Process Equipment Design

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Lecture –39
Design of Crystallizer-1

Hello everyone. This is 8th week and we are in 4th lecture of 8th week and overall it is 39th lecture of the course Process Equipment Design and I welcome you all in this lecture. So, as far as this lecture is concerned in this lecture we are going to cover the topic crystallization. So, in this lecture we will define crystallization, we will see different form of the crystal and then we will discuss the crystallization process depending upon the solubility curve.

And after that in subsequent lecture we will discuss about the design of crystallizer. So, let us start this lecture with crystallization. So, what is basically crystallization? Crystallization is the process to form the product in a definite shape. Usually, we do not focus on the shape whatever product we want if that product is of given quality or the acceptable quality we consider that.

But in engineering process some of the products are form in a definite shape I am not speaking about the size, size may vary, but shape will be very definite. So, that shape we call as a crystal. When the product is made in the form of crystal the process by which it is made we call that as crystallization. So, in this lecture we will consider the crystallization process in detail. So, let us start that.

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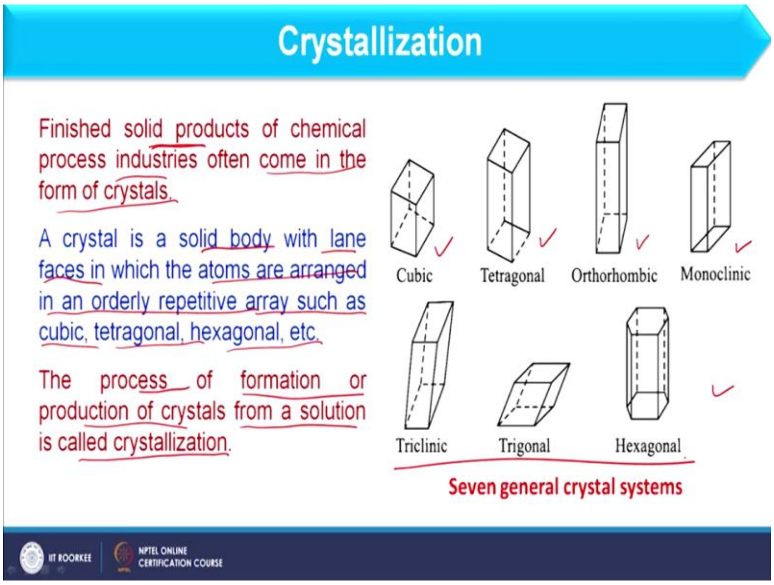

Crystallization

Finished solid products of chemical process industries often come in the form of crystals.

A crystal is a solid body with lane faces in which the atoms are arranged in an orderly repetitive array such as cubic, tetragonal, hexagonal, etc.

The process of formation or production of crystals from a solution is called crystallization.

So, as I have told you that finished solid products of chemical process industries often come in the form of crystal. So, basically if I am saying a crystal it means it has a definite shape. What these shapes are that we will discuss. So, as far as the crystal is concerned it is a solid body with the lane faces in which the atoms arranged in an orderly repetitive array such as cubic, tetragonal, hexagonal etcetera.

So, you see it has a definite array whatever particles are available in the product these particle take its step in a definite array or we can say in a definite format and so we call that as a crystal and that array maybe a cubical shape, a hexagonal, octagonal or you can say any that kind of shape or you can say any other shape, but that shape is very definite. So, what is basically crystallization?

The crystallization is the process of formation or production of crystals from a solution we consider that as a crystallization. So, that is basically when feed is available it is in the form of solution, but the product is in the form of solid. So, that we consider as crystallization process and if you see in this image we have several general crystal system such as cubic, tetragonal, orthorhombic, monoclinic and similarly we have many others.

So, these shapes are very definite. So, if I give some example if you say that you are dealing with mica for example. So, what is the shape of mica? The shape of mica is a plane sheet. When you break the mica particle it will be in the form of fine sheets. So, in that way we consider that it has a definite shape. In the similar line we can come across with different other examples also. So, that is basically a particular crystal.

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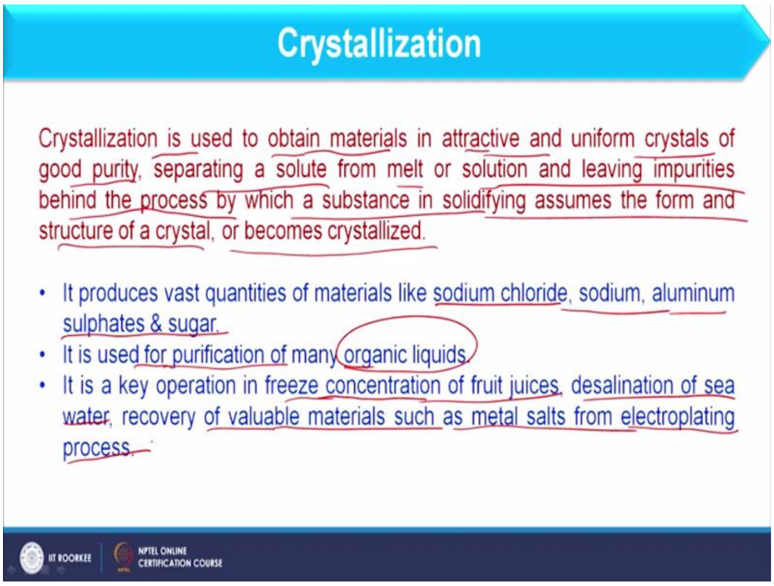

