Mass Transfer Operations II
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Lecture No 29
Solid Liquid Phase Equilibrium, Theory of Crystallization

Welcome back to mass transfer operations 2. We were discussing on crystallization. Now we will be discussing on solid liquid phase equilibrium and theory of crystallization. So before entering into the solid liquid phase equilibrium we should learn the terminologies for saturation.

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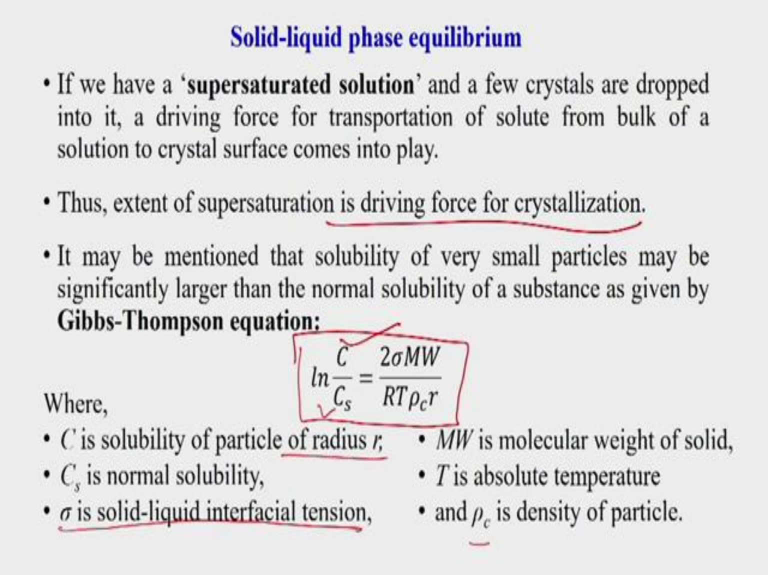

Solid-liquid phase equilibrium

- If we have a '**supersaturated solution**' and a few crystals are dropped into it, a driving force for transportation of solute from bulk of a solution to crystal surface comes into play.
- Thus, extent of supersaturation is driving force for crystallization.
- It may be mentioned that solubility of very small particles may be significantly larger than the normal solubility of a substance as given by **Gibbs-Thompson equation:**

$$\boxed{ln\frac{C}{C_s} = \frac{2\sigma MW}{RT\rho_c r}}$$

Where,

- C is solubility of particle of radius r,
- C_s is normal solubility,
- σ is solid-liquid interfacial tension,
- MW is molecular weight of solid,
- T is absolute temperature
- and ρ_c is density of particle.

That is we can say a quasi static state of one solution where we can say the capacity of the solute inside this solution is exceptionally higher than the regular solubility limit. That we can say if we have a supersaturated solution and a few crystals are dropped into it, a driving force for the transportation of the solute from the bulk of the solution to the crystal surface comes into the play. So thus the extent of super saturation is the driving force for the crystallization.

It may be mentioned that the solubility of the very small particles may be significantly larger than the normal solubility of the substances that is given by this Gibbs-Thompson equation that is ln C by Cs is equal to 2 into sigma into MW by RT into rho c into r where C is the, you can say, solubility of the particle of radius r, where Cs is the normal solubility. So this additional solubility actually comes into the picture when we have these very tiny particles. .

Say whenever we will be discussing about the solubility curve of these any salt or any organic materials, then we discuss this one the solubility of the regular crystals, but whenever the regular crystals are converted into small particles then their solubility level actually increases and that is why we can say in a particular temperature and pressure the solubility actually increases from the regular solubility and due to that constant temperature and pressure. The capacity of the solvent to dissolve the solute increases and that is why the super saturation is created and where sigma actually the solid-liquid interfacial tension, MW is the molecular weight of the solid and T the absolute temperature and rho c is the density of the particle.

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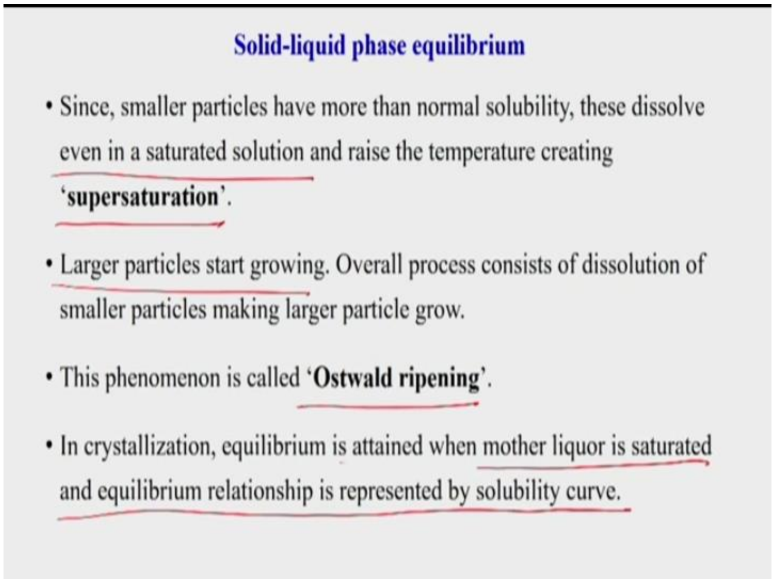

Solid-liquid phase equilibrium

- Since, smaller particles have more than normal solubility, these dissolve even in a saturated solution and raise the temperature creating '**supersaturation**'.
- Larger particles start growing. Overall process consists of dissolution of smaller particles making larger particle grow.
- This phenomenon is called '**Ostwald ripening**'.
- In crystallization, equilibrium is attained when mother liquor is saturated and equilibrium relationship is represented by solubility curve.

So since the smaller particles have more than normal solubility these dissolve even in a saturated solution. That is why you say in a saturated solution we can say saturated solution means the maximum amount of the solute is present at that particular temperature and pressure and raise the temperature creating this super saturation. So larger particles then starts growing and overall process consist of dissolution of the smaller particles making larger particular grow. So these phenomena is called Ostwald ripening or this way, the particles will be associated in all 3 directions in all XYZ directions and then big crystal will be formed.

In crystallization equilibrium is attained when mother liquor actually is saturated and equilibrium relationship is represented by the solubility curve. So whenever we have this supposed this feed and say when it is super saturated in a particular temperature and pressures we say this is the magma. Whenever from this magma this crystal is separated then whatever this exhaust fluid will be there that we say that is the mother liquor. So there solubility of the solute will be there at the temperature and pressure but due to this super saturation this more amount of the solutes will be present inside the solvent. That is why sometimes we get less crystal yield also we will be discussing in detail that in the regular cases.

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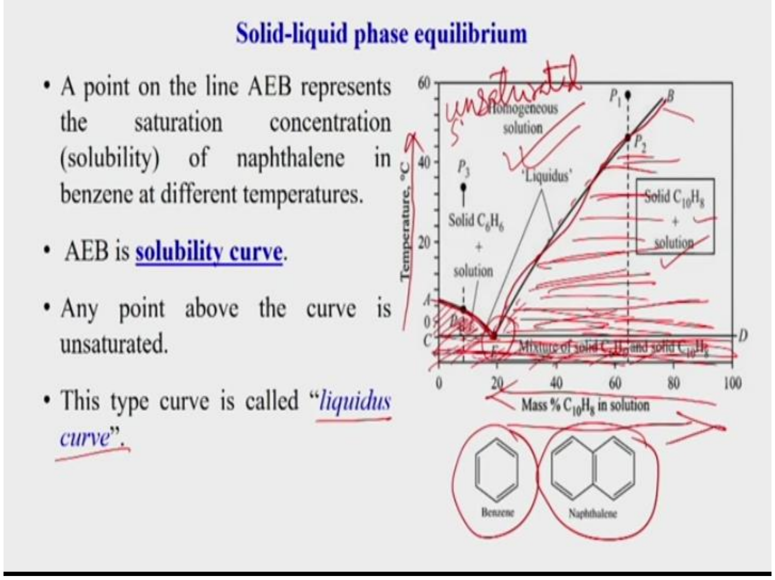

Solid-liquid phase equilibrium

- A point on the line AEB represents the saturation concentration (solubility) of naphthalene in benzene at different temperatures.
- AEB is **solubility curve**.
- Any point above the curve is unsaturated.
- This type curve is called "*liquidus curve*".

So now this one whenever will be discussing about the say solid-liquid phase equilibrium. If it is a pure solute like this any salt or any say sugar or any type of organic materials then with increasing temperature in generally we can say these solubility increases. That is why whenever you input these if we draw this, a temperature and say solute concentration, then we get a or in general we get this linearly increasing curve.

