Mass Transfer Operation 2

Professor. Chandan Das

Department of Chemical Engineering,

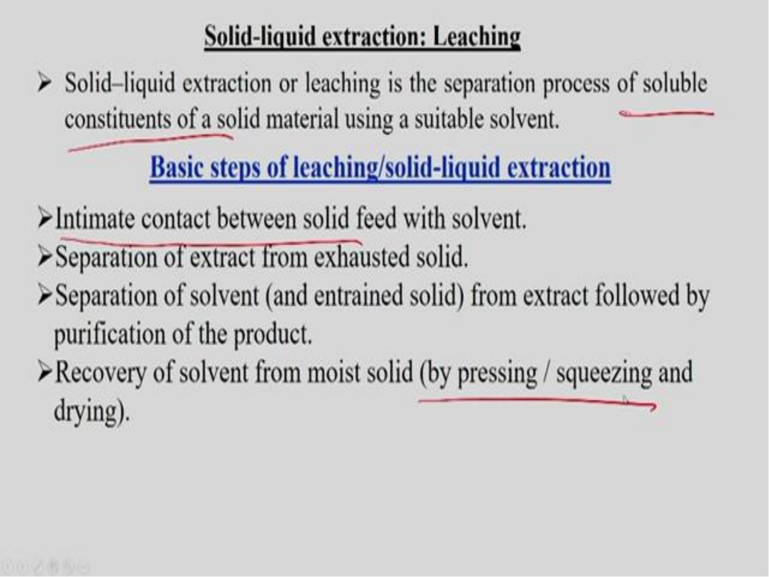
Indian Institute of Technology, Guwahati

Lecture-31

Concluding remarks: Part 2

Now, we will be discussing about the solid liquid extraction that if the fourth chapter that is whatever we have learned in chapter 3 that is the liquid - liquid extraction in place of these liquid the carrier addition in place of the carrier solvent it is a solid inert like the inside this one the target component is there and we are adding the solvent from the outside extracting solvent and then the remaining process will remain same.

(Refer Slide Time: 01:00)



Solid-liquid extraction: Leaching

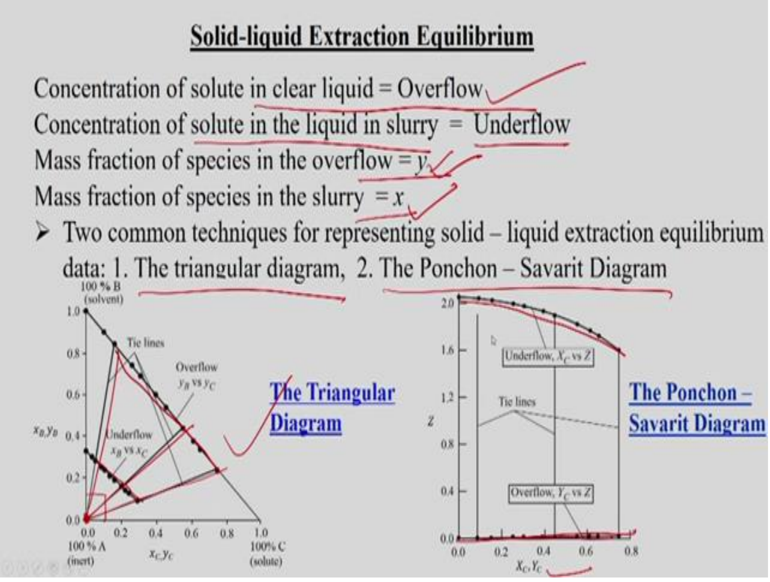
- Solid–liquid extraction or leaching is the separation process of soluble constituents of a solid material using a suitable solvent.

Basic steps of leaching/solid-liquid extraction

- Intimate contact between solid feed with solvent.
- Separation of extract from exhausted solid.
- Separation of solvent (and entrained solid) from extract followed by purification of the product.
- Recovery of solvent from moist solid (by pressing / squeezing and drying).

So, the solid liquid extraction or leaching process leaching is the separation process of the soluble constituents of a solid material using a suitable solvent. The basic steps of the leaching or solid liquid extraction process are like, intimate contact between the solid feed and with the solvent there separation of the extract from the exhausted solid, then separation of the solvent like this and entrained solid from the extract followed by this purification of the product. Then recovery of the solvent from moist solid just by pressing or squeezing like this and then drying.

(Refer Slide Time: 01:38)



Solid-liquid Extraction Equilibrium

Concentration of solute in clear liquid = Overflow

Concentration of solute in the liquid in slurry = Underflow

Mass fraction of species in the overflow = y

Mass fraction of species in the slurry = x

- Two common techniques for representing solid – liquid extraction equilibrium data: 1. The triangular diagram, 2. The Ponchon – Savarit Diagram

The Triangular Diagram

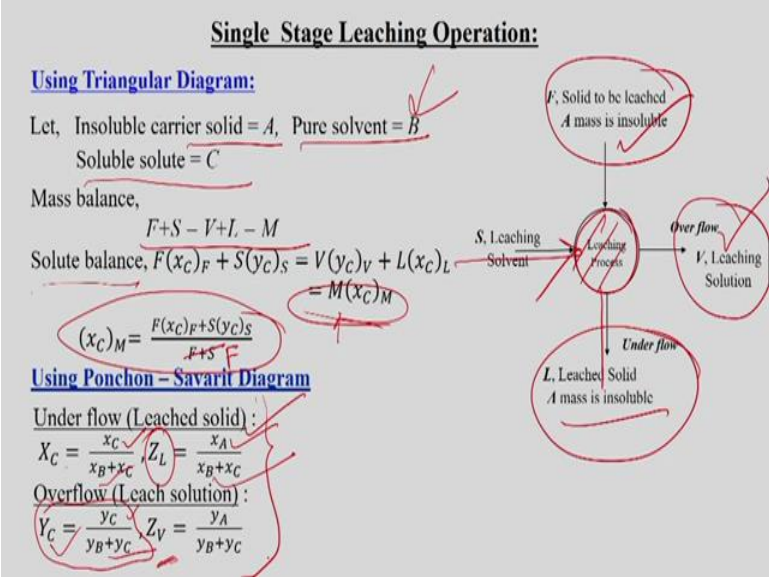
The Ponchon – Savarit Diagram

Like this Solid Liquid Extraction Equilibrium, it is equivalent to that of the liquid liquid extraction equilibrium like this concentration of the solute in the clear liquid that is overflow, then concentration of the solute in the liquid in the slurry that we say this an underflow or this like carrier solvent here is this inert solid, so that is underflow.

The mass fraction of the species in the overflow that is y, and mass fraction of the species in the slurry is x. We are more interested in the overflow. So the 2 common techniques for the representing solid liquid extraction equilibrium data are triangular diagram and the Ponchon Savarit diagram.

That is overflow actually lies in these BC line and underflow lies between these one and all the tie line actually originates from the A point. That is in at solid point, or for Ponchon Savarit one in the xc and yc most of the overflow points actually will be like coinciding but values are very less small and underflow lines are will be like this one with high values.

(Refer Slide Time: 03:08)



Single Stage Leaching Operation:

Using Triangular Diagram:

Let, Insoluble carrier solid = A, Pure solvent = B

Soluble solute = C

Mass balance,

$$F+S - V+L - M$$

Solute balance, $F(x_C)_F + S(y_C)_S = V(y_C)_V + L(x_C)_L$

$$= M(x_C)_M$$

$$(x_C)_M = \frac{F(x_C)_F+S(y_C)_S}{\cancel{F+S}\ F}$$

Using Ponchon – Savarit Diagram

Under flow (Leached solid) :

$$X_C = \frac{x_C}{x_B+x_C}, Z_L = \frac{x_A}{x_B+x_C}$$

Overflow (Leach solution) :

$$Y_C = \frac{y_C}{y_B+y_C}, Z_V = \frac{y_A}{y_B+y_C}$$

Like the single stage operation that is for extraction whatever we have discussed the same thing is applied here means the leaching process suppose we have the solid to be least means this is one particular solid with insoluble A mass insoluble or inert is there, then here actually in leaching process we are adding this leaching solvent like extracting solvent, then under flow will be there where the inert will be coming with the small amount of this one target component say C.