Crystallization

Crystallization is used to obtain materials in attractive and uniform crystals of good purity, separating a solute from melt or solution and leaving impurities behind the process by which a substance in solidifying assumes the form and structure of a crystal, or becomes crystallized.

- It produces vast quantities of materials like sodium chloride, sodium, aluminum sulphates & sugar.
- It is used for purification of many organic liquids.
- It is a key operation in freeze concentration of fruit juices, desalination of sea water, recovery of valuable materials such as metal salts from electroplating process.

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So, as far as crystallization process is concerned it is used to obtain material in attractive and uniform crystals of good purity, separating a solute from the melt or solution and leaving impurities behind the process by which a substance in solidifying assumes the form and structure of a crystal or becomes crystallized. So, you see when we have the solution and the product the product mainly consist of the solute which is available in the solution.

So, when that solute takes a definite shape of a particles it leaves the solvent behind and we consider that solute is crystallized. So, we have different examples of the product which are available in the form of crystal and these are when we consider the sodium chloride, sodium, aluminum sulfates and sugars. So, when you consider the manufacturing of the sodium chloride or we can say the sugar it has a definite shape.

So, in these industries crystallizer are very important unit and which usually occur after the evaporation because when we have the evaporation we got the solution with high concentration and that concentration is sufficient to be used in crystallizer. So, usually in sugar industry we can say sodium chloride industry there we consider crystallizer as a main unit.

And secondly we can consider crystallization as a purification of many organic liquids. So, when we purify the organic liquid how we remove the impurity that is done through crystallization because when we have the solution impurity can occupy a particular shape and that can be removed in the form of crystal. So, when solvent is available we consider that as a pure organic solvent.

And that can be purified by the crystallization process. Further, we have different applications of crystallization such as it is used to freeze concentration of the fruit juice, desalination of sea water as I have told you that it is used to prepare sodium chloride and further we can also consider this to remove the impurity and to generate the drinkable water from the sea water.

So, it is also part of the crystallization, but mainly it is not used to prepare drinkable water. It is basically used to prepare the solid which we consider as a sodium chloride. It is further used for recovery of valuable material such as metal salts from the electroplating process. So, you can consider that crystallization is used in different processes in chemical industries. So, now we will see that how this crystallization occurs. So, for that we will consider on the solution where I am having a particular solute.

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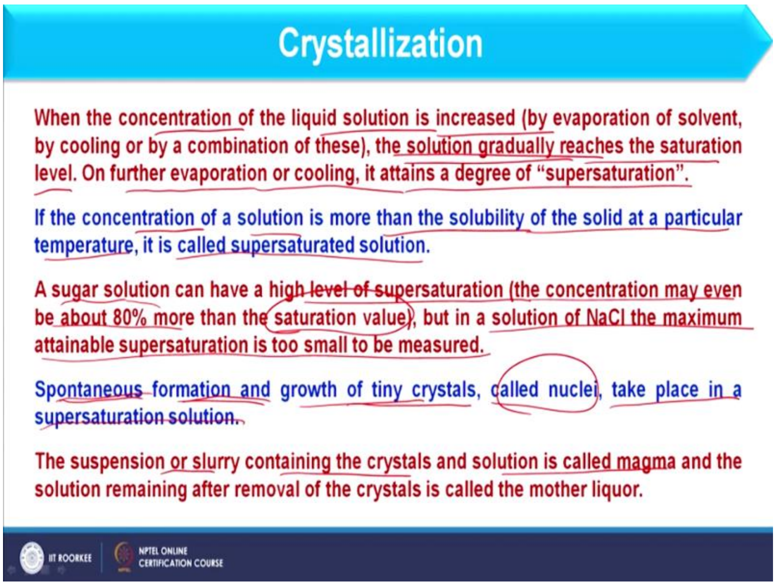

Crystallization

When the concentration of the liquid solution is increased (by evaporation of solvent, by cooling or by a combination of these), the solution gradually reaches the saturation level. On further evaporation or cooling, it attains a degree of "supersaturation".

If the concentration of a solution is more than the solubility of the solid at a particular temperature, it is called supersaturated solution.

A sugar solution can have a high level of supersaturation (the concentration may even be about 80% more than the saturation value), but in a solution of NaCl the maximum attainable supersaturation is too small to be measured.