So that curve above this curve we can say that is the unsaturated one and below this one the saturated and which one is excess that will be coming out as the say precipitate or , one solid phase. So below this one saturated and excess amount is separated as the solid phase and above this one, it will be remain in the unsaturated condition and on the curve actually you can say this one saturation point is there but whenever we have the mixed solid mixture then in general we do not have that simplicity and their solubility curves are more complicated.

If we take the example of say benzene and say naphthalene, then we can learn that in case of that type of 2 solid mixtures, their solubility curves are not linear or not simple. Like, if we start from this A to E to say we can say this to B, so this is actually we can say a solubility curve for this benzene and naphthalene mixture. So in this x axis, this naphthalene concentration is increasing in the right hand side, or benzene concentration is increasing in the left-hand side. Temperature is increasing in the y-axis.

And so that is why we say in any point on this curve we can say on this one on A, E and B. So any point we can say this is a solubility point or we can say saturation point or we can say saturation concentration of naphthalene in benzene at different temperatures or the vice versa. So that is why we say this is the solubility curve but you see this one the solubility curve is not simple like any other solubility curve.

Here you see this one, say this lowest point is there the below this one any of the mixture will remain in the solid condition but the thing is that say if we start from A to E there when the benzene concentration is more and since suppose in this zone actually from A, E and C, these zone whenever we will be decreasing the temperature then we will be getting that say solid benzene will be separated because that is in the huge amount and the solution will contain this naphthalene but whenever we will be talking about this right hand side suppose in this zone in between say B, E, D there you see this one if we decrease the temperature we will be getting this solid naphthalene and this benzene in the solution because this benzene concentration is lower here and this the arms actually are called this liquidus curve.

So this one supposed AE and EB these are called all liquidus curve. So above this curve means A E B these are all we can say this homogeneous solution of this is you can say this one unsaturated. So this is unsaturated because in that zone, the solution actually will demand more solutes to be dissolved as the temperature is very high and below this curve, , these are all saturated and based on the composition the few amount of the solid will be separated from the solute solution mixture and whenever we will be talking about C E D below this one in any of the compositions we can say and at that temperature always these will be in the solid form, so in this zone, these are in the solid form.

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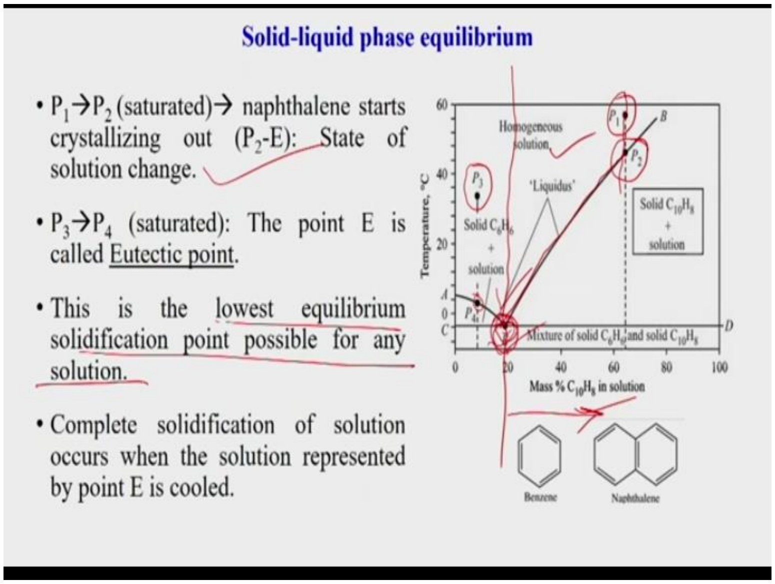

Solid-liquid phase equilibrium

- $P_1 \rightarrow P_2$ (saturated)$\rightarrow$ naphthalene starts crystallizing out (P_2-E): State of solution change.
- $P_3 \rightarrow P_4$ (saturated): The point E is called Eutectic point.
- This is the lowest equilibrium solidification point possible for any solution.
- Complete solidification of solution occurs when the solution represented by point E is cooled.

Now you see if we start from a point P1 say suppose one will be this one more than say 20 percent naphthalene concentration and one will be discussing about the less than 20 percent naphthalene concentration or we will be discussing where one composition where naphthalene is more will be discussing one composition where benzene is more. Suppose this naphthalene is more this is the composition like P1 and temperature is 60 degrees Celsius and we are decreasing the temperature and keeping there pressure constant and then when it will be reaching point P2 then we can say this is the saturation point means above this one it was unsaturated one. That is why it was homogeneous solution. So whenever it will be reaching point 2 it reaches the saturation point.

Then, again if we decrease the temperature, then it will follow this route, like this it will be following this route. And temperature as temperature will be decreasing then composition of the mixture will be decreasing means this excess amount of the naphthalene actually will be coming out as the crystal. So that is why is naphthalene composition will be decreasing and it will be reaching one point that is E. So at around say minus 5 degree Celsius. It will be reaching where we can say 20 percent naphthalene is there and 80 percent benzene will be there because the remaining amount, say if we say it is a 65 percent of naphthalene was there in the beginning so now it is only 20 percent. So the rest amount actually is separated as the crystal.

So that is why, it will be following P1 to P2 to E. So that is and then the minimum point where all the pages will be coexisting means the solution means a phase will be there and solid phase also will be coexisting. And if we take one composition where benzene is more and say naphthalene is less, suppose say if we take the composition like 10 percent say we can say naphthalene and say 90 percent Benzene is there. So mostly it is benzene. So whenever it will be reaching this point P4 then it will be, we can say, it is a saturation point. Then if we decrease again the temperatures then it will go to this point like this again it will follow this path from P4 to E it will be coming and then at that time what will happen, this benzene will be separated. That is why it is we can say naphthalene concentration will go on increasing and then when it will be reaching point E then both whatever the residue was there means say in the solution that will be now all these on solids will be separated from the system.

So this point E actually called Eutectic point. So this is we can say this is the lowest equilibrium solidification point possible for any solution. So whenever we have this eutectic mixture then that is the lowest equilibrium solidification point. So complete solidification of the solution occurs when the solution is represented by point E. That is in that composition is cooled, so complete solidification will take place and that time it will not follow any of the, we can say routes like this like P2 to E or P4 to E, like this it will not follow any solubility curve or saturation curve. So there actually we can say the entire composition will be converted into a solid crystals and we know that below this whatever composition is it will be solidified and then crystal will be separated. That actually from this we can say equilibrium curve this one expect.

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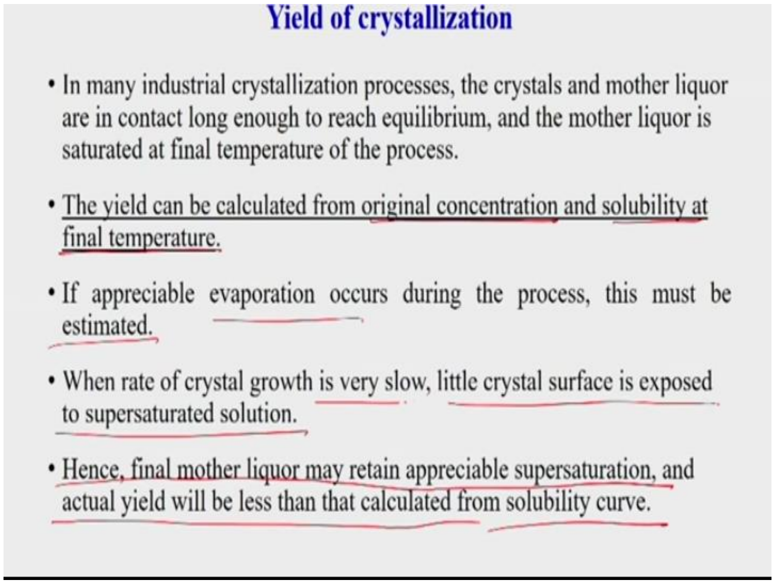

Yield of crystallization

- In many industrial crystallization processes, the crystals and mother liquor are in contact long enough to reach equilibrium, and the mother liquor is saturated at final temperature of the process.
- The yield can be calculated from original concentration and solubility at final temperature.
- If appreciable evaporation occurs during the process, this must be estimated.
- When rate of crystal growth is very slow, little crystal surface is exposed to supersaturated solution.
- Hence, final mother liquor may retain appreciable supersaturation, and actual yield will be less than that calculated from solubility curve.

