formulas. Within these compounds, two types of defects are typically observed.

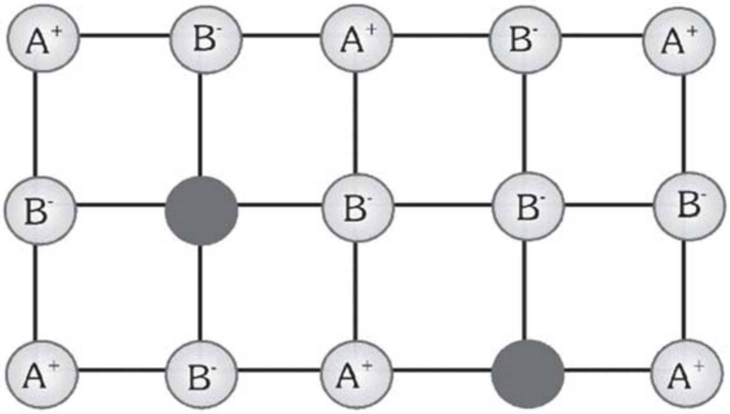
(i) Schottky defect,

(ii) Frenkel defect

### (i) Schottky defect

This defect arises when one cation and one anion are absent from their designated positions, resulting in the formation of a pair of holes. The overall charge of the crystal remains neutral because the number of missing positive ions (cations) matches the number of missing negative ions (anions).

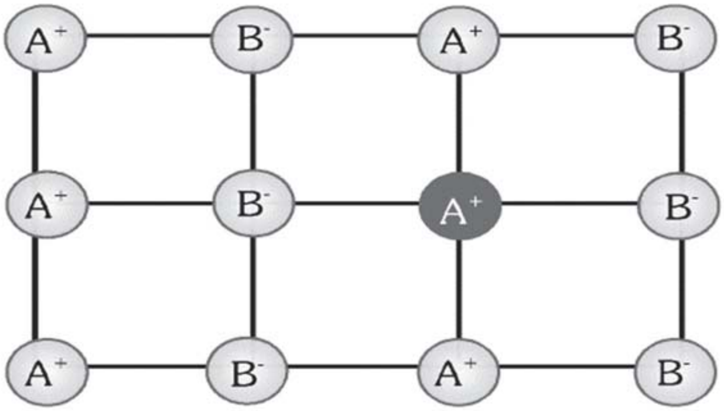
- Schottky defects commonly occur in ionic compounds where the radius ratio [ $r^+/r^-$] is relatively close to unity. This defect is more likely when there is minimal difference in size between the cations and anions.
- For a Schottky defect, the co-ordination numbers of the ions must be high. Examples of ionic solids exhibiting this defect include NaCl, CsCl, KCl, KBr, and others.
- The consequences of a Schottky defect include a decrease in the density of the crystal, a slight increase in electrical conductivity through an ionic mechanism, and a reduction in the lattice energy or stability of the crystal due to the presence of numerous voids.



Schottky defect

### (ii) Frenkel defect

This defect arises when an ion departs from its designated position in the lattice and occupies an interstitial site, resulting in the creation of a hole or vacancy in the lattice.



**Frenkel defect**

The crystal's electroneutrality is preserved as the count of positive and negative ions remains equal. Due to their small size, positive ions often vacate their lattice positions to occupy interstitial sites.

Frenkel defect is observed in ionic compounds with a low radius ratio [ $r^+/r^-$]. This defect is prominent when there is a substantial difference in size between cations and anions, and the ions have low co-ordination numbers.

Examples are ZnS, AgBr, AgI, AgCl.

**Consequences of Frenkel Defect**

- The proximity of similar charges has a tendency to elevate the dielectric constant of the crystal.
- A crystal exhibiting a Frenkel defect conducts electricity to a limited extent through an ionic mechanism.
- The density of the crystal remains unchanged.

## [B] non-stoichiometric defect

These defects are noticeable in compounds containing transitional elements. They occur as a result of an excess of either metal ions or non-metal ions in the compound.

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

A compound may exhibit an excess of metal ions if a negatively charged anion is missing from its designated lattice site, resulting in the creation of a 'void' that is filled by an electron. Ionic crystals that are prone to Schottky defects may also manifest this type of metal excess defect. In the case of alkali metal halides heated in an atmosphere of vapors of the alkali metal, anion vacancies are generated. The halide ions (anions) migrate from their designated lattice sites to the crystal's surface, where they combine with the newly formed metal cations. The electrons lost by the metal atoms as they diffuse through the crystal are known as F-centers. The primary outcome of a metal excess defect is the development of color in the crystal. For instance, when a NaCl crystal is heated in an atmosphere of Na vapors, it acquires a yellow hue. Similarly, when a KCl crystal is heated in an atmosphere of potassium vapors, it takes on a violet appearance.

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

This defect type is characteristic of crystals prone to displaying the Frenkel defect. An extra positive ion is positioned in the interstitial site, and to maintain electrical neutrality, an electron is present in the adjacent interstitial site. ZnO serves as an example demonstrating this defect. When ZnO is heated, it releases oxygen in a reversible process. The surplus Zn++ ions occupy the interstitial sites, while electrons are encapsulated in the neighboring interstitials. The yellow color observed in heated ZnO is attributed to these trapped electrons, and these electrons also account for the electrical conductivity of the ZnO

### Doping

Doping refers to the incorporation of a small quantity of foreign impurity into the host crystal, leading to an elevation in the crystal's electrical conductivity. Specifically, when group 14 elements like Si and Ge are doped with elements from group 15, such As, an excess of electrons is introduced into the crystals, resulting in the formation of n-type semiconductors. On the other hand, doping group 14 elements with group 13 elements, such as Indium, generates holes or electron deficiencies in the crystals, thereby producing p-type semiconductors. In the context of semiconductors, the symbol 'p' signifies the flow of positive charge.