Spontaneous formation and growth of tiny crystals, called nuclei, take place in a supersaturation solution.

The suspension or slurry containing the crystals and solution is called magma and the solution remaining after removal of the crystals is called the mother liquor.

When the concentration of the liquid solution is increased and how we can increase the concentration of the solution either by evaporation of the solvent or by cooling or the combination of these two. So, the solution gradually reaches the saturation level when we further evaporate it or cool it, it attains a degree of super saturation. So, that is very important word when we are considering crystallization the solution should be at super saturation condition.

You may consider that the solution of sugar in water at a particular temperature when you keep on stirring the sugar is mixed in the water very easily and form a solution. When you keep on increasing the temperature the solubility of sugar in the water will also keep on increasing. So, more and more sugar can be put in the water and solution can be obtained. Now, when we further decrease the temperature of the solution then what will happen?

Whatever sugar is available it will be available in the form of precipitate because it will not be soluble anymore because temperature we already have reduced. So, in that case you can see small particles of sugar in the solution and that particles are basically the crystals. So, how it happens because we reduce the temperature and when we reduce the temperature the saturation condition become super saturation condition.

So, that is very common example of crystallization process that you can carry out at your houses also. So, let us discuss it further. If the concentration of a solution is more than the solubility of the solid at a particular temperature it is called as super saturated solution. So, as I have explained this to you with the example of sugar and water. So, you can consider the super saturated condition in that solution.

So, further if I consider the example of sugar solution it can have a high level of super saturation. The concentration may even about 80% more than the saturation value, but in the solution of sodium chloride the maximum attainable super saturation is too small to be measured. So, in sugar solution super saturation condition occurs with significant amount of sugar however that is very less when we are considering sodium chloride.

So, basically what happens in crystallization spontaneous formation and growth of tiny crystals which we call as nuclei takes place in a super saturation solution. So, when we consider the super saturation condition it means that whatever solute is available it forms crystal, but crystal has a definite size initially it is not in the form of crystal it is very small particles or we consider that as tiny crystal in other word it is called nuclei.

So, initially very small particles are formed and then continuously formation of solute over the surface of tiny crystal we have definite size crystals, but it is basically start on the nuclei and that occurs at super saturation condition. So, the suspension or slurry containing the crystals the solution is called magma. So, when we have the super saturation solution and when I am having small crystals in this we consider that as a magma.

And when the crystal is removed from the solution whatever liquid remains there that we consider as solvent or that is also called as mother liquor. It does not mean that solute will not be there, solute will be there, but solute concentration in a mother liquor is very less because most of the solute we can remove in the form of crystals. So, you see usually it has three component.

First is crystal second magma when we have the solution along with crystal and third we have the mother liquor when crystal is removed from the solution.

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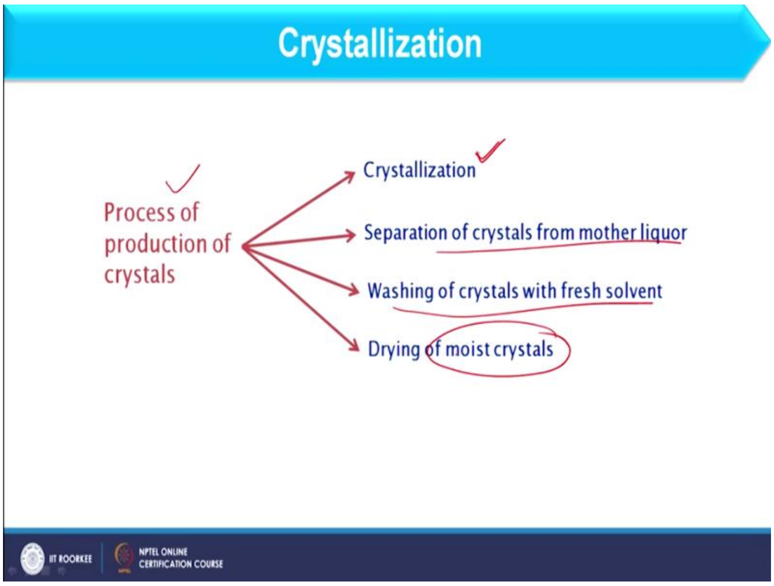

Crystallization

Process of production of crystals

- Crystallization
- Separation of crystals from mother liquor
- Washing of crystals with fresh solvent
- Drying of moist crystals

So, as far as crystallization process is concerned it has different steps. So, process of production of crystal the first step is the crystallization itself then we have separation of crystals from the mother liquor then washing of the crystal with fresh solvent to remove the impurities from the crystal and then dry the moist crystal. So, in this way we have different steps which we should follow to make the product of different shapes that we consider as crystals. Now, let us see few points about super saturation.