So now we will be discussing about the yield of the crystallization process. So this is very important parameter actually for the crystallization or if we say this crystallization is efficient then we need to calculate the yield like this. In many industrialization crystallization process the crystals and mother liquor are in contact long enough to reach the equilibrium. So and the mother liquor is a saturated and final temperature of the process, that is of the constant pressure. So that yield can be calculated from the original concentration say that is in the unsaturated condition whatever the original concentration was there this that will be definite and the solubility at the final temperature.

That is whenever the temperature is decreased then what is the final temperature and then at that temperature what is the solubility limit and what was the initial concentration? So from this difference actually will be getting how much amount of crystal actually is separated. So in the beginning what was the concentration and at that time what is the solubility that is not so important because that is we know that at the higher temperature it will remain in the unsaturated condition. But the original concentration is required because the remaining amount will be separated as the crystal. So if this one appreciable evaporation occurs during the process this must be estimated. So whenever this some amount of evaporation takes place, then we can say the water amount actually will be changing from the original solution.

So that needs to be considered and based on that if the some amount of the water is evaporated then the yield actually will be increasing. So in any process if there is evaporation yield will be more, if there is no evaporation then yield will be less because that time the we can see the total amount of mass which will be separated that will be lower. Then whenever the mass that will be separated if some amount of water is evaporated because you see solubility is dependent on the temperature and pressure and say this one in a particular temperature how much amount of solute is present per unit mass of the water or solvent. So that is why we can say if evaporation is there we need to consider this one means whenever we will be doing water balance or solute balance then we need to consider this water amount also.

When the rate of crystal growth is very slow then little crystal surface is exposed to the saturated supersaturated solution. So that is sometimes required to add the we can see foreign particles or we can say it is one solid interface where the crystallization process will be enhanced where this process is very slow but a hence then final mother liquor may retain appreciable super saturation and actual yield will be less than the calculated from the solubility curve that what who actually tried to explain that due to the super saturation in a particular solubility limit in a particular temperature the mother liquor will contain more amount of the solute then its solubility limit. That is why the actual yield will be lesser that will be calculated for the solubility curve to the hooker. This is solubility curve ball situation carp.

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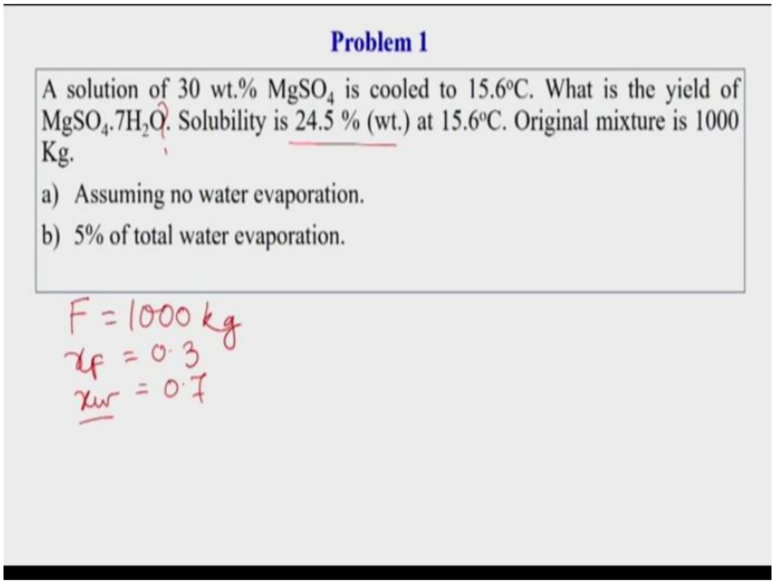

Problem 1

A solution of 30 wt.% $MgSO_4$ is cooled to 15.6°C. What is the yield of $MgSO_4.7H_2O$. Solubility is 24.5 % (wt.) at 15.6°C. Original mixture is 1000 Kg.

a) Assuming no water evaporation.

b) 5% of total water evaporation.

$F = 1000$ kg

$x_F = 0.3$

$x_w = 0.7$

Now, we will be solving one problem that how the yield actually is calculated in case of this water evaporation or without water evaporation. This is a very simple problem. Like this is solution of 38 percent magnesium sulphate is cooled to 15.6 degrees Celsius. So initial temperature will be definitely the room temperature and we assume that this at room temperature whatever 30 percent magnesium sulfate is there that is unsaturated solution and what is the yield of this magnesium sulphate 7 H2O, we need to calculate this one.

So solubility is 24.5 percent that is in weight percent actually at 15.6 degree Celsius. Original mixture is a 1000 kg. Now we need to assume that there is no (evaporation) water evaporation and we need to consider when 5 percent water is evaporated. So in the beginning what we will be doing say we will take the, supposed to feed is equal to 1000 kg then xf will be 0.3 then xw will be 0.7, this water because in case of the crystallization water has a role also. We need to consider that also and say in this we can say solubility this one at 15.6 degrees Celsius is this one 24.5.

So it will be converting from so mother liquor will contain 0.245, this one x mother liquor will be 0.245. So now what will you be doing this one? So we need to calculate this say molecular weight. We can say this one molecular weight of MgSO4 so that is we can say 120.4 and molecular weight of MgSO4.7H2O will be 120.4 plus 126. That will be say 246.5 that is, so this water molecule is 18 into 7 126.1. So we will be doing this both water balance and say the magnesium sulphate 7 H2O balance for this system.

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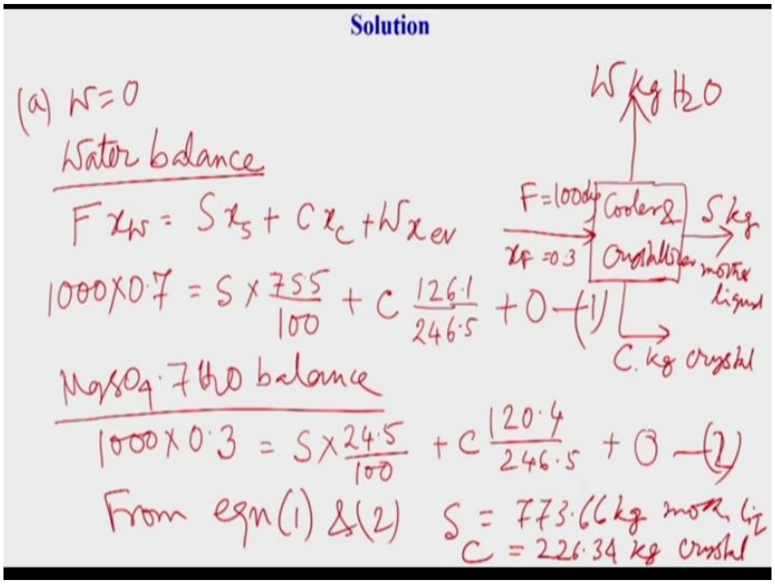

Solution

(a) $W=0$

Water balance

$$F x_W = S x_S + C x_C + W x_{ev}$$

$$1000 \times 0.7 = S \times \frac{75.5}{100} + C\,\frac{126.1}{246.5} + 0 \quad (1)$$

$MgSO_4 \cdot 7H_2O$ balance

$$1000 \times 0.3 = S \times \frac{24.5}{100} + C\,\frac{120.4}{246.5} + 0 \quad (2)$$

From eqn (1) & (2) $S = 773.66$ kg mother liq
$C = 226.34$ kg crystal

Suppose for the first case no water evaporation is there. Suppose for case a we will take this one. This we can say cooler and crystallizer so feed is F is equal to say 1000 kg and xf is 0.3. Now it will be converting into 3 different streams. So firstly like so we can say C kg crystal, then it is S kg mother liquor and say suppose W kg water. So if for first case this W is equal to 0. We will be doing that say water balance. Water balance we will be doing suppose F xw is equal to S into xs plus say c into xc plus W into say x let us take evaporated. So F is equal to say 1000 kg into xw is equal to 0.7, that S we do not know.

S into xs is equal it is we can say crystal, crystal will be say 24.5 percent is crystal is there and that is why the remaining amount will be there, So 100 minus 24.5 that is you can say 75.5 divided by 100 and plus say crystal will be say for this case also water will be 7 H2O and that is 126.1 divided by say total is 246.5 plus water is equal to 0. And say if we do MgSO4 7H2O balance then we will be getting this one. Say F xf so 1000 into 0.3 is equal to S into the rest amount, this means solid 24.5 in the mother liquor divided by you can say this one 100 plus say C into remaining amount, 120.4 divided by 246.5, this plus if evaporated is nothing.