And the overflow will be there that is actually our interest like this, like this this insoluble carrier so this on A, like equivalent to carrier solvent in the liquid liquid extraction process then pure solvent that is actually added like this starting solvent, then soluble solute that is the target component present in the inert.

And we will be doing the mass balance:

F+S=V+L=M

If we do the solute balance:

$$F(x_C)_F + S(y_C)_S = V(y_C)_V + L(x_C)_L = M(x_C)_M$$

So, using **Ponchon Savarit**

Under flow (Leached solid) : $X_C = \frac{x_C}{x_B+x_C}$, $Z_L = \frac{x_A}{x_B+x_C}$

Overflow (Leach solution) : $Y_C = \frac{y_C}{y_B+y_C}$, $Z_V = \frac{y_A}{y_B+y_C}$

$F' =$ kg non solid

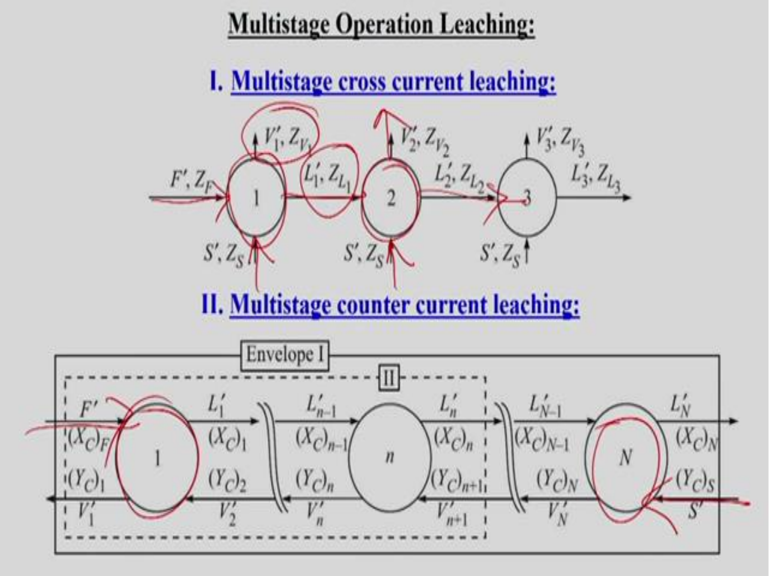
$$Z'_F = \frac{\text{kg solid}}{\text{kg non solid}}$$

Material balance, $F' + S' = L' + V' = M'$

Solute balance, $F'Z'_F + S'Z'_S = L'Z'_L + V'Z'_V = M'Z'_M$

$$Z'_M = \frac{F'Z'_F + S'Z'_S}{F' + S'}$$

(Refer Slide Time: 05:12)



Multistage Operation Leaching:

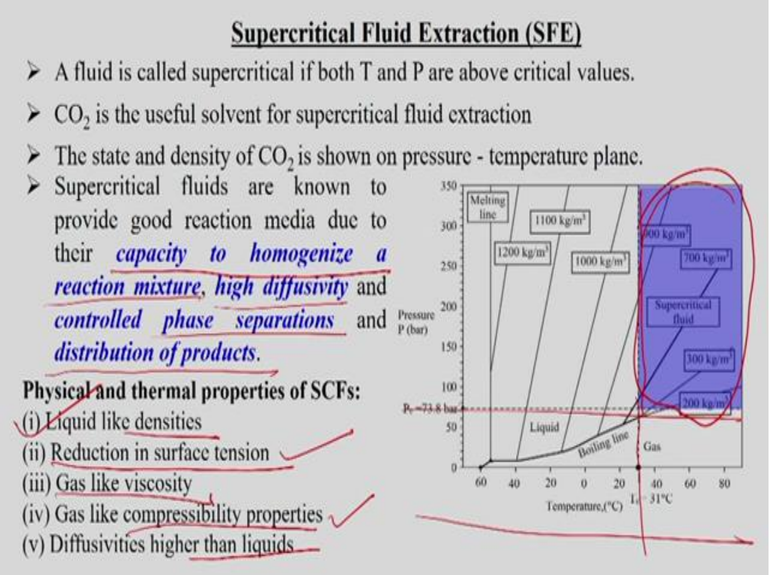
I. Multistage cross current leaching:

II. Multistage counter current leaching:

Like this Multistage leaching operation similar to that of the extraction process, suppose this feed is entering and extracting solvent is added then we have this overflow then underflow, then underflow of the stage 1 will be the feed to the stage 2, then again we are adding solvent and then we are getting overflow like that is continued.

And in case of the multistage counter current process so here feed is entering at stage 1 and solvent is adding from the last stage, that is N stage and the procedure is same like whatever we have discussed in case of the solid liquid liquid extraction process.

(Refer Slide Time: 05:54)



Supercritical Fluid Extraction (SFE)

- A fluid is called supercritical if both T and P are above critical values.
- CO_2 is the useful solvent for supercritical fluid extraction
- The state and density of CO_2 is shown on pressure - temperature plane.
- Supercritical fluids are known to provide good reaction media due to their *capacity to homogenize a reaction mixture, high diffusivity* and *controlled phase separations* and *distribution of products.*

Physical and thermal properties of SCFs:

(i) Liquid like densities
(ii) Reduction in surface tension
(iii) Gas like viscosity
(iv) Gas like compressibility properties
(v) Diffusivities higher than liquids

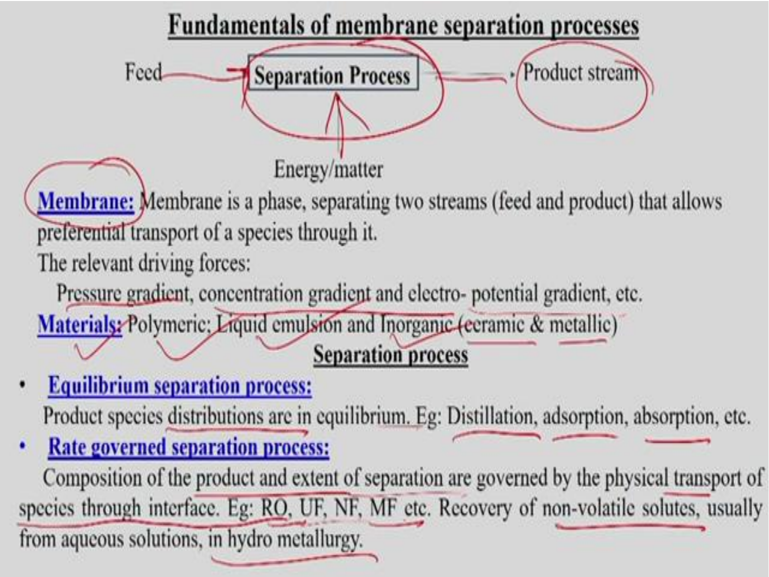
And another point actual we discuss this under this solid liquid extraction process or leaching that is the super critical feed extraction that is in this in case of this this one what is called

TBT diagram, suppose this above a critical particular temperature and above a critical pressure there is 1 zone where it is actually to behaving as supper critical fluid.