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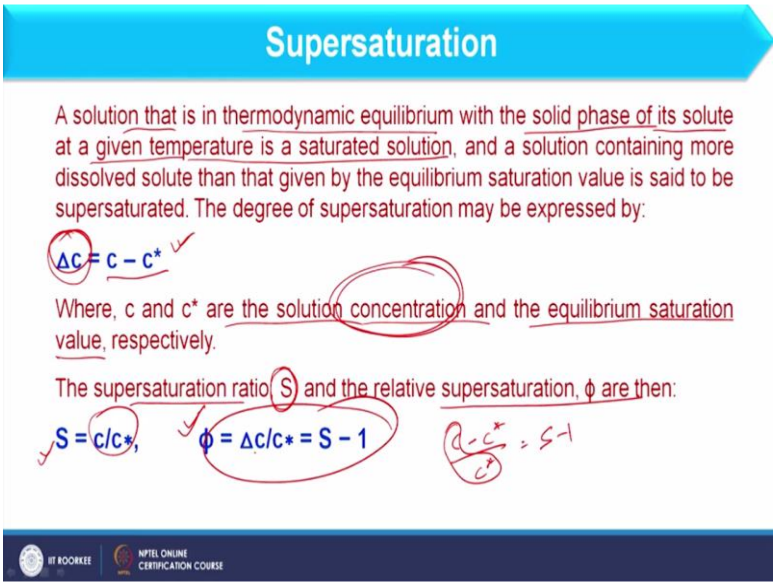

Supersaturation

A solution that is in thermodynamic equilibrium with the solid phase of its solute at a given temperature is a saturated solution, and a solution containing more dissolved solute than that given by the equilibrium saturation value is said to be supersaturated. The degree of supersaturation may be expressed by:

$\Delta c = c - c^*$

Where, c and c* are the solution concentration and the equilibrium saturation value, respectively.

The supersaturation ratio S and the relative supersaturation, ϕ are then:

$S = c/c_*$, $\phi = \Delta c/c_* = S - 1$

$\frac{c - c^*}{c^*} = S - 1$

So, what is super saturation? A solution that is in thermodynamic equilibrium with the solid phase of its solute at a given temperature is called as saturated solution. I mean when the solvent and solute is at equilibrium condition at a particular temperature that is very important at a particular temperature we consider that as a saturated solution. And when the solution considers more solute then that is available at equilibrium condition we call that as super saturation condition.

So, what is the degree of super saturation that must be the concentration at present when I am considering it a super saturation solution and the concentration at the equilibrium condition when it is a saturated solution. So, degree of super saturation is basically c – c star where c and c star are the solution concentration which is at the super saturation condition and the equilibrium saturated value that is this value.

So, difference of these two will be the degree of super saturation and further we have super saturation ratio which can be represented as S and a relative super saturation psi we can obtain as here I am having capital S which is the super saturation ratio c – c star and then we can have relative super saturation that is psi value. So, that is basically delta c / c star so you can consider that c – c star divided by c star so this is nothing, but the S – 1 so simple derivation is there. So, in that way you can relate relative super saturation and super saturation ratio.

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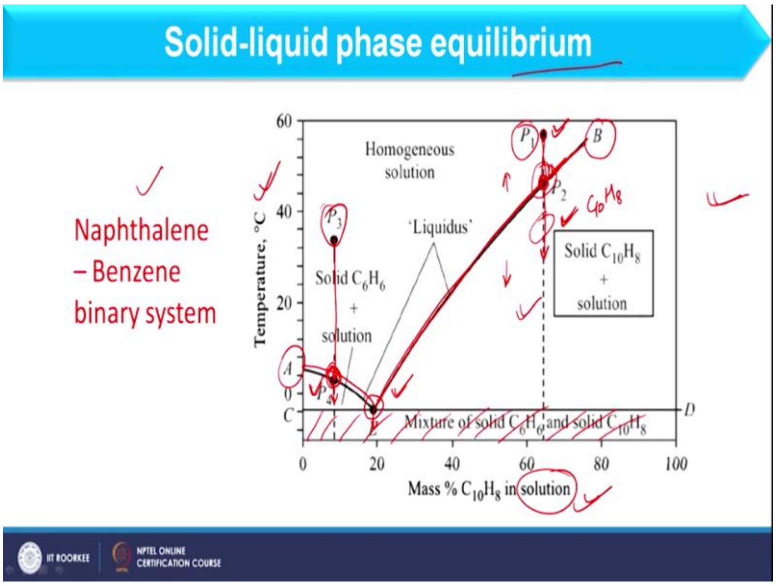

Solid-liquid phase equilibrium

Naphthalene – Benzene binary system

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And now we have very important diagram and this diagram we consider as solid liquid phase equilibrium. So, if you focus on this particular graph it is showing naphthalene benzene binary system and binary system for what? This is basically solid liquid phase equilibrium. So, when we consider temperatures as well as concentration of the solution. Solution means when I am having naphthalene in benzene.