So we have now this supposed this equation 1, this is equation say 2. So from this equation 1 and 2 we can say if we do the manipulation we will be getting from from equation 1 and 2 we will be getting say S is equal to so we can say 773.66 kg. So that is we can say that is the mother liquor and crystal that will be equal to the remaining amount say to 226.34kg say crystal. When there is no evaporation, then we will be getting to 226.34 kg crystal and 773.66 kg mother liquor, so that will be divided into 2 parts and W will be 0.

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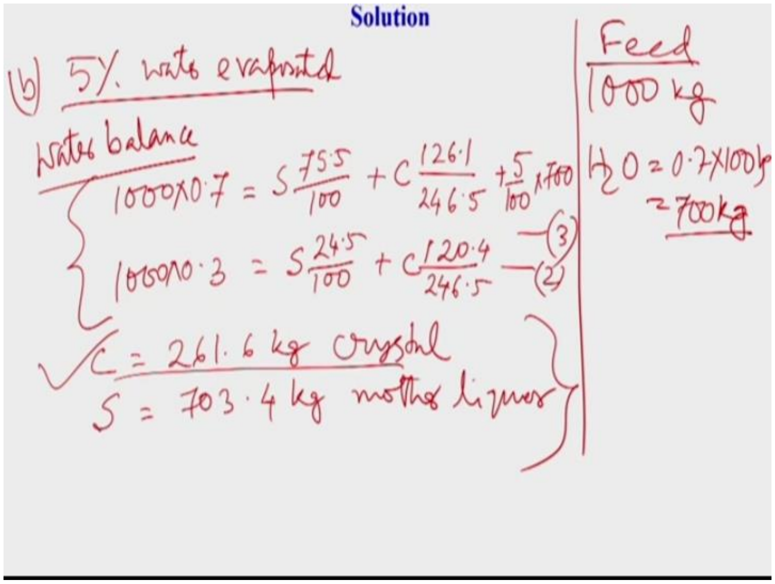


Solution

(b) 5% water evaporated

Water balance

$1000 \times 0.7 = S\frac{75.5}{100} + C\frac{126.1}{246.5} + \frac{5}{100} \times 700$ — (3)

$1000 \times 0.3 = S\frac{24.5}{100} + C\frac{120.4}{246.5}$ — (2)

✓ C = 261.6 kg crystal

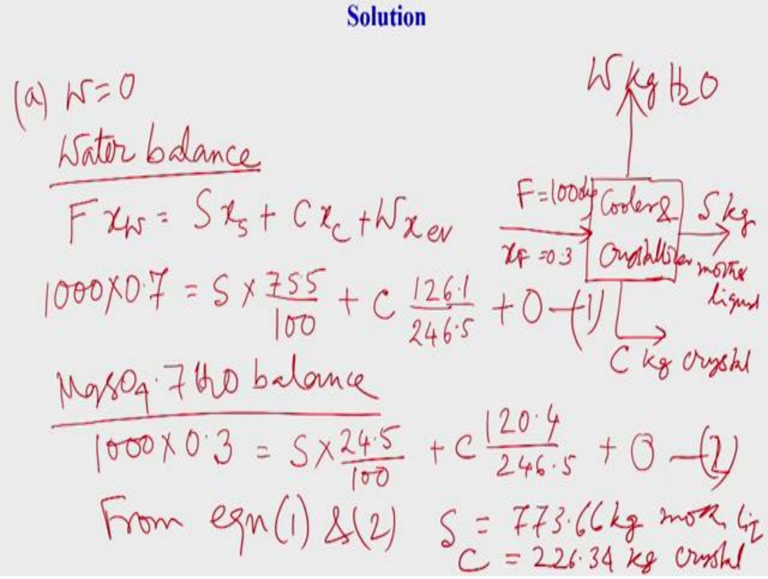
S = 703.4 kg mother liquor

Feed

1000 kg

$H_2O = 0.7 \times 1000$ kg

= 700 kg



Solution

(a) W = 0

Water balance

$F x_w = S x_s + C x_c + W x_{ev}$

$1000 \times 0.7 = S \times \frac{75.5}{100} + C\frac{126.1}{246.5} + 0$ — (1)

$MgSO_4 \cdot 7H_2O$ balance

$1000 \times 0.3 = S \times \frac{24.5}{100} + C\frac{120.4}{246.5} + 0$ — (2)

From eqn (1) & (2) S = 773.66 kg mother liq

C = 226.34 kg crystal

But whenever we have the 5 percent water loss, like this 5 percent water evaporated. So then we have this, say for water balance we will be doing then water balance. We will be doing the water balance like this, say F into xw that is 0.7 that will be S into like this whatever water 75.5 by 100 in this mother liquor plus in crystal water will be like this 126.1 by 246.5 plus say this one that total water actually was there like for this case, out of this 1000 kg in this feed, 1000 kg feed, water was actually 0.7 into 1000 kg, so that is you can say 700 kg.

So this is actually 700 kg, out of this 700 kg 5 percent is evaporated so 5 by 100 into 700. So that is that is you can see equation 3 and we have this equation 2 like this 1000 into 0.3 is equal to a S into 24.5 by say 100 plus C into 120.4 divided by 246.5, so that is equation 2. So from these 2 equations will be getting now, if we just manipulate these 2 equations we will be getting that C is equal to 261.6 kg, so crystal and mother liquor will be equal to 703.4 kg mother liquor. So whenever there will be evaporation we will be getting more crystal or we can say the yield is more. So in case of this without evaporation that was only 226.34 kg crystal, whenever only 5 percent water is evaporated then it is increased from 226.34 kg to 261.6 kg. So that, when the evaporation is there we will be getting more yield.

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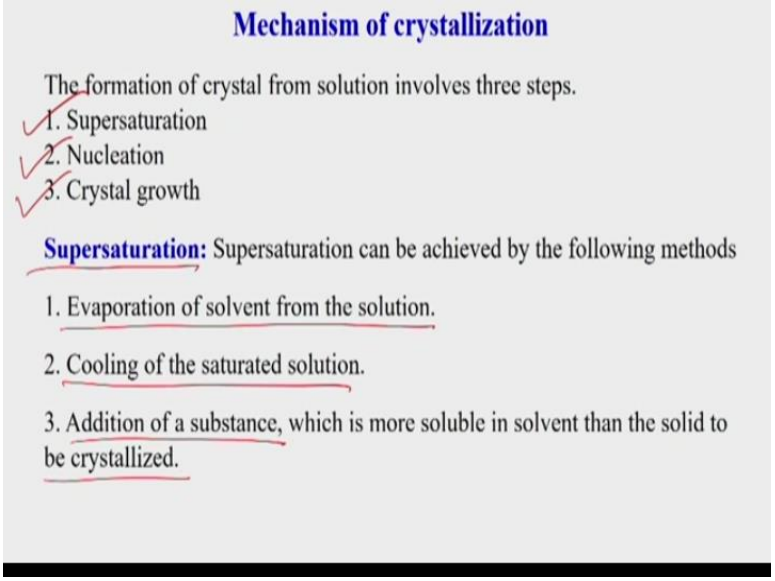

Mechanism of crystallization

The formation of crystal from solution involves three steps.

1. Supersaturation
2. Nucleation
3. Crystal growth

Supersaturation: Supersaturation can be achieved by the following methods

1. Evaporation of solvent from the solution.
2. Cooling of the saturated solution.
3. Addition of a substance, which is more soluble in solvent than the solid to be crystallized.

Now we will be discussing about the mechanism of crystallization. So the formation of the crystal actually from the solution involves these 3 steps. The first step is this we can say the supersaturation. How we can make the supersaturation, then the second step will be nucleation means nucleus formation, then we can say the third step will be crystal good. Once crystal growth is complete then it will be separated from this mother liquor means say this one from this feed and we can say that will be separated and that will be purified, cleaned, dried and then it will be used for the final application. So this supersaturation whatever we discussed till now that can be achieved by the following methods like this evaporation of the solvent from the solution.

So if we evaporate this one then supersaturation will be created like this. That is one way and another one is the cooling of the saturated solution just if we cool down the saturation solution then also or sometimes by cooling and heating like this in a cyclic order say whenever we will be first will be heating, then we will be cooling or then again heating and cooling, that way also supersaturation will be created because whenever we have these big crystals or we can say these big materials there their solubility will be low because the solubility also is dependent on this specific surface area. Whenever we are converting this into small particles, then we can say the solubility will be increasing. If we cool down then, , if we cool down the saturated solution then supersaturation also will be created or sometimes addition of a substance like this which is more soluble in solvent than the solute to be crystallized then also supersaturation also is created.