So, a fluid is called supercritical if both temperature and pressure are above critical point. CO2 is useful solvent for the supercritical fluid extraction process. The, this one state and density of this CO2 is shown on pressure temperature plane, then supercritical fluids are known to provide this good reaction medium due to their this capacity to homogenize a reaction mixture high diffusivity and controlled phase separations and distribution of the products.

So that is one of this green extraction process with this high efficiency, physical and thermal properties of the supercritical fluids are like this liquid like densities are there for the supercritical fluid the reduction in the surface tension, then Gas like viscosity that is required then gas like compressibility also that is also good and diffusivities value actually is higher than the liquid and the we sometimes the extraction ability is so many folds higher than that of these liquid.

(Refer Slide Time: 07:52)



Fundamentals of membrane separation processes

Membrane: Membrane is a phase, separating two streams (feed and product) that allows preferential transport of a species through it.

The relevant driving forces:

Pressure gradient, concentration gradient and electro- potential gradient, etc.

Materials: Polymeric; Liquid emulsion and Inorganic (ceramic & metallic)

Separation process

- **Equilibrium separation process:**
  Product species distributions are in equilibrium. Eg: Distillation, adsorption, absorption, etc.
- **Rate governed separation process:**
  Composition of the product and extent of separation are governed by the physical transport of species through interface. Eg: RO, UF, NF, MF etc. Recovery of non-volatile solutes, usually from aqueous solutions, in hydro metallurgy.

Now, we will be discussing this membrane separations technology there this we have already discuss this fundamentals of the membrane separation process like say if we say this is the process then feed is entering and we are suppose suppling energy or matter, then products are actually formed like this, so for that we described this membrane as we say phase, separating two streams like this feed and product that allows the preferential transport of a species through this barrier.

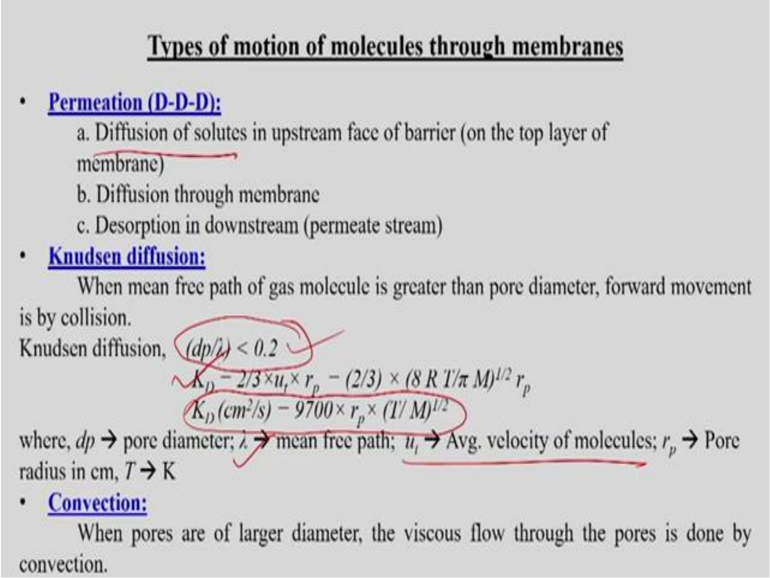
Generally, we say this semipermeable barrier and it preferential is separate a particular component and means resisting one and allowing the other two pass through it. The relevant driving forces are like pressure gradient then concentration gradient then electro potential gradient etcetera. Like this the material are like this polymeric liquid emulsion then some inorganic like this like ceramic and metallic.

So, in separations processes at so far we have learned about this humidification, then dehumidification, then drying, then extraction, leaching, absorption, adsorption or and other processes, most of the processes are actually equilibrium separation processes like product species equilibrium distribution are in equilibrium, like say distillation or adsorption, absorption wherever the separation is controlled by the equilibrium.

When the process reaches it equilibrium then this physical separation stops and we need to break the equilibrium so that we get the separation. But now in membrane separation processes we will be learning something about different thing like it is the rate governed serration processes composition of the product and extent of separation are actually governed by the physical transport of the species through the interface, like reverse osmosis, ultrafiltration, Nano filtration, micro filtration et cetera.

And recovery of non-volatile solutes like sometimes aqueous solutions, in hydro metal of metallurgy. This are all rate governed separation processes, there equilibrium is not stablished at all.

(Refer Slide Time: 10:27)



Types of motion of molecules through membranes

- **Permeation (D-D-D):**
  a. Diffusion of solutes in upstream face of barrier (on the top layer of membrane)
  b. Diffusion through membrane
  c. Desorption in downstream (permeate stream)
- **Knudsen diffusion:**
  When mean free path of gas molecule is greater than pore diameter, forward movement is by collision.
  Knudsen diffusion, $(dp/\lambda) < 0.2$
  $$K_D = 2/3 \times u_t \times r_p = (2/3) \times (8 R T/\pi M)^{1/2} r_p$$
  $$K_D (cm^2/s) = 9700 \times r_p \times (T/M)^{1/2}$$
  where, dp → pore diameter; λ → mean free path; u_t → Avg. velocity of molecules; r_p → Pore radius in cm, T → K
- **Convection:**
  When pores are of larger diameter, the viscous flow through the pores is done by convection.

Like this this types of motion of the molecules through the membranes that is one is the permeation D-D-D concept like this a diffusion of the solutes in the upstream face of the barrier and then diffusion through the membrane and then desorption in the downstream.

And another one is Knudsen diffusivities, say when the mean free path of gas molecules especially is greater than that of the pore diameter through which the gas will be permitting then forward movement actually is done by collision. And then Knudsen diffusivities actually or Knudsen diffusion controls the transport of the gas species through the pores.

Knudsen diffusion, $(dp/\lambda) < 0.2$

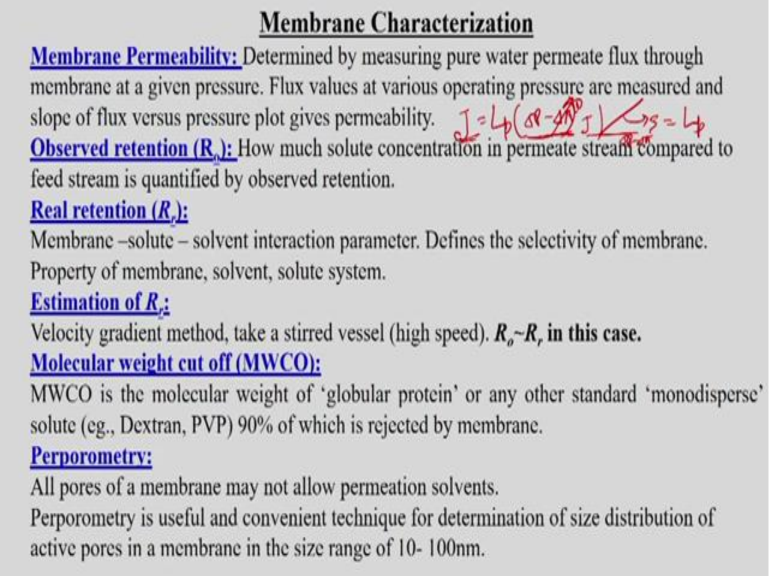
$$K_D = 2/3 \times u_t \times r_p = (2/3) \times (8 R T/\pi M)^{1/2} r_p$$

$$K_D (cm^2/s) = 9700 \times r_p \times (T/M)^{1/2}$$

where, dp → pore diameter; λ → mean free path; u_t → Avg. velocity of molecules; r_p → Pore radius in cm, T → K

When pores are larger diameter the viscous flow through the pores is done by this convection also, sometimes convective this one flow is there also.

(Refer Slide Time: 12:32)



Membrane Characterization

Membrane Permeability: Determined by measuring pure water permeate flux through membrane at a given pressure. Flux values at various operating pressure are measured and slope of flux versus pressure plot gives permeability.