So naphthalene is solid, benzene is solvent. So, when I am considering this graph if you focus on this line that is A to E and then B. This particular graph from A to E and then B this graph we consider as solid liquid phase equilibrium line and above this we consider unsaturation condition and below this we consider super saturation condition. So, this curve basically we call as saturation condition also.

So, let us see if I am having point P 1 in this. So, this point P 1 is at high temperature and when we cool this it will reach to P 2 point. So, while reducing this we can consider that the solution from unsaturation condition can be reached at saturation condition at point P 2. So, this is the case when naphthalene is dissolved in benzene. So, here I am having a saturation solution.

Now, if we further cool it then what will happen in the same concentration we are reducing the temperature it means this is the condition where crystal will be formed and this particular region we call as super saturation condition. So, at this point when we reduce the temperature further the crystal of naphthalene will form and as far as saturation condition is concerned we can have saturation condition while varying the concentration at different temperature from B to E.

And this is basically concentration of the solution and in the similar line when I am considering point P 3 let us say. So, in this point P 3 when I am reducing the temperature further it will reach to point P 4. So, P 4 is basically the saturation point where it is available at saturation curve. When we further reduce its temperature then what will happen here benzene will be solidify or crystal will be form of the benzene.

So, here you see we can have the crystal of the naphthalene, but here we have crystal of the benzene and all these will depend on the temperature and concentration. So, this curve from A to E it is basically the saturation condition where temperature and concentration will vary. Now, when I am considering point E is basically called as eutectic point and when we consider this point E.

And reduce the temperature further we consider this section when the whole solution is solidify either it is benzene or naphthalene. So, beyond point E whole solution will be solidify however above point E it will depend on the curve where naphthalene will be crystallized or where benzene will be crystallized. So, in this way we consider solid liquid phase equilibrium and this curve directs us that at what condition we can form the crystal of a particular solute. And further we will discuss the solubility curve.

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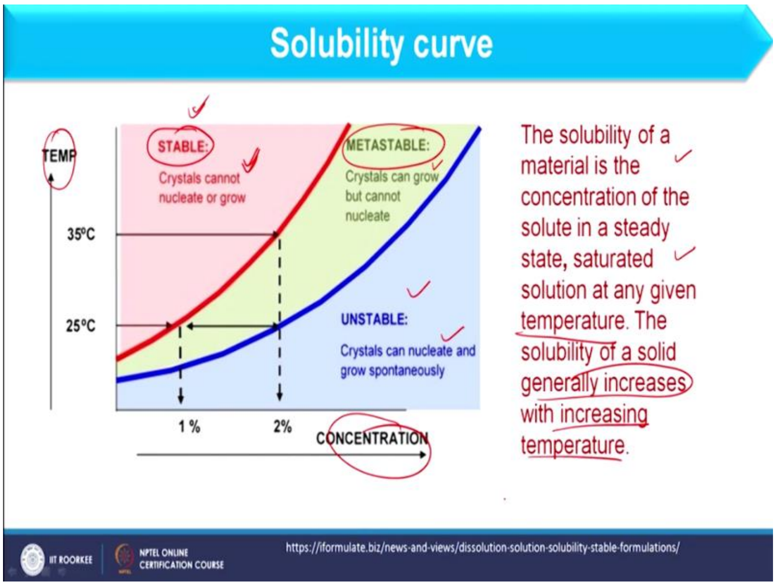

Solubility curve

The solubility of a material is the concentration of the solute in a steady state, saturated solution at any given temperature. The solubility of a solid generally increases with increasing temperature.

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So, basically what is solubility? When we consider the solubility it is basically the ability of a solute to dissolve in a solvent and that we consider as solubility. Now here we will discuss the solubility curve. If you see this here I am having temperature as well as concentration. So, the solubility of the material is the concentration of solute in steady state saturated solution at any given temperature.

The solubility of solid generally increases with increasing temperature. So I think this is the known factor. And further if we focus on the solubility curve here I am having three different condition. First is the stable condition where crystal cannot nucleate or growth. So, that is basically the solution is at saturation condition or less than that. So, next is we are having metastable state where crystal can grow, but cannot nucleate.

It means crystals are formed randomly. Nucleation means first tiny crystals will be formed and because over that solute will be deposited. So, in metastable state we do not have any nucleation crystal are formed randomly and next I am having unstable condition where crystals can nucleate and grow spontaneously. So, this is basically the solubility curve where you can focus that at a particular temperature how much solute should be involved or should be dissolved in the solvent so that crystals can be formed. So, this is the basic aim of the solubility curve.