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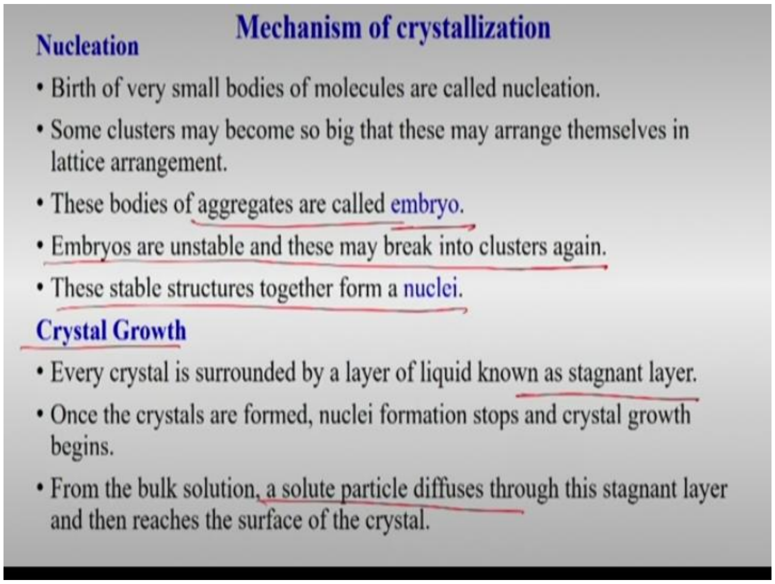

Mechanism of crystallization

Nucleation

- Birth of very small bodies of molecules are called nucleation.
- Some clusters may become so big that these may arrange themselves in lattice arrangement.
- These bodies of aggregates are called embryo.
- Embryos are unstable and these may break into clusters again.
- These stable structures together form a nuclei.

Crystal Growth

- Every crystal is surrounded by a layer of liquid known as stagnant layer.
- Once the crystals are formed, nuclei formation stops and crystal growth begins.
- From the bulk solution, a solute particle diffuses through this stagnant layer and then reaches the surface of the crystal.

Then we can say that is nucleation that is a nucleus formation. So that is we can say the birth of the very small bodies of the molecules are called nucleation or nucleus formation. Some clusters may become so weak that these may arrange themselves in the lattice arrangement. So in the beginning also we discussed that crystallization is one repetitive process. That it repeats the unit crystals in all 3 directions in XYZ direction it repeats. So in the lattice arrangement actually it will be added and these bodies of these what is called aggregates actually are called embryo, these embryos are unstable and these may break into the clusters again.

These stable structures together form a nuclei. Once this nuclei is formed or we can say that nucleus is formed then we cannot stop this, we can say, crystal growth, like this then crystal growth starts. So every crystal is surrounded by a layer of liquid that is we can say this one as the stagnant layer. Once the crystals are formed, the nuclei formation stops and crystal growth actually begins. So from the bulk solution a solute particle diffuses through the stagnant layer and then reaches the surface of the crystal and then all the surface, these are all we can say, these combines and then form the big big crystal.

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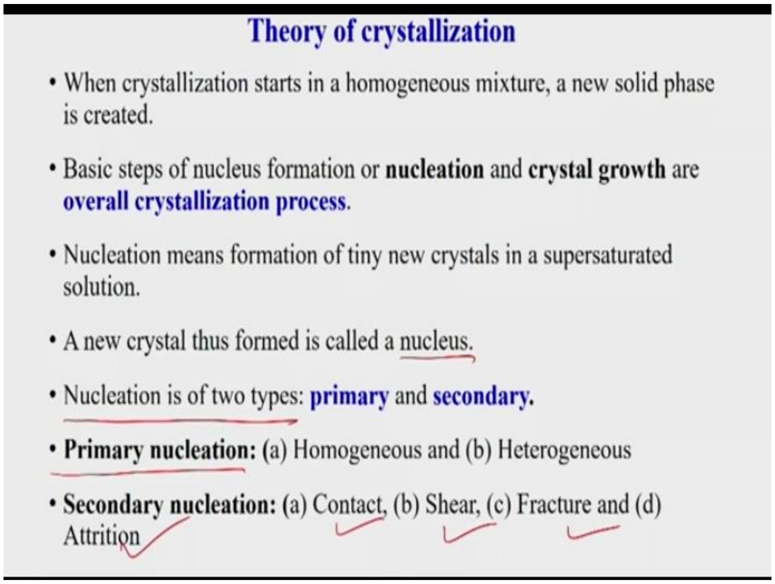

Theory of crystallization

- When crystallization starts in a homogeneous mixture, a new solid phase is created.
- Basic steps of nucleus formation or **nucleation** and **crystal growth** are **overall crystallization process**.
- Nucleation means formation of tiny new crystals in a supersaturated solution.
- A new crystal thus formed is called a nucleus.
- Nucleation is of two types: **primary** and **secondary.**
- **Primary nucleation:** (a) Homogeneous and (b) Heterogeneous
- **Secondary nucleation:** (a) Contact, (b) Shear, (c) Fracture and (d) Attrition

Now we will be discussing about the theory of the crystallization. So when the crystallization starts in a homogeneous mixture a new phase is created. So the basic steps of nucleus formation or nucleation and crystal growth are overall crystallization process. So in the beginning we have this we need to make the supersaturation by any means. Then we have the nucleation and once nucleation is done then crystal growth will be there. The combination of the nucleation and crystal growth is called this crystallization process.

So nucleation means a formation of these tiny new crystals in a supersaturated solution. A new crystal thus formed is called this nucleus. Then this nucleation is of 2 types. One is the primary nucleation, another is the secondary nucleation. The primary nucleation is also 2 types that is sometimes we have this homogeneous nucleation, sometimes we have heterogeneous nucleation and for the secondary nucleation, there are 4 different types of nucleation, like this contact then shear, fracture and then attrition. Either of these 4 different types of the secondary nucleation processes are available there for the industrial applications.

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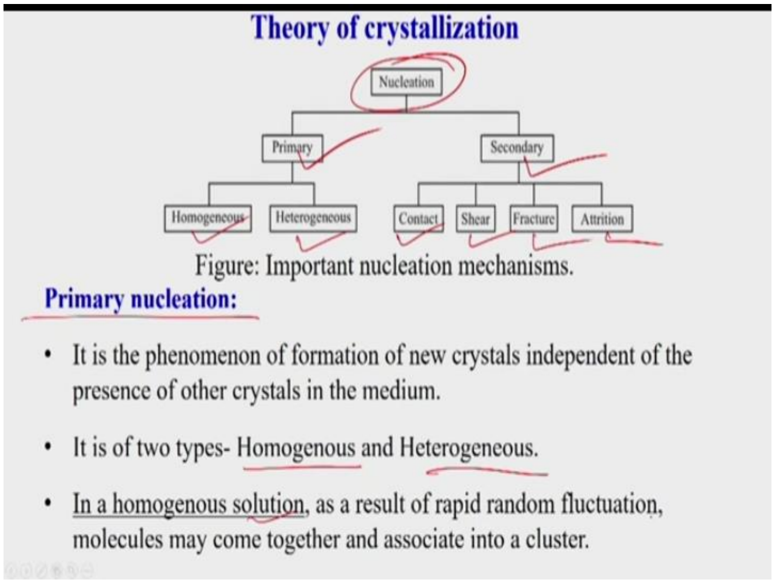

Theory of crystallization

Nucleation
Primary
Secondary
Homogeneous
Heterogeneous
Contact
Shear
Fracture
Attrition

Figure: Important nucleation mechanisms.

Primary nucleation:

- It is the phenomenon of formation of new crystals independent of the presence of other crystals in the medium.
- It is of two types- Homogenous and Heterogeneous.
- In a homogenous solution, as a result of rapid random fluctuation, molecules may come together and associate into a cluster.

So now we can summarize this one like this say nucleation process, like this primary is there and secondary. Primary is the homogeneous and heterogeneous and secondary is contact, shear, fracture and attrition like this. In primary nucleation it is the phenomena of the formation of these new crystals that is independent of the presence of other crystals in the medium. So that is primary, by any means new crystal is formed or we can we say this tiny surface or we can solid surface is created without the addition or without the help of any other solid surfaces. It is of 2 types like this homogeneous and heterogeneous. In a homogeneous solution actually, as a result of rapid and random fluctuation, molecules may come together and associate into a cluster.