$J = L_p(\Delta P - \Delta\pi)$ J $\Delta P - \Delta\pi$ $S = L_p$

Observed retention (R_o): How much solute concentration in permeate stream compared to feed stream is quantified by observed retention.

Real retention (R_r):

Membrane –solute – solvent interaction parameter. Defines the selectivity of membrane. Property of membrane, solvent, solute system.

Estimation of R_r:

Velocity gradient method, take a stirred vessel (high speed). **R_o~R_r in this case.**

Molecular weight cut off (MWCO):

MWCO is the molecular weight of 'globular protein' or any other standard 'monodisperse' solute (eg., Dextran, PVP) 90% of which is rejected by membrane.

Perporometry:

All pores of a membrane may not allow permeation solvents.

Perporometry is useful and convenient technique for determination of size distribution of active pores in a membrane in the size range of 10- 100nm.

Then we have learned in detail about the membrane characterisation in terms of permeability that is the ability of the membrane to permeate the solvent through that at a given pressure and if the permeability value is very high then it is highly productive or through (())(12:54) is very high. Flux values at various operating pressures are measured and the slope of the flux versus pressure plot gives the permeability.

As the as per the Darcy's law:

$J=Lp(\Delta P-\Delta\pi)$

where ($\Delta P-\Delta\pi$) is the driving force and this flux that we can see if we plot this one J verses ($\Delta P-\Delta\pi$) then you will be getting 1 slope, this straight line the slope actually will be getting s is equal to nothing but Lp.

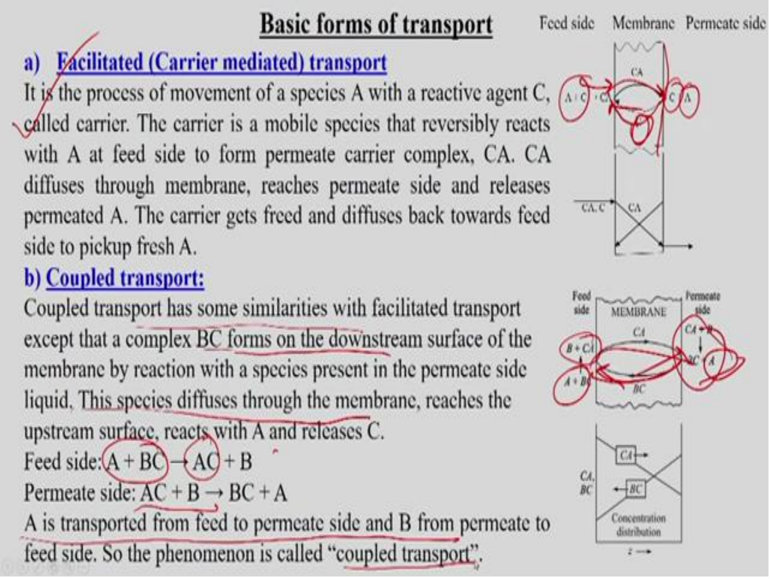
If we take pure water then this $\Delta\pi$ will be 0, so Lp is equal to J is equal to Lp into del P. And another term actually we have learned that is this observed retention, how much solute concentration in the permeate stream compared to the feed stream is quantified by this observed retention.

And real retention was like this membrane solute solvent interaction parameter that is defines the selectivity of the membrane. Property of then this property this is the property of the membrane solvent solute system. And R R actually is estimated in using this velocity gradient method or a we need to take stirred start vessel then with high speed then this one observed retention and real retention will be same in that case.

Then other important characteristic was like molecular weight cut off. Then molecular weight cut off of the is the molecular of the globular protein or any other standard monodispersed solute like this that is like Dextran PVP or PVA like this 90 percent of which is rejected by the membrane their corresponding value actually is terminate molecular weight cut off.

Then Perporometry there is all pores of a membrane may not allow this permeation of the solvent. So, then perporometry is useful and convenient technique for determination of the size distribution of the active pores in a membrane in the size range of 10 to 100 Nano meter.

(Refer Slide Time: 15:15)



Basic forms of transport

a) Facilitated (Carrier mediated) transport

It is the process of movement of a species A with a reactive agent C, called carrier. The carrier is a mobile species that reversibly reacts with A at feed side to form permeate carrier complex, CA. CA diffuses through membrane, reaches permeate side and releases permeated A. The carrier gets freed and diffuses back towards feed side to pickup fresh A.

b) Coupled transport:

Coupled transport has some similarities with facilitated transport except that a complex BC forms on the downstream surface of the membrane by reaction with a species present in the permeate side liquid. This species diffuses through the membrane, reaches the upstream surface, reacts with A and releases C.

Feed side: $A + BC \rightarrow AC + B$

Permeate side: $AC + B \rightarrow BC + A$

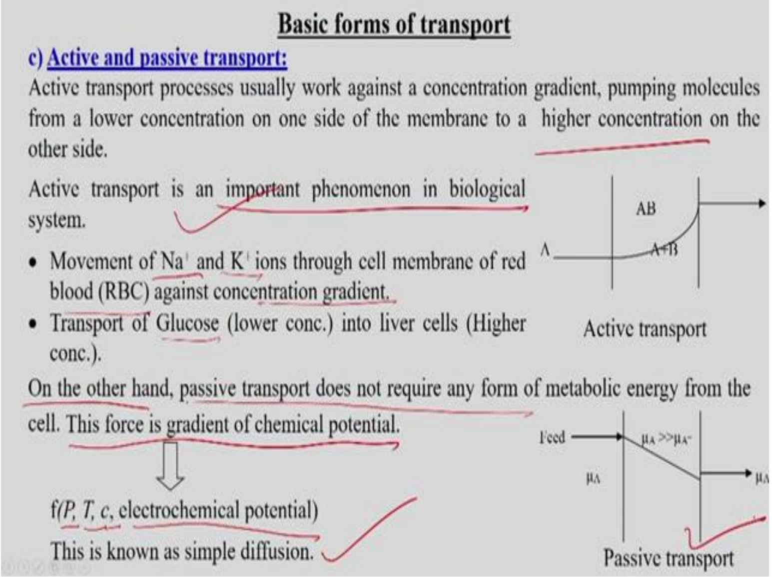
A is transported from feed to permeate side and B from permeate to feed side. So the phenomenon is called "coupled transport".

Now the basic forms of the transport like this one of this facilitated transport like this carrier mediated transport and like this first one like this, A plus C that will coming as CA and it will be transport porting to this opposite side of the membrane and then it will be separated into C and A and carrier will be coming back to the back side of the feed.

And then this is carrier mediated transport, whenever we will be talking about this coupled transport, this coupled transport actually has some similarities with the facilitated transport except that of the complex BC, forms on the downstream surface like this one where only C came back in case of the facilitated transport of the membrane by reaction with these species present in the permeate side of the liquid.

This species diffuses through the membrane, reaches the upstream surface reacts with A and releases C like this, this case. So, feed side we have this A plus BC like this A plus BC we have or like B plus C whatever may be then CA will be transporting. Then AC will be there and B will be and permeate side AC is coming here and then reacting with B to release A and then BC will come back, so A is transported from feed to permeate side and B from B from permeate to feed side. So, the phenomenon is called the coupled transport.

(Refer Slide Time: 16:53)



Basic forms of transport

c) Active and passive transport:

Active transport processes usually work against a concentration gradient, pumping molecules from a lower concentration on one side of the membrane to a higher concentration on the other side.

Active transport is an important phenomenon in biological system.

- Movement of Na^+ and K^+ ions through cell membrane of red blood (RBC) against concentration gradient.
- Transport of Glucose (lower conc.) into liver cells (Higher conc.).

