

Mass Transfer Operations II
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Lecture No 28
Crystallization

Welcome back to mass transfer operations 2.

What is crystal?

Crystal is a solid body with plane faces in which the atoms are arranged in an ordinary repetitive array. Most crystals are anisotropic; their mechanical, electrical, magnetic and optical properties are often different in different directions.

What is crystallization?

Crystallization is a process where solid particles are formed from a homogeneous phase. When crystals are produced by cooling a saturated solution, process is called solution crystallization. When crystals are produced by cooling a molten solid in absence of any solvent, it is called melt crystallization. Some liquids (e.g., ammonium oleate) that exhibit anisotropy at temperatures just above their melting points are called liquid crystals because of their similarity with crystalline solids.

Types of crystal geometry

Crystals are classified into seven general systems:

1. **Cubic System:** Three equal axes at right angles to each other
2. **Tetragonal system:** Three axes at right angles to each other, one longer than others.
3. **Orthorhombic:** Three axes are right angles to each other, all of different lengths.
4. **Monoclinic:** Three unequal axes, two at right angles in plane and the third at some different angle to the plane.
5. **Triclinic:** Three unequal axes at unequal angles to each other and not 30° , 60° or 90° .
6. **Trigonal (Rhombohedral):** Three equal and equally inclined axes.

7. **Hexagonal:** Six equal axes in one plane at 120° to each other and a seventh axis at right angle to this plane.

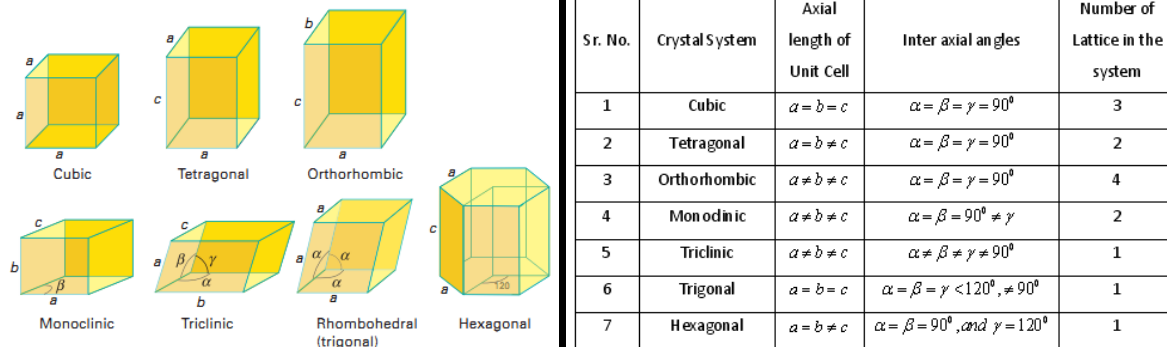


Figure 1. Seven crystal systems.

Major steps in crystallisation process

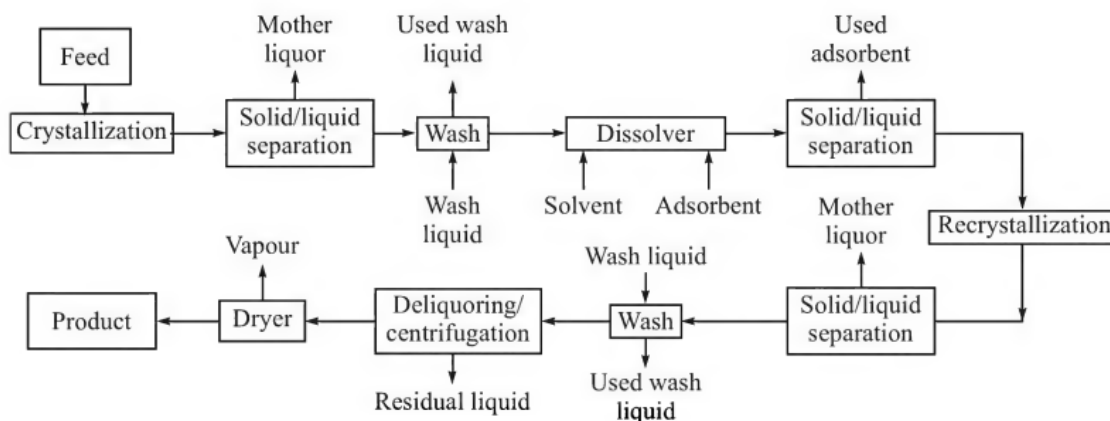


Figure: The major steps in the process of crystallization.