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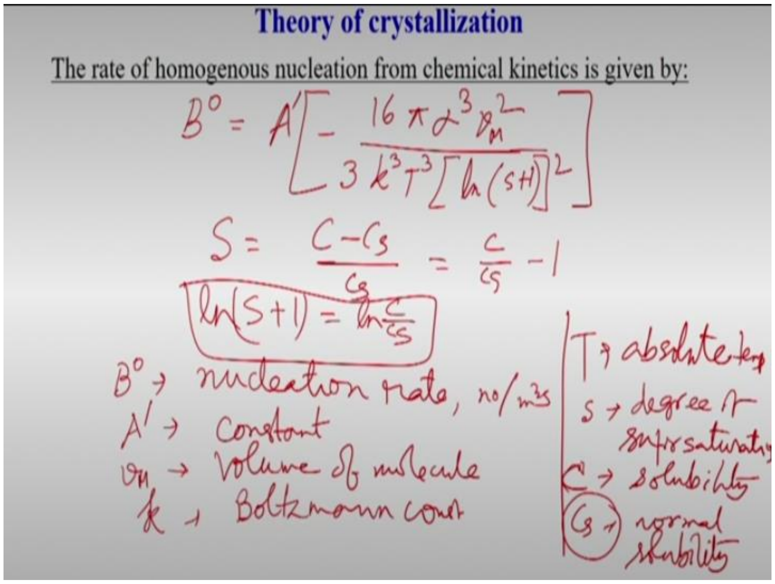

Theory of crystallization

The rate of homogenous nucleation from chemical kinetics is given by:

$$B^0 = A'\left[-\frac{16\pi\sigma^3 v_M^2}{3k^3T^3[\ln(S+1)]^2}\right]$$

$$S = \frac{C-C_s}{C_s} = \frac{C}{C_s} - 1$$

$$\boxed{\ln(S+1) = \ln\frac{C}{C_s}}$$

$B^0 \rightarrow$ nucleation rate, no/m³s

$A' \rightarrow$ Constant

$v_M \rightarrow$ Volume of molecule

$k \rightarrow$ Boltzmann const

$T \rightarrow$ absolute temp

$S \rightarrow$ degree of supersaturation

$C \rightarrow$ solubility

$C_s \rightarrow$ normal solubility

And the rate of this homogeneous nucleation this chemical kinetics is given by like this you can write this one. This B prime is equal to say A prime into minus 16 pi sigma cube into vm to the power 2 divided by 3 k cube T cube into ln S plus 1 whole square. So where this S is equal to, actually S is equal to C minus Cs that is what we can say driving force by Cs and if you just manipulate this one is equal to C by Cs minus 1. So this S plus 1 will be equal to C by CS. If we take logarithm in both the cases then it will be like ln S plus 1 is equal to ln C by Cs.

So here B prime actually is called say nucleation rate. So that will be we can say this number per meter cube per second and this A prime is actually, that is we can say these are constant, that is you can say system dependent and this vm actually is volume of molecule. Then this k is Boltzmann Constant and T is absolute temperature and S is degree of supersaturation, how much supersaturation is there that is S. We will be solving some problems then we will be clearing this one and C is we can say solubility and Cs is actually normal solubility. That is we can say that whatever we will be getting the Cs that is from the graph and this C actually that is, during this supersaturation what is the solubility that is much more higher than the Cs value.

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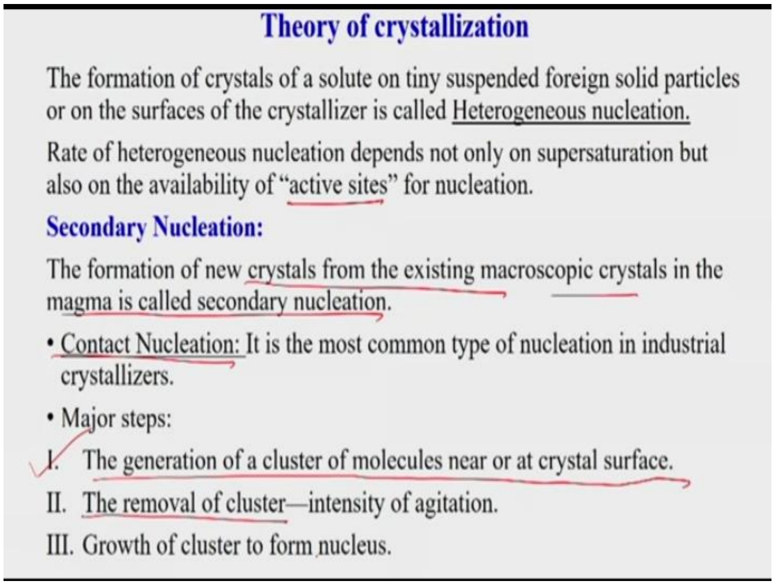

Theory of crystallization

The formation of crystals of a solute on tiny suspended foreign solid particles or on the surfaces of the crystallizer is called Heterogeneous nucleation.

Rate of heterogeneous nucleation depends not only on supersaturation but also on the availability of "active sites" for nucleation.

Secondary Nucleation:

The formation of new crystals from the existing macroscopic crystals in the magma is called secondary nucleation.

- Contact Nucleation: It is the most common type of nucleation in industrial crystallizers.
- Major steps:

I. The generation of a cluster of molecules near or at crystal surface.
II. The removal of cluster—intensity of agitation.
III. Growth of cluster to form nucleus.

So the formation of the crystals of a solute in tiny suspended foreign solid particles or on the surface of the crystallizer is called this Heterogeneous nucleation and the rate of this heterogeneous crystallization depends not only the supersaturation but also the availability of the active sites. So how much active sites are present for the, we can say the nucleation that also controls the heterogeneous nucleation. Now whenever we will be talking about the secondary nucleation the formation of the new crystals actually from the existing microscopic crystals in the magma actually is called secondary nucleation. So for that we have 4 different types of nucleation. The first one is this contact nucleation. It is the most common type of nucleation in the industrial crystallizer. The major steps are like these, first step is the generation of the cluster of molecules near or at the crystal surface like this we need to generate the cluster. Then the removal of the cluster, then growth of the cluster to form the nucleus.

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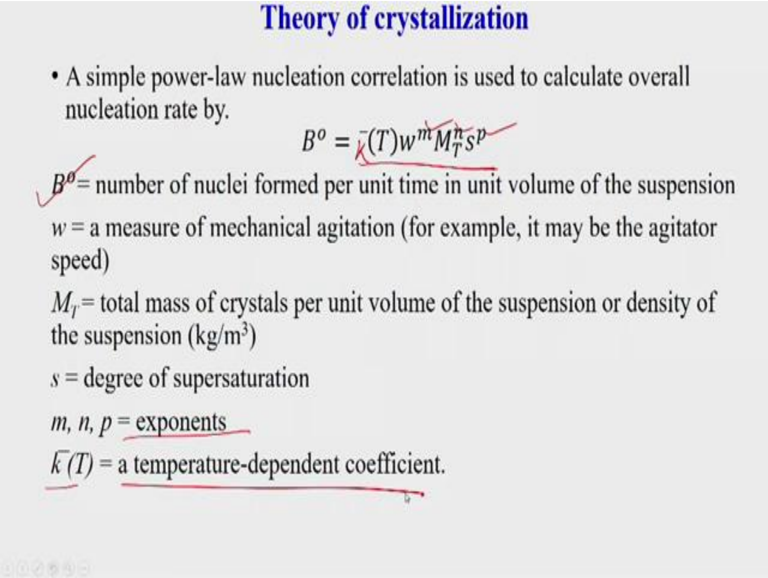

Theory of crystallization

- A simple power-law nucleation correlation is used to calculate overall nucleation rate by.

$$B^o = \bar{k}(T) w^m M_T^n s^p$$

B^o = number of nuclei formed per unit time in unit volume of the suspension

w = a measure of mechanical agitation (for example, it may be the agitator speed)

M_T = total mass of crystals per unit volume of the suspension or density of the suspension (kg/m^3)

s = degree of supersaturation

m, n, p = exponents

$\bar{k}(T)$ = a temperature-dependent coefficient.