On the other hand, passive transport does not require any form of metabolic energy from the cell. This force is gradient of chemical potential.

⇩

f(*P*, *T*, *c*, electrochemical potential)

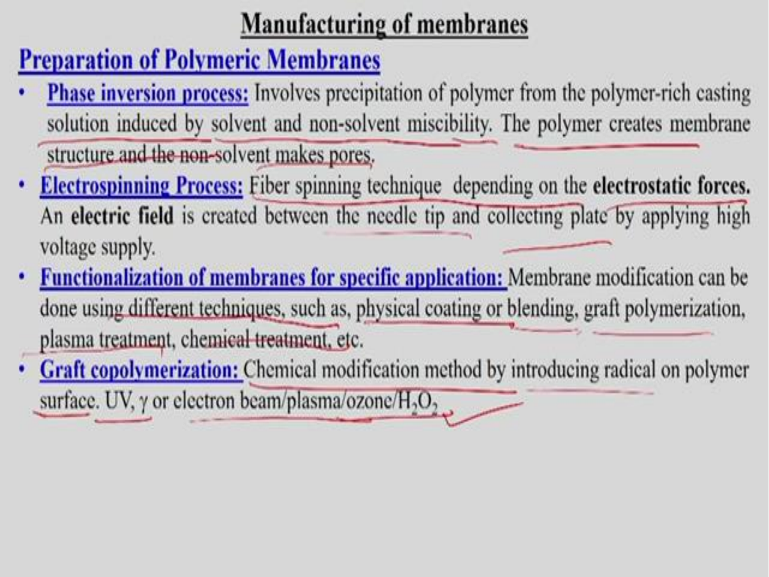
This is known as simple diffusion.

Now, this active and passive transport is there through the membrane like this, this are the basic form of the transport. Active transport processes usually work against a concentration gradient, this pumping molecules from a lower concentration on one side of the membrane to a higher concentration on the other side like this. So, that is why we can see this one that is active transport is an important phenomenon in biological system.

Movement of like sodium plus and kot potassium plus ions through the cell membrane of red blood cells against the concentration gradient is example of this active transport. Transport of this glucose like this and lower concentration into liver cells are like at the higher concentration also.

On the other hand, this passive transport does not require any form of this metabolic energy from the cell. This force is the gradient of the chemical potential. Like this pressure temperature concentration electrochemical potential so this is known as simple diffusion. This is the passive transport.

(Refer Slide Time: 18:04)



Manufacturing of membranes

Preparation of Polymeric Membranes

- **Phase inversion process:** Involves precipitation of polymer from the polymer-rich casting solution induced by solvent and non-solvent miscibility. The polymer creates membrane structure and the non-solvent makes pores.
- **Electrospinning Process:** Fiber spinning technique depending on the **electrostatic forces.** An **electric field** is created between the needle tip and collecting plate by applying high voltage supply.
- **Functionalization of membranes for specific application:** Membrane modification can be done using different techniques, such as, physical coating or blending, graft polymerization, plasma treatment, chemical treatment, etc.
- **Graft copolymerization:** Chemical modification method by introducing radical on polymer surface. UV, γ or electron beam/plasma/ozone/H_2O_2.

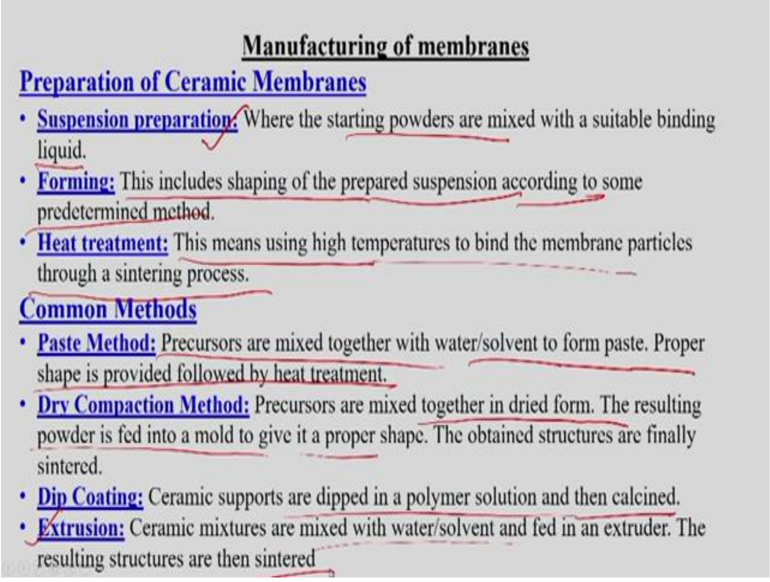
So, now this manufacturing of the membrane like this preparation of the polymeric membrane there are so many techniques one major or important technique is this phase inversion technique, it involves the precipitation of polymer from the polymer rich casting solution induced by the solvent and non-solvent miscibility. The polymer creates membrane structure and the non-solvent actual make the pores.

An another process is the electrospinning process like this fibber spinning technique depending on the electrostatic force that this one fibbers are form. Then an electric field is created between the needle tip and the collecting plate by applying the high voltage supply. And then from there actually using this spinning the field actually is formed.

Then functionalization of the membrane for specific applications are this one is very this standard technique membrane modification can be done using this different technique, such as this physical coating or blending, graft polymerization, then plasma treatment, chemical treatment et cetera.

Then graft copolymerization that is also one important manufacturing process like chemical modification method by introducing this radical on the polymeric surface like this using this UV or gamma or electron beam or plasma or ozone or hydrogen peroxide, this graft copolymerization also is the done for the polymeric membranes.

(Refer Slide Time: 19:51)



Manufacturing of membranes

Preparation of Ceramic Membranes

- **Suspension preparation:** Where the starting powders are mixed with a suitable binding liquid.
- **Forming:** This includes shaping of the prepared suspension according to some predetermined method.
- **Heat treatment:** This means using high temperatures to bind the membrane particles through a sintering process.

Common Methods

- **Paste Method:** Precursors are mixed together with water/solvent to form paste. Proper shape is provided followed by heat treatment.
- **Dry Compaction Method:** Precursors are mixed together in dried form. The resulting powder is fed into a mold to give it a proper shape. The obtained structures are finally sintered.
- **Dip Coating:** Ceramic supports are dipped in a polymer solution and then calcined.
- **Extrusion:** Ceramic mixtures are mixed with water/solvent and fed in an extruder. The resulting structures are then sintered

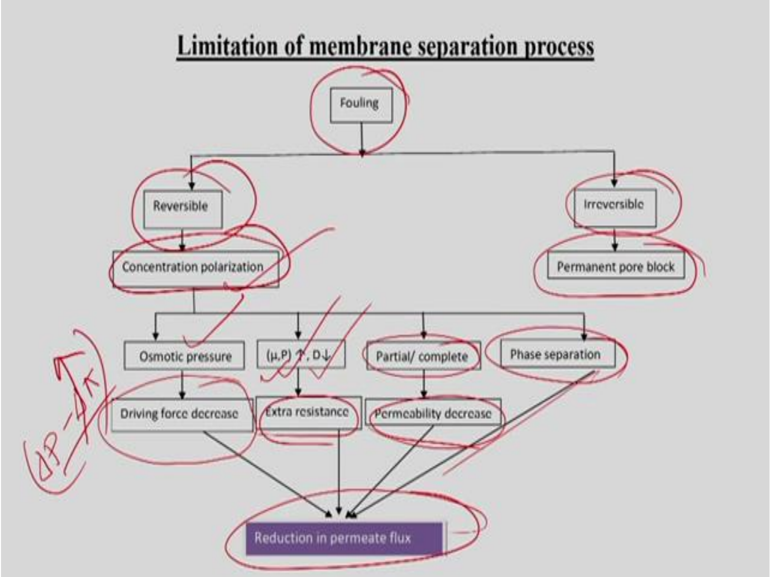
Now, this for ceramic membranes the preparations of ceramic membranes are done by mostly the suspension preparation for the starting powders are mixed with a suitable binding liquids. Then forming is done this shaping of the prepared suspension according to some predetermined method. Then heat treatment is done this means this one using high temperature to bind the membrane particles through sintering process.