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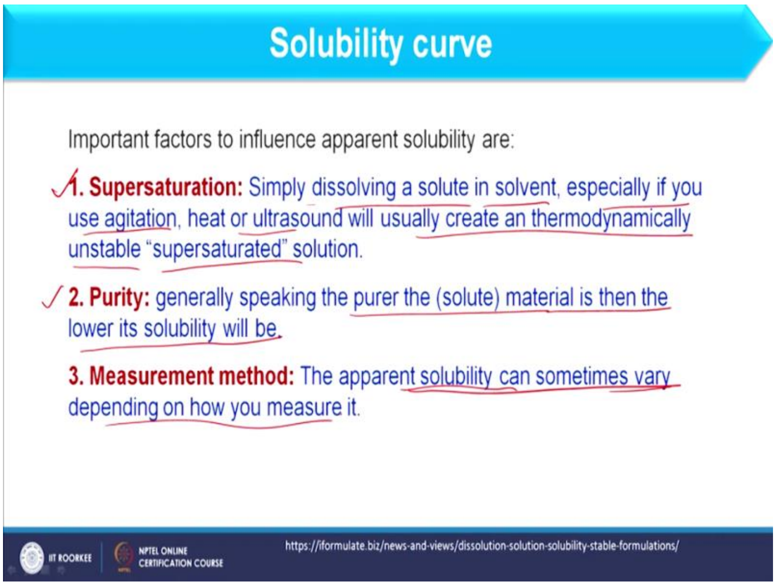

Solubility curve

Important factors to influence apparent solubility are:

✓ 1. **Supersaturation:** Simply dissolving a solute in solvent, especially if you use agitation, heat or ultrasound will usually create an thermodynamically unstable "supersaturated" solution.

✓ 2. **Purity:** generally speaking the purer the (solute) material is then the lower its solubility will be.

3. **Measurement method:** The apparent solubility can sometimes vary depending on how you measure it.

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Next, we have some important factors which affect the apparent solubility and these are the super saturation the very important point. Simple dissolving a solute in solvent especially if you use agitation heat or ultrasound will usually create a thermodynamically unstable that is super saturated solution. So, next point we have the purity. So generally speaking the purer the solute material is than the lower its solubility will be.

And it will also depend on the measurement method. The apparent solubility can sometimes vary depending on how you measure it.

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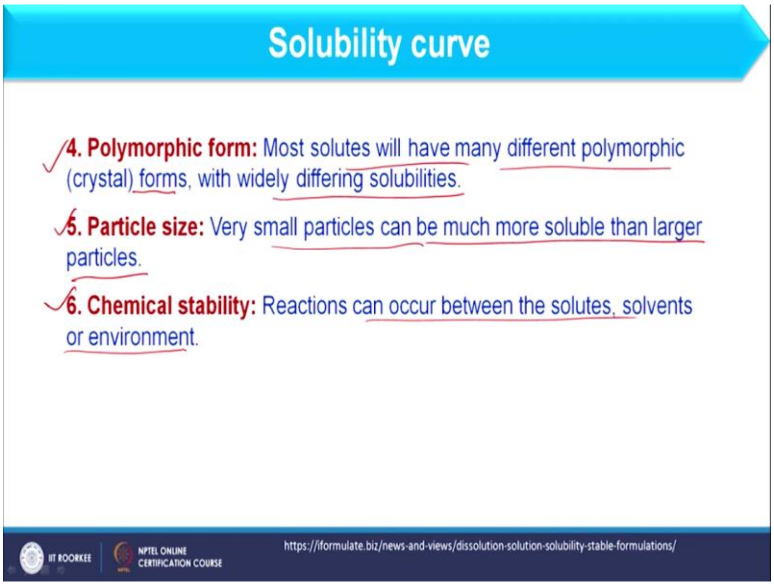

Solubility curve

4. Polymorphic form: Most solutes will have many different polymorphic (crystal) forms, with widely differing solubilities.

5. Particle size: Very small particles can be much more soluble than larger particles.

6. Chemical stability: Reactions can occur between the solutes, solvents or environment.

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So, along with this there are number of factors on which the apparent solubility depends and these are polymorphic form. So, more solutes will have many different polymorphic form and that we consider as the crystal with widely differing solubilities. And now we have the particle size very small particles can be much more soluble than the larger particles. So, solubility will depend on the solute particles also.

And then we have the chemical stability reactions can occur between solute, solvent or environment. So, basically we should avoid the chemical disability and we should consider that solute, solvent should not react with the environment or react with each other. So, all these factor depends on the apparent solubility.