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:

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:**

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

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 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 C_s is equal to 2 into σ into MW by RT into ρ_c into r where C is the, you can say, solubility of the particle of radius r , where C_s is the normal solubility. So this additional solubility actually comes into the picture when we have these very tiny particles. .

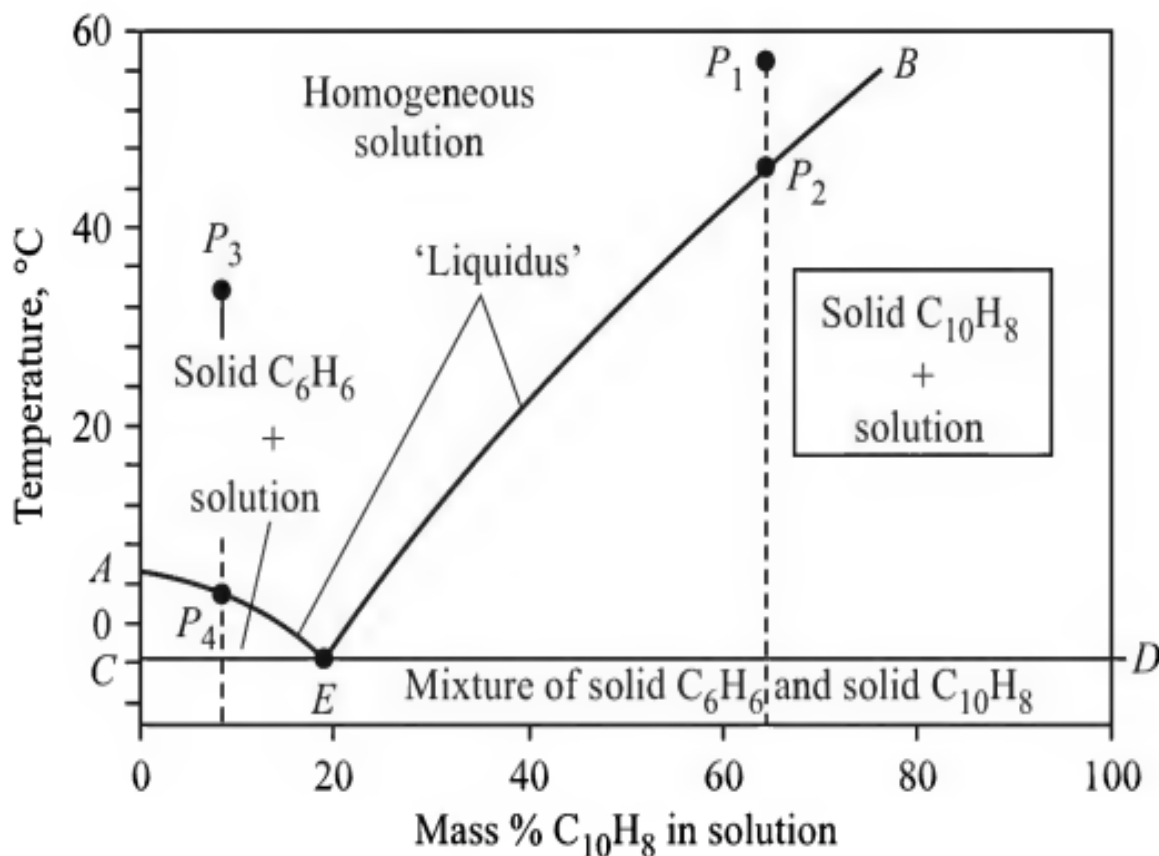
Say whenever we will be discussing about the solubility curve of these any salt or any organic materials, then we discuss this one the solubility of the regular crystals, but whenever the regular crystals are converted into small particles then their solubility level actually increases and that is why 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 σ actually the solid-liquid interfacial tension, MW is the molecular weight of the solid and T the absolute temperature and ρ_c is the density of the particle.