Then some common methods are like this paste method like these precursors are mixed together with water solvent to form this paste. Then proper shape is given using the dyes. Another one is the dry compaction method, the precursors are mixed with mixed together in dried from. The resulting powder actually is fed into the mould to give a it a proper shape. The obtained structures are actually finally sintered

(20:47).

Another one is the dip coating method like this ceramic supports are dipped in polymeric solution and then calcined. Means it is burned and another important method is the extrusion the ceramic mixtures are mixed with the water or solvent and then fed in extruder. The resulting structures are then say burned actually.

(Refer Slide Time: 21:12)



Limitation of membrane separation process

Fouling

Reversible

Irreversible

Concentration polarization

Permanent pore block

Osmotic pressure

$(\mu, P)\uparrow, D\downarrow$

Partial/ complete

Phase separation

Driving force decrease

Extra resistance

Permeability decrease

Reduction in permeate flux

$\Delta P - \Delta\pi$

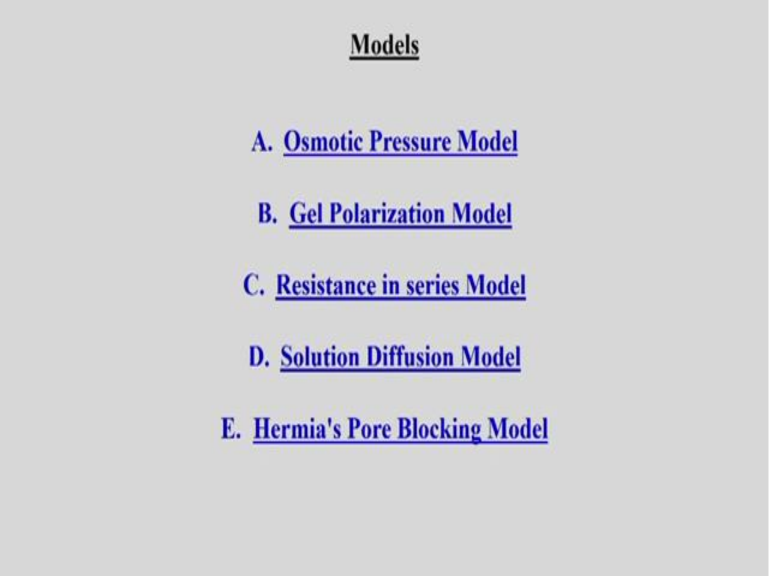
Then we have already discussed in detail about the limitation of the membrane separation processes like this we also highlighted that the fouling is the major drawback of the membrane separation processes because as this is the red separations processes with time the solutes will be deposited on the membrane surface and then fouling will take place. And that fouling may be of 2 type like 1 is the reversible fouling and another is the irreversible fouling.

The reversible fouling is due to this concentration polarization or deposition of the solute on the membrane surface and the irreversible fouling is due to the permanent pore blocking. For this concentration polarization osmotic pressure is developed then viscosity pressure will be increasing then diffusivity will be decreasing then partial or complete pore blocking will take place then phase separation also will take place.

Then due to this osmotic pressure development driving force will be decreasing because CC driving force was del P minus delta pi as it is increasing so $\Delta P - \Delta\pi$ will go on decreasing then extra resistance will be created and permeability will be decreasing.

And ultimately this reduction in the permeate flux, so that is one of the drawbacks. So, there are so many methods to decrease the fouling of the membrane separation processes.

(Refer Slide Time: 22:49)



Models

A. Osmotic Pressure Model

B. Gel Polarization Model

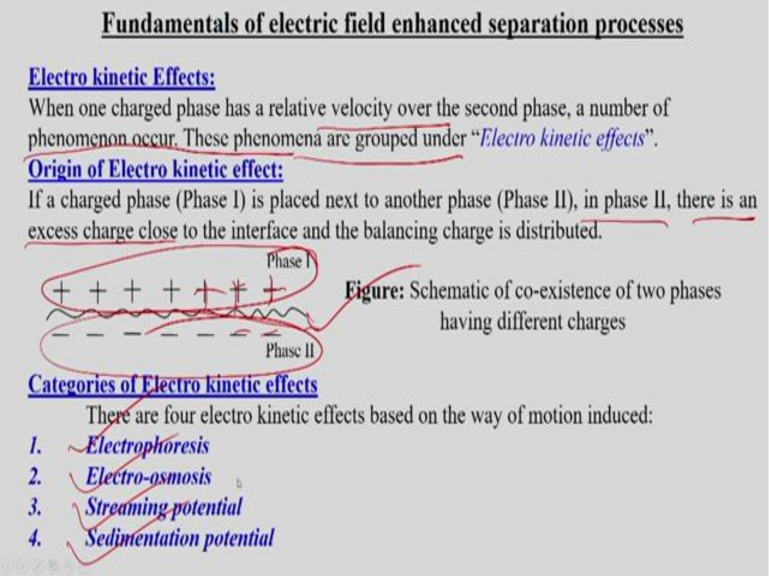
C. Resistance in series Model

D. Solution Diffusion Model

E. Hermia's Pore Blocking Model

Now this different module we have discussed in detail about this say model like this osmotic pressure model then gel polarization model, resistance in series model, solution diffusion model and then Hermia's pore blocking model.

(Refer Slide Time: 22:58)



Fundamentals of electric field enhanced separation processes

Electro kinetic Effects:

When one charged phase has a relative velocity over the second phase, a number of phenomenon occur. These phenomena are grouped under "*Electro kinetic effects*".

Origin of Electro kinetic effect:

If a charged phase (Phase I) is placed next to another phase (Phase II), in phase II, there is an excess charge close to the interface and the balancing charge is distributed.

Figure: Schematic of co-existence of two phases having different charges

Categories of Electro kinetic effects

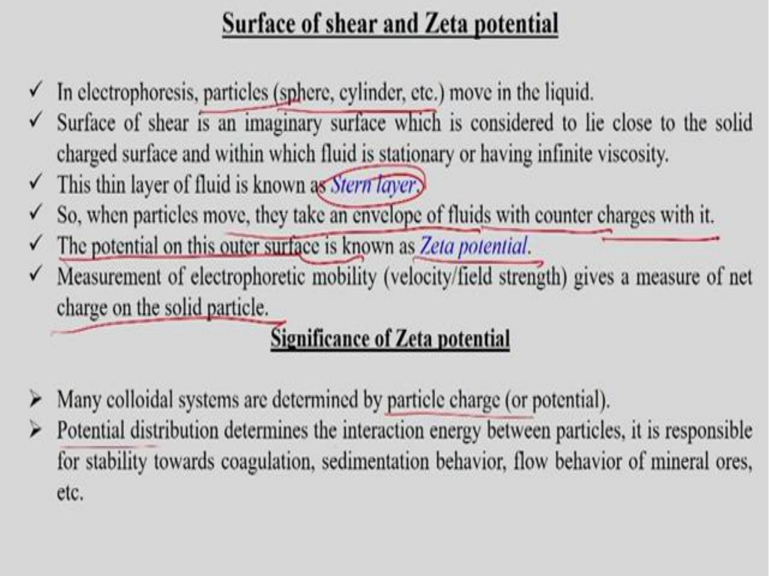
There are four electro kinetic effects based on the way of motion induced:

1. *Electrophoresis*
2. *Electro-osmosis*
3. *Streaming potential*
4. *Sedimentation potential*

And then we have discussed in detail about the fundamentals of the electric field enhanced separation processes. In the membranes and for that actually initially we discussed about the electro kinetic effects like the on one charged phase has a relative velocity over the second phase, a number of phenomenon actually occur. This phenomenon is general is grouped as electro kinetic effect like this.