And for that actually we can say a simple power-law nucleation correlation actually is used to calculate the overall nucleation rate like B prime is equal to that is we can say T into w to the power we can say m into M to the power n into Sp where B prime is number of nucleus formation and w is the measure of the mechanical agitation and MT that is we can say total mass of the per crystal volume and S actually is the this one degree of supersaturation. Then this m, n and p these are different exponents and it is also system specific and k prime actually this is a temperature-dependent coefficient, so that is also the system specific.

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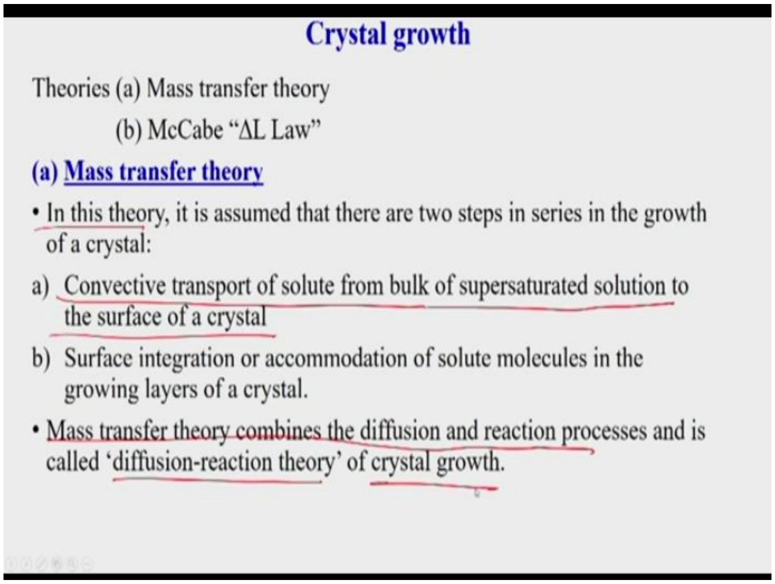

Crystal growth

Theories (a) Mass transfer theory

(b) McCabe "ΔL Law"

(a) Mass transfer theory

- In this theory, it is assumed that there are two steps in series in the growth of a crystal:

a) Convective transport of solute from bulk of supersaturated solution to the surface of a crystal

b) Surface integration or accommodation of solute molecules in the growing layers of a crystal.

- Mass transfer theory combines the diffusion and reaction processes and is called 'diffusion-reaction theory' of crystal growth.

Now there are 2 different theories actually for the crystal growth, these are widely accepted. One is this mass transfer, this is mostly accepted theory and second one is McCabe delta L Law. The first one is this mass transfer theory that is in this theory, it is assumed that there are 2 steps in the series, in the growth of the crystals like this the first step will be like convective transport of the solute from bulk of the supersaturated solution to the surface of the crystal. So that is convective transfer is taking place from the bulk to the crystal surface. Then second one is a surface integration or accommodation of the solute molecules in a repetitive way actually in the growing layer of the crystal, so the mass transfer theory combines the diffusion and reaction processes and is called this diffusion reaction theory of the crystal growth.

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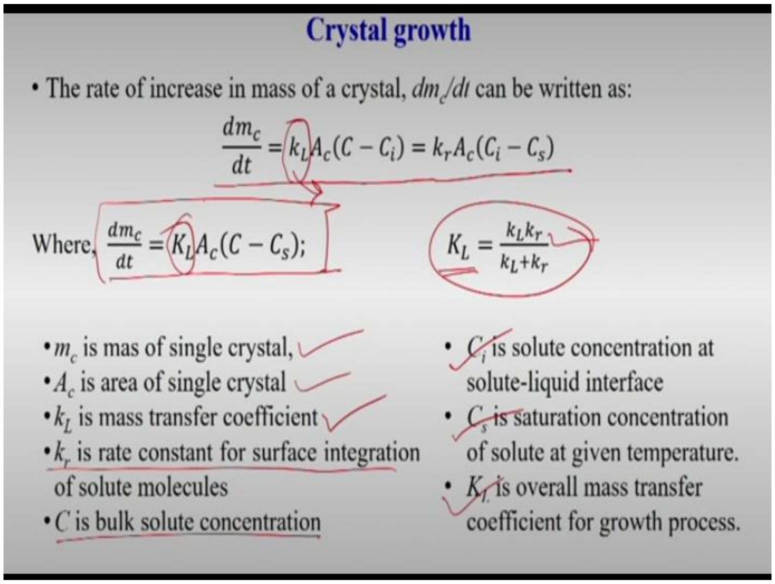

Crystal growth

- The rate of increase in mass of a crystal, dm_c/dt can be written as:

$$\frac{dm_c}{dt} = k_L A_c (C - C_i) = k_r A_c (C_i - C_s)$$

Where, $\boxed{\frac{dm_c}{dt} = K_L A_c (C - C_s);}$ $\quad K_L = \frac{k_L k_r}{k_L + k_r}$

- m_c is mas of single crystal,
- A_c is area of single crystal
- k_L is mass transfer coefficient
- k_r is rate constant for surface integration of solute molecules
- C is bulk solute concentration
- C_i is solute concentration at solute-liquid interface
- C_s is saturation concentration of solute at given temperature.
- K_L is overall mass transfer coefficient for growth process.

And the rate of the increase of the mass of the crystal that dm c by dt can be written as this dm c by dt is equal to small kl into Ac into C minus Ci that is equal to kr into Ac into Ci minus Cs where in the individual mass transfer coefficient can be replaced by overall mass transfer coefficient by like this dmc by dt is equal to Kl into Ac into C into Cs where the scale is just by overall mass transfer coefficient is equal to KL that is Kl is equal to, we can say the mass transfer coefficient and kr is equal to we can say rate constant for the surface integration divided by kl plus kr.

So there mc, the mass of the single crystal, then Ac is the area of the single crystal, kl is the mass transfer coefficient, kr is the constant and C is the bulk solute concentration. Ci is the solute concentration at the interface, then Cs the saturation concentration and KL is the overall mass transfer coefficient. So from this equation we can say what is the rate of the crystal growth that we can calculate from this equation by using either of the in terms of individual mass transfer coefficient or in terms of overall mass transfer coefficient where actually KL is actually represented in terms of individual mass transfer coefficient as well as the mass transfer rate constant.

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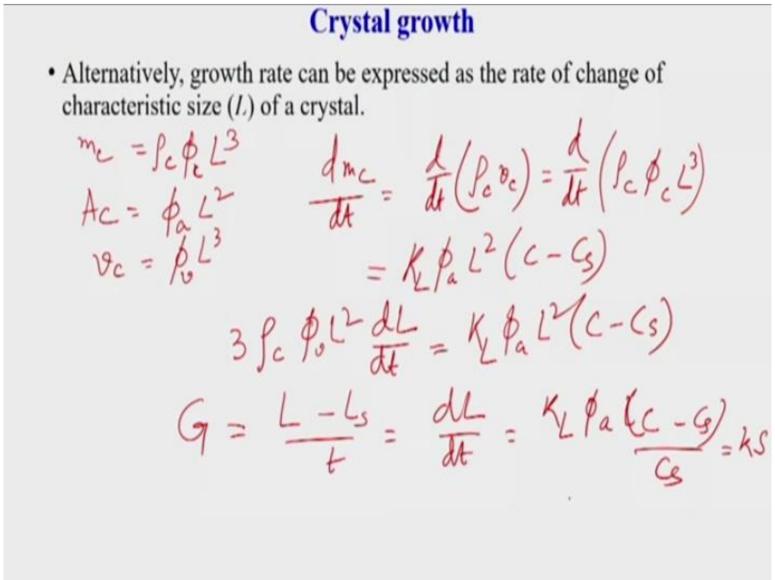
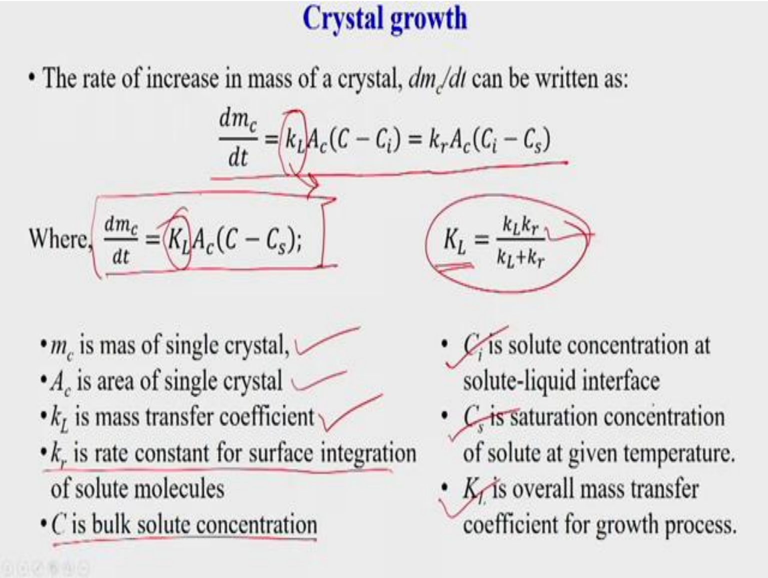