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.

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.

In Crystallization, equilibrium is attained when mother liquor is saturated and equilibrium relationship is represented by solubility curve.



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”.

- $P_1 \rightarrow P_2$ (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.

5. Yields : 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.

Problem 1: A solution of 30 wt% MgSO_4 is cooled to 15.6°C . What is the yield of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Solubility is 24.5 % (wt) at 15.6°C . Original mixture is 1000Kg.

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 $7\text{H}_2\text{O}$, 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 x_f will be 0.3 then x_w 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 .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 MgSO_4 so that is we can say 120.4 and molecular weight of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 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 for water balance and say the magnesium sulphate 7 H_2O balance for this system.

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Solution

(a) $W=0$
Water balance
 $F x_w = S x_s + C x_c + W x_{ev}$
 $1000 \times 0.7 = S \times \frac{75.5}{100} + C \times \frac{126.1}{246.5} + 0 - (1)$

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ balance
 $1000 \times 0.3 = S \times \frac{24.5}{100} + C \times \frac{120.4}{246.5} + 0 - (2)$

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

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 x_F 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 $F x_w$ is equal to S into x_s plus say c into x_c plus W into say let us take evaporated. So F is equal to say 1000 kg into x_w is equal to 2.7, that S we do not know.

S into x_s we can say it is equal it is we can say crystal. Crystal will be so 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 H_2O

and that is 126.1 divided by say total is 246.5 plus water is equal to 0. And say if we do $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ balance then we will be getting this one. Say F x f 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 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

$$1000 \times 0.7 = S \frac{75.5}{100} + C \frac{126.1}{246.5} + \frac{5}{100} \times 1000$$

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

$$C = 261.6 \text{ kg crystal}$$

$$S = 703.4 \text{ kg mother liquor}$$

Feed
1000 kg
 $H_2O = 0.7 \times 1000$
 $\approx 700 \text{ kg}$

Solution

(a) $W=0$

Water balance

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

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

MgSO₄ · 7H₂O balance

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

From eqn (1) & (2)

$$S = 773.66 \text{ kg mother liq}$$

$$C = 226.34 \text{ kg crystal}$$

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 x_w 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.

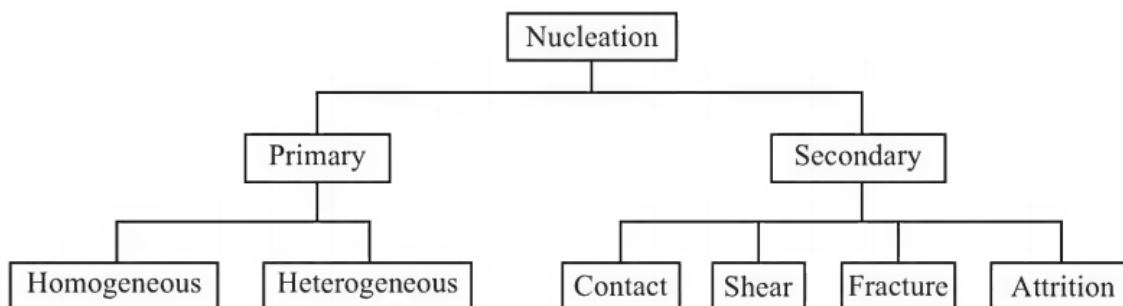
So this is actually 700 kg, out of this 700 kg 5 percent is evaporated so 5 by 100 into 700. So that is that is you can see equation 3 and we have this equation 2 like this 1000 into 0.3 is equal to a S

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.

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 is also divided into two categories; homogeneous and heterogeneous. Contact, shear, fracture and attrition are secondary nucleation.



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.