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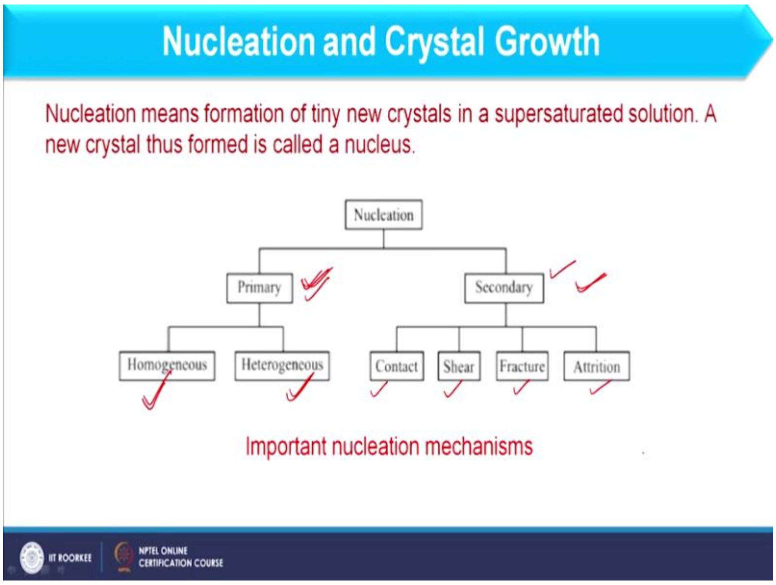

Nucleation and Crystal Growth

Nucleation means formation of tiny new crystals in a supersaturated solution. A new crystal thus formed is called a nucleus.

- Nucleation
  - Primary
    - Homogeneous
    - Heterogeneous
  - Secondary
    - Contact
    - Shear
    - Fracture
    - Attrition

Important nucleation mechanisms

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And now we will discuss nucleation and crystal growth. So, as far as nucleation is concerned basically we have two types of nucleation. The first is the primary nucleation and then we have the secondary nucleation. What is primary nucleation? Primary nucleation are that nucleation where the nuclei is not available it means the crystals are formed randomly. And secondary nucleation means some nucleates or nuclei are already available and further growth of the crystal occurs on these nuclei or nucleates.

So, secondary nucleation means when I am already having nuclei inside this and primary means nuclei are not available, crystals are formed randomly. So, as far as primary nucleation is concerned it is basically of two types homogenous and heterogeneous and secondary nucleation can occur with the contact with shear fracture and attrition. So, these are basically nucleation mechanisms which are consider in crystallization process. When the solution is at super saturated condition.

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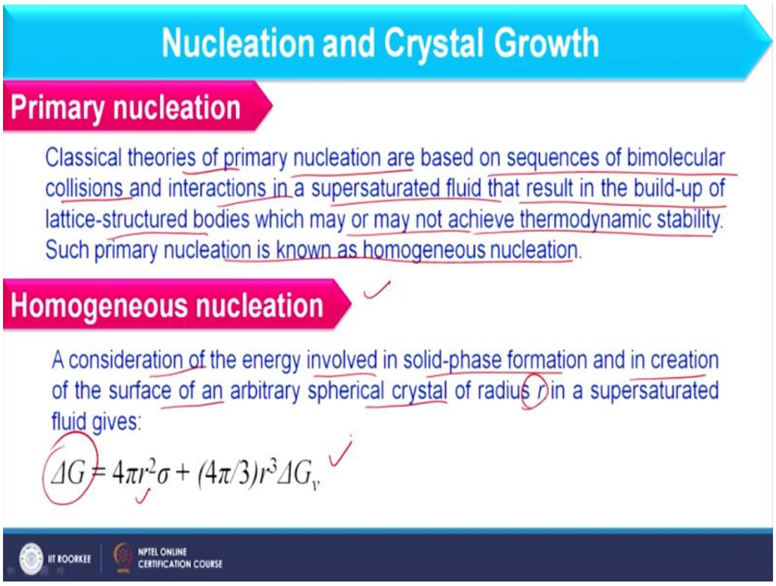

Nucleation and Crystal Growth

Primary nucleation

Classical theories of primary nucleation are based on sequences of bimolecular collisions and interactions in a supersaturated fluid that result in the build-up of lattice-structured bodies which may or may not achieve thermodynamic stability. Such primary nucleation is known as homogeneous nucleation.

Homogeneous nucleation

A consideration of the energy involved in solid-phase formation and in creation of the surface of an arbitrary spherical crystal of radius r in a supersaturated fluid gives:

$$\Delta G = 4\pi r^2\sigma + (4\pi/3)r^3\Delta G_v$$

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So, what is primary nucleation basic definition I have already told you, now see its further. So, classical theories of primary nucleation are based on sequences of bimolecular collusions, interaction of super saturated fluid that result in the buildup of lattice structured body which may or may not achieve thermodynamic stability. So, such prime nucleation is known as homogenous nucleation.

So, as far as homogenous nucleation is concerned so in this nucleation a consideration of the energy involved in solid phase formation and in creation of the surface of an arbitrary physical crystal of the radius r in super saturated solution gives. So as far as energy involvement is considered it is basically pi / 4 r square sigma + 4 pi / 3 r cube delta Gv.