So, for that we discussed about the origin of the electro kinetic effects, like if a charged phase like this suppose this phase 1 is placed next to another phase like this phase 2, so then so there is an excess charge close to that of the interface and the balancing charge is distributed like this. So suppose this plus minus plus minus this will be distributed and and then we have discussed about the categories of the electro kinetic effects like electrophoresis, electro osmosis, streaming potential, then sedimentation potential.

(Refer Slide Time: 24:06)



Surface of shear and Zeta potential

- ✓ In electrophoresis, particles (sphere, cylinder, etc.) move in the liquid.
- ✓ Surface of shear is an imaginary surface which is considered to lie close to the solid charged surface and within which fluid is stationary or having infinite viscosity.
- ✓ This thin layer of fluid is known as *Stern layer*.
- ✓ So, when particles move, they take an envelope of fluids with counter charges with it.
- ✓ The potential on this outer surface is known as *Zeta potential*.
- ✓ Measurement of electrophoretic mobility (velocity/field strength) gives a measure of net charge on the solid particle.

Significance of Zeta potential

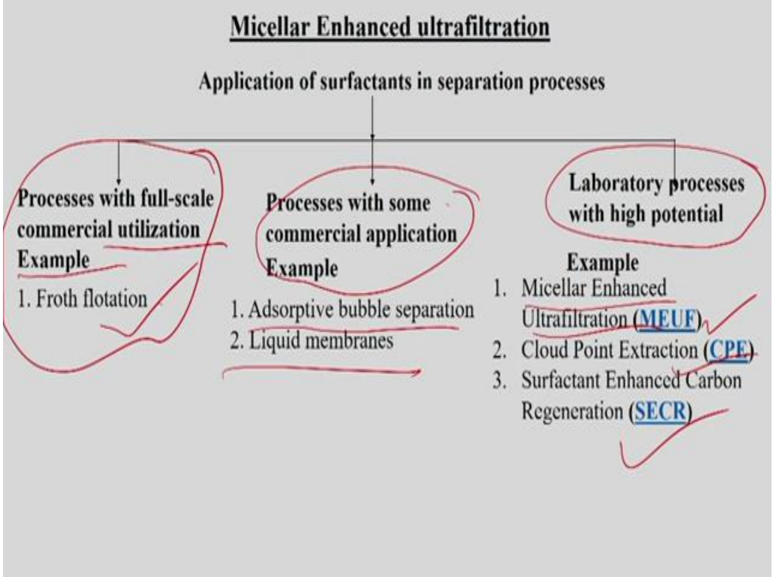
- ➢ Many colloidal systems are determined by particle charge (or potential).
- ➢ Potential distribution determines the interaction energy between particles, it is responsible for stability towards coagulation, sedimentation behavior, flow behavior of mineral ores, etc.

Then we have discussed in detail about the surface and shear and surface of the shear and the zeta potential. So, in electrophoresis these particles like this this sphere or cylinders move in the liquid and then surface of the shear is an imaginary surface actually which is considered to lie close to the solid charged surface and within which the fluid is stationary or having this infinity infinite viscosity.

This film, this thin film layer actually of the fluid is knowns as the stern layer. And so when particles move, they take an envelope of this fluids with counter charges with it. So, the potential on this outer surface is known as zeta potential. And the measurement of electrophoretic mobility gives a measure of this this one net charge actually on the solid particles.

And we have discussed in detail about the significance of the zeta potential. Like many colloidal systems are determined by the particle charge or this potential. And potential distribution determines the interaction energy between this particles, it is responsible for stability toward the coagulation, sedimentation behaviour, flow behaviour of this mineral ores, et cetera.

(Refer Slide Time: 25:37)



Micellar Enhanced ultrafiltration

Application of surfactants in separation processes

Processes with full-scale commercial utilization
Example
1. Froth flotation

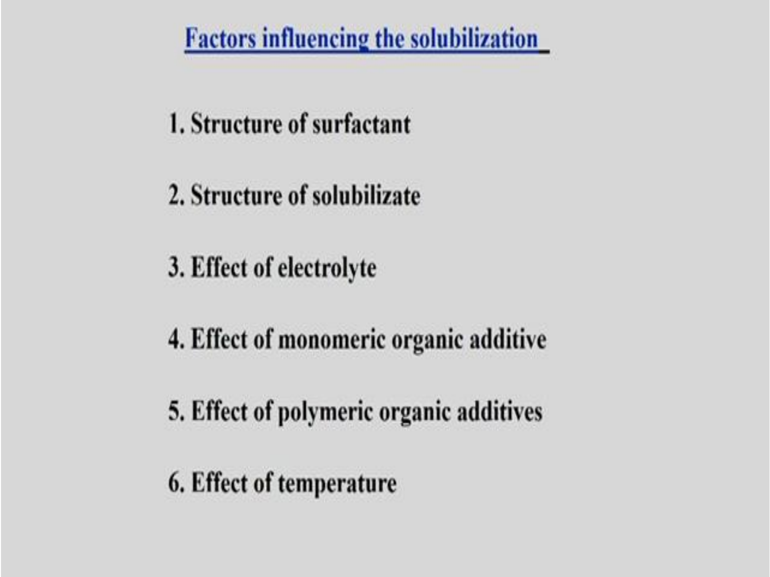
Processes with some commercial application
Example
1. Adsorptive bubble separation
2. Liquid membranes

Laboratory processes with high potential
Example
1. Micellar Enhanced Ultrafiltration (MEUF)
2. Cloud Point Extraction (CPE)
3. Surfactant Enhanced Carbon Regeneration (SECR)

Then we have discussed in detail about the micellar enhanced ultrafiltration where if the surfactants are solubilised over there critical micelle concentration then micelle is formed then this micellar will be able to trap these solutes and then make the big globules.

Then this one process with full scale commercial utilization examples are like froth flotation is there process with some commercial application like this adsorptive bubble separation or liquid membraned are there and laboratory processes with high potential like this micellar enhanced ultrafiltration MEUF, then cloud point extraction CPE and then surfactant enhanced carbon regeneration SECR.

(Refer Slide Time: 26:33)

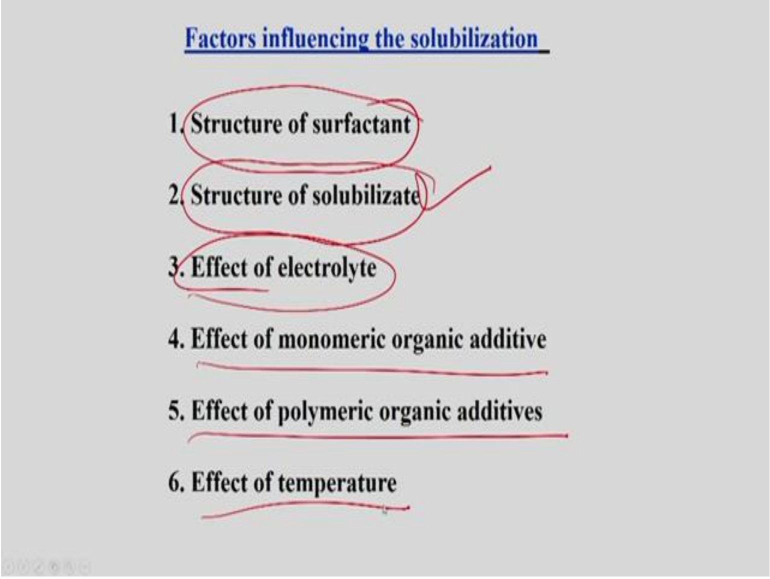


Factors influencing the solubilization

1. Structure of surfactant
2. Structure of solubilizate
3. Effect of electrolyte
4. Effect of monomeric organic additive
5. Effect of polymeric organic additives
6. Effect of temperature

Then in surfactant based separation process or MEUF there actually we have discussed the surfactant are surface active agents like may be ionic surfactant then non-ionic surfactants, zwitterionic surfactant are there but as the ionic surfactant are of 2 types like this cationic surfactant like CPC cetyl pyridinium chloride or anionic surfactant are like sodium dodecyl sulfate or like these or sometime this in aqueous solution CPC and SDS both are divided into this one ionic forms like cetyl pyridinium plus and dodecyl sulfate minus.