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

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 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:

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

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

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

$B^0 \rightarrow$ 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 v_m 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 C_s that is what we can say driving force by C_s and if you just manipulate this one is equal to C by C_s minus 1. So this S plus 1 will be equal to C by C_s . If we take logarithm in both the cases then it will be like $\ln S$ plus 1 is equal to $\ln C$ by C_s .

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 v_m 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 C_s is actually normal solubility. That is we can say that whatever we will be getting the C_s 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 C_s 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. And for that actually we can say a simple power-law nucleation correlation actually is used to calculate the overall nucleation rate like B' 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 S^p where B' is number of nucleus formation and w is the measure of the mechanical agitation 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' 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, $\frac{dm_c}{dt} = K_L A_c (C - C_s);$ $K_L = \frac{k_L k_r}{k_L + k_r}$

<ul style="list-style-type: none"> 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 ✓ 	<ul style="list-style-type: none"> 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. ✓
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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 k_L into A_c into C minus C_i that is equal to k_r into A_c into C_i minus C_s where in the individual mass transfer coefficient can be replaced by overall mass transfer coefficient by like this dm_c by dt is equal to K_L into A_c into C into C_s where the scale is just by overall mass transfer coefficient is equal to K_L that is K_L is equal to, we can say the mass transfer coefficient and k_r is equal to we can say rate constant for the surface integration divided by k_L plus k_r .

So there m_c , the mass of the single crystal, then A_c is the area of the single crystal, k_L is the mass transfer coefficient, k_r is the constant and C is the bulk solute concentration. C_i is the solute concentration at the interface, then C_s the saturation concentration and K_L 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 K_L is actually represented in terms of individual mass transfer coefficient as well as the mass transfer rate constant.

Crystal growth

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

$$m_c = \rho_c \phi_c L^3$$

$$A_c = \phi_a L^2$$

$$v_c = \phi_v L^3$$

$$\frac{dm_c}{dt} = \frac{d}{dt}(\rho_c v_c) = \frac{d}{dt}(\rho_c \phi_c L^3)$$

$$= K_L \phi_a L^2 (C - C_s)$$

$$3 \rho_c \phi_v L^2 \frac{dL}{dt} = K_L \phi_a L^2 (C - C_s)$$

$$G = \frac{L - L_s}{t} = \frac{dL}{dt} = K_L \phi_a \frac{(C - C_s)}{C_s} = k_s$$

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

<ul style="list-style-type: none"> 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 ✓ 	<ul style="list-style-type: none"> 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. ✓
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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 m_c that will be say we can say, ρ_c into ϕ_c into L^3 . We know already that is A_c is equal to ϕ_a and L^2 and V_c that will be like this ϕ_v into L^3 .

So now we have this dm_c/dt that will be is equal to d by dt into we can say m_c will be converting into ρ_c into V_c that is equal to d by dt into ρ_c into V_c is equal to ϕ_c into L^3 . That is we can say this is capital L into ϕ_a into L^2 into $C - C_s$ from the previous equation

or 3 into ρ C into ϕ v into L square into dL dt . That will be equal to $K_L \phi a L$ square into C minus C_s . Just by manipulation we are getting this one and there actually we can say growth rate we can say L minus L_s by t that will be nothing but dL by dt that is equal to $K_L \phi a L$ square into so that is ϕa into C minus C_s by C_s that will be equal to k_s where k that is you can say we are getting this one is equal to k into C minus C_s by C_s , so that also we can say k is coming from this part K_L into this ϕa .

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Crystal growth

L_s is seed size and G is crystal growth

$$k = \frac{K_L \phi a G}{3 \rho_c \phi_0} \quad \text{and} \quad S = \frac{C - G}{G}$$

$$G = \frac{dL}{dt} = k' \left(\frac{C - G}{C_s} \right)^2 = k' S^2$$

$k, k' \rightarrow$ depend on

- a) temp
- b) environment (agitation, crystal geom)
- c) crystal size

Then we can say this L_s is seed size and G is a measure of crystal growth, therefore k we can say will be like this, K_L into ϕa into C_s by 3 into ρ_c into ϕ v and S will be C minus C_s by C_s . 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 C_s by C_s 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.

All systems don't obey McCabe ΔL Law

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