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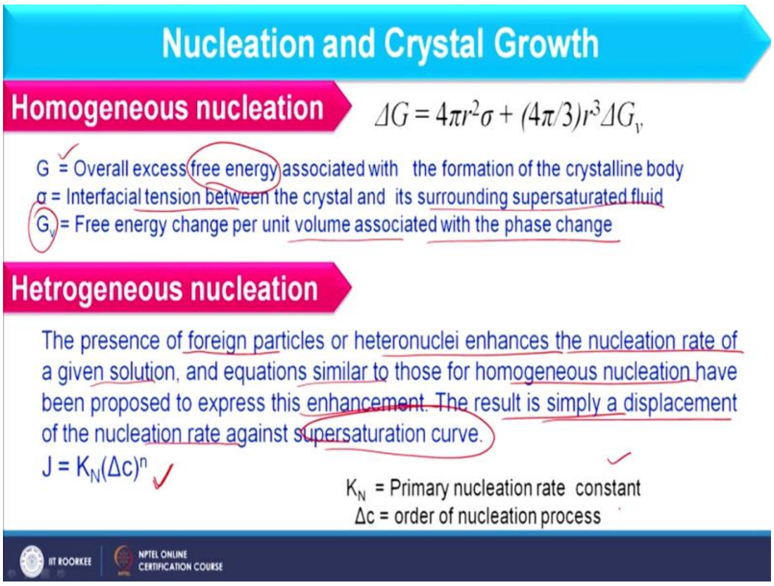

Nucleation and Crystal Growth

Homogeneous nucleation $\Delta G = 4\pi r^2\sigma + (4\pi/3)r^3\Delta G_v$

G = Overall excess free energy associated with the formation of the crystalline body
σ = Interfacial tension between the crystal and its surrounding supersaturated fluid
G_v = Free energy change per unit volume associated with the phase change

Hetrogeneous nucleation

The presence of foreign particles or heteronuclei enhances the nucleation rate of a given solution, and equations similar to those for homogeneous nucleation have been proposed to express this enhancement. The result is simply a displacement of the nucleation rate against supersaturation curve.

$J = K_N(\Delta c)^n$

K_N = Primary nucleation rate constant
Δc = order of nucleation process

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So, what these parameters are let us see that. G is the overall excess free energy associated with the formation of crystalline body and sigma is interfacial tension between crystal and the solution and further Gv is the free energy change per unit volume associated with the phase change. So, in this way you can compute the energy involvement when I am considering homogenous nucleation.

In the similar line heterogeneous nucleation is the presence of foreign particles or heteronuclei enhances the nucleation rate of a given solution. The equations similar to those for homogenous nucleation have been proposed to express this enhancement. Further, we can consider the result is simply a displacement of nucleation rate against the super saturation curve.

So, you see here I am having this expression where KN is the primary nucleation rate constant and delta c is the order of nucleation process. So, in this way you can consider homogenous nucleation and heterogeneous nucleation.

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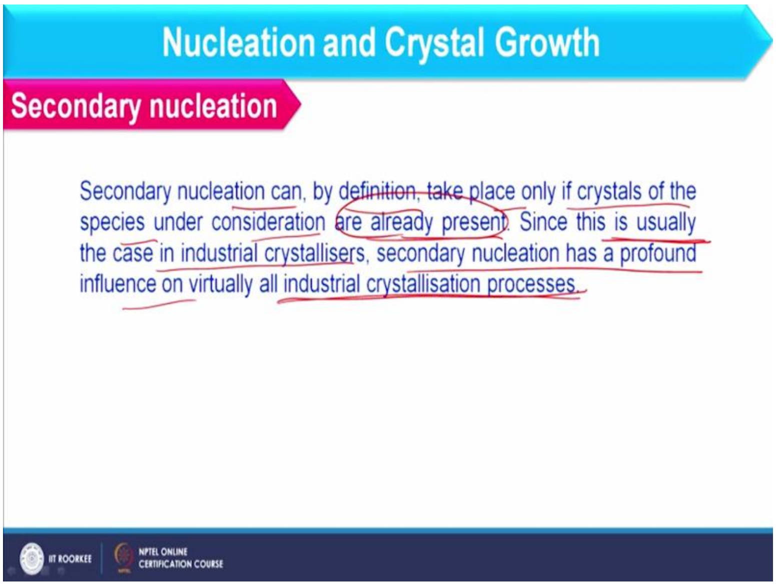

Nucleation and Crystal Growth

Secondary nucleation

Secondary nucleation can, by definition, take place only if crystals of the species under consideration are already present. Since this is usually the case in industrial crystallisers, secondary nucleation has a profound influence on virtually all industrial crystallisation processes.

So, let us focus on secondary nucleation. As I have already told you it is developed based on some nuclei or nucleates. So, secondary nucleation can by definition can take place only if crystal of a species under consideration are already present. So that I have already told you and since this is usually the case in industrial crystallizer secondary nucleation has a profound influence on virtually all industrial crystallization processes.

So, at industrial level we usually consider secondary nucleation because in that nuclei are already available. So, we will discuss the concept of crystallization and design of crystallizer in subsequent lectures also. So that is all for now. Thank you.