Crystal growth

- Alternatively, growth rate can be expressed as the rate of change of characteristic size (*L*) of a crystal.

$$m_c = \rho_c \phi_c L^3$$
$$A_c = \phi_a L^2$$
$$v_c = \phi_v L^3$$

$$\frac{dm_c}{dt} = \frac{d}{dt}(\rho_c v_c) = \frac{d}{dt}(\rho_c \phi_c L^3)$$
$$= K_L \phi_a L^2 (c - C_s)$$
$$3 \rho_c \phi_v L^2 \frac{dL}{dt} = K_L \phi_a L^2 (c - C_s)$$
$$G = \frac{L - L_s}{t} = \frac{dL}{dt} = K_L \phi_a \frac{(c - C_s)}{C_s} = kS$$



Crystal growth

- The rate of increase in mass of a crystal, dm_c/dt can be written as:

$$\frac{dm_c}{dt} = k_L A_c (C - C_i) = k_r A_c (C_i - C_s)$$

Where, $\frac{dm_c}{dt} = K_L A_c (C - C_s)$; $K_L = \frac{k_L k_r}{k_L + k_r}$

- m_c is mas of single crystal,
- A_c is area of single crystal
- k_L is mass transfer coefficient
- k_r is rate constant for surface integration of solute molecules
- C is bulk solute concentration
- C_i is solute concentration at solute-liquid interface
- C_s is saturation concentration of solute at given temperature.
- K_L is overall mass transfer coefficient for growth process.

So alternatively this growth rate can be expressed as the rate of the change of the characteristic size also. That is L of the crystal so that is very simply done by using this we can say this size factor or length factor or like this where we can say we will be writing this way like this MC that will be say we can say, rho c into phi c into L cube. We know already that is Ac is equal to phi a and L square and Vc that will be like this phi v into L cube.

So now we have this dmc dt that will be is equal to d by dt into we can say mc will be converting into rho c into Vc that is equal to d by dt into rho c into Vc is equal to phi c into L cube. That is we can say this is capital L into phi a into L square into C minus Cs from the previous equation or 3 into rho C into phi v into L square into dL dt. That will be equal to KL phi a L square into C minus Cs. Just by manipulation we are getting this one and there actually we can say growth rate we can say L minus Ls by t that will be nothing but dL by dt that is equal to KL phi a L square into so that is phi a into C minus Cs by Cs that will be equal to ks where k that is you can say we are getting this one is equal to k into C minus Cs by Cs, so that also we can say k is coming from this part Kl into this phi a..

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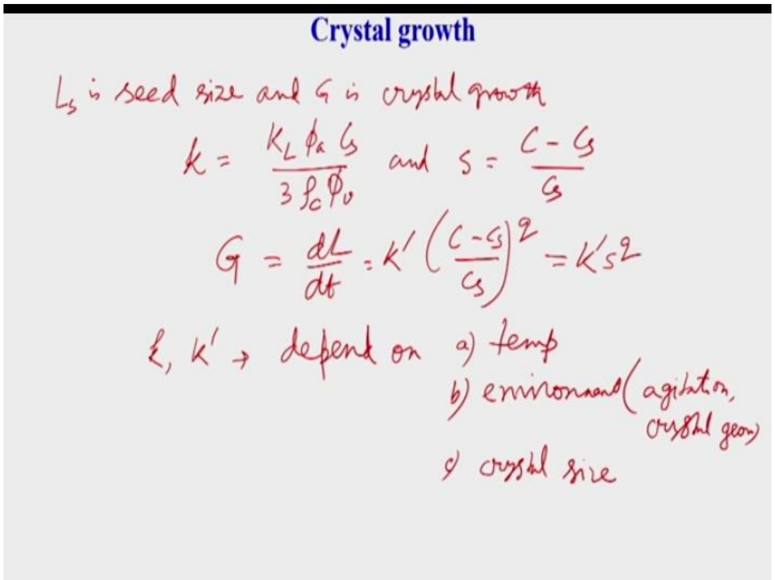

Crystal growth

L_s is seed size and G is crystal growth

$$k = \frac{K_L \phi_a C_s}{3 \rho_c \phi_v} \quad \text{and} \quad S = \frac{C - C_s}{C_s}$$

$$G = \frac{dL}{dt} = k' \left(\frac{C - C_s}{C_s}\right)^q = k' s^q$$

$k, k' \rightarrow$ depend on a) temp

b) environment (agitation, crystal geom)

c) crystal size

Then we can say this Ls is seed size and G is a measure of crystal growth, therefore k we can say will be like this, KL into phi a into Cs by 3 into rho c into phi v and S will be C minus Cs by Cs. So now we can get this G that is will be able to say dL by dt that will be K prime into C minus Cs by Cs into to the power q that will be we can say K prime into S to the power q. So just we can say k and K prime these depend actually, depend on we can say like temperature then environment like this like how much agitation is actually taking place then crystal geometry, what type of crystal actually is there whether body centre, cubic or face centre, cubic or hexagonal closed packing, so crystal geometry like this and then we can say finally crystal size, crystal size also is we can say the controlling parameter.

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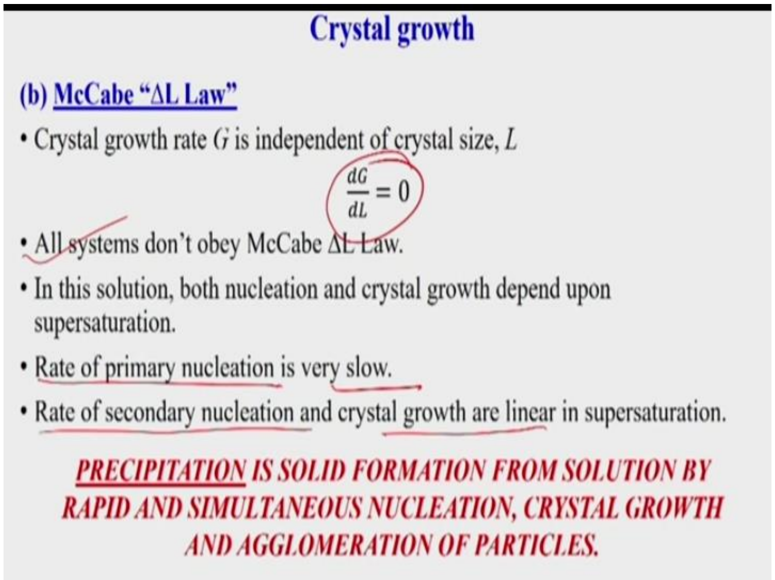

Crystal growth

(b) McCabe “ΔL Law”

- Crystal growth rate G is independent of crystal size, L

$$\frac{dG}{dL} = 0$$

- All systems don’t obey McCabe ΔL Law.
- In this solution, both nucleation and crystal growth depend upon supersaturation.
- Rate of primary nucleation is very slow.
- Rate of secondary nucleation and crystal growth are linear in supersaturation.

PRECIPITATION IS SOLID FORMATION FROM SOLUTION BY RAPID AND SIMULTANEOUS NUCLEATION, CRYSTAL GROWTH AND AGGLOMERATION OF PARTICLES.

So then the second one that is McCabe delta L Law, there actually we can say this crystal growth rate G is independent of the crystal size L. So that is why dG by dL that is equal to 0. So all systems do not obey this McCabe delta L Law. In the solution actually in case of this McCabe delta L Law both nucleation and crystal growth depend upon these for supersaturation but rate of this primary nucleation is very slow and the rate of the secondary nucleation and crystal growth are linear in the supersaturation. So now at the end of this discussion we can differentiate between these crystallization and precipitation like this.

So this precipitation that is, in the solid formation from the solution by rapid and simultaneous nucleation, crystal growth and agglomeration of the particles. But in case of the crystallization, whatever we have learnt till now that the say whenever we have this supersaturation then we will be getting this nucleation then we can say crystal growth.

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Thank You

Next class

Design of crystallizer, Crystallization equipment

So thank you very much, in the next class we will be discussing about design of the crystallizer and crystallization equipment.