(Refer Slide Time: 27:12)

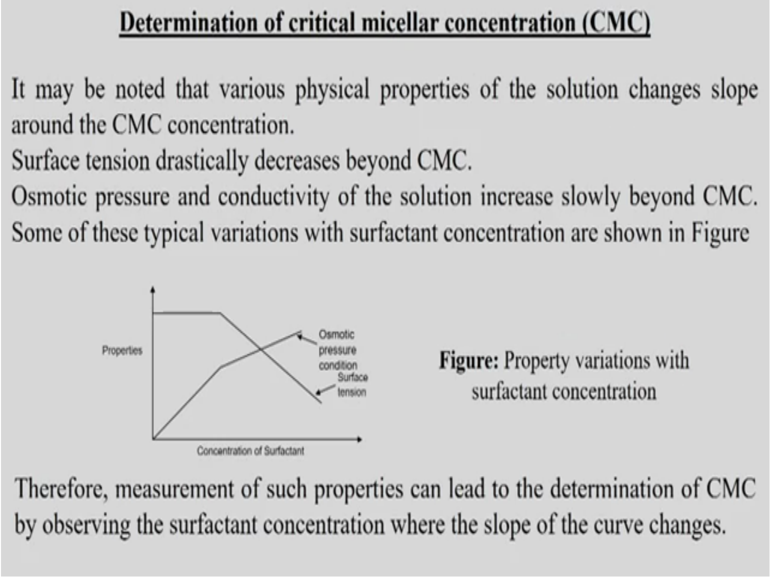


Factors influencing the solubilization

1. Structure of surfactant
2. Structure of solubilizate
3. Effect of electrolyte
4. Effect of monomeric organic additive
5. Effect of polymeric organic additives
6. Effect of temperature

And the factors that influencing the solubilisation are like this structure of the surfactant like this and structure of the solubilizate which we actually try to trap using the surfactant, then effect of the electrolyte then effect of the monomeric organic additive, then effects of the polymeric organic additives, then effect of temperature also.

(Refer Slide Time: 27:34)



Determination of critical micellar concentration (CMC)

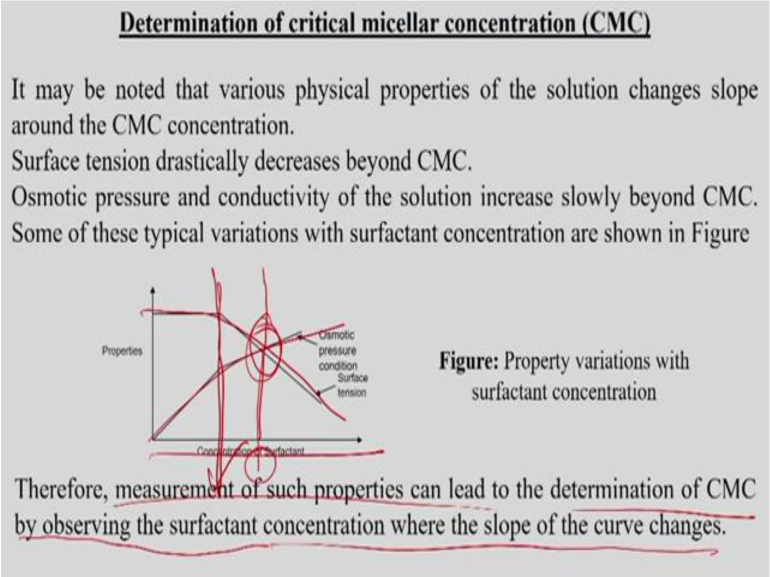
It may be noted that various physical properties of the solution changes slope around the CMC concentration.
Surface tension drastically decreases beyond CMC.
Osmotic pressure and conductivity of the solution increase slowly beyond CMC.
Some of these typical variations with surfactant concentration are shown in Figure

Figure: Property variations with surfactant concentration

Therefore, measurement of such properties can lead to the determination of CMC by observing the surfactant concentration where the slope of the curve changes.

Then we learned something about the critical micellar concentration, so that beyond a particular concentration of the monomer, the these from globules and enter into the bulk of the solution like this like one globule. So, these globules or agglomerates of monomers are spherical in shape to have the minimum surface energy and is known as the micelles. So, whenever we say this one minimum amount of concentration of surfactant required to make that micelle is called critical micellar concentration or CMC.

(Refer Slide Time: 28:11)



Determination of critical micellar concentration (CMC)

It may be noted that various physical properties of the solution changes slope around the CMC concentration.
Surface tension drastically decreases beyond CMC.
Osmotic pressure and conductivity of the solution increase slowly beyond CMC.
Some of these typical variations with surfactant concentration are shown in Figure

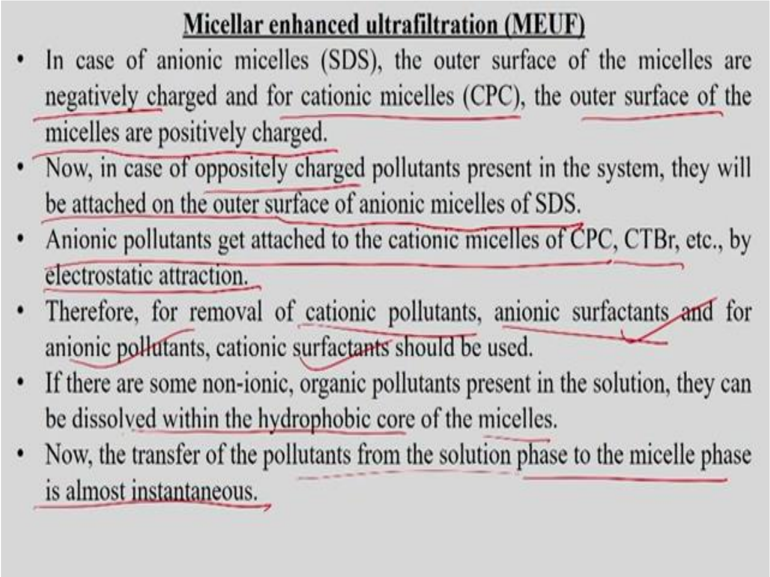
Figure: Property variations with surfactant concentration

Therefore, measurement of such properties can lead to the determination of CMC by observing the surfactant concentration where the slope of the curve changes.

Now we also discuss the determination of the critical micellar concentration for different surfactants like this a concentration of surfactant is plotted with surface tension and osmotic pressure where it cut actually from there it gives this the concentration of the critical micellar concentration.

So, therefore the measurement of such properties can lead to the determination of the CMC by observing the surfactant concentration where slope of the curve changes or where like this, this one or where the appropriate change in the properties change place, like this may be CMC or sometimes sometimes when these different properties actually intersect each other that will also is a CMC value.

(Refer Slide Time: 28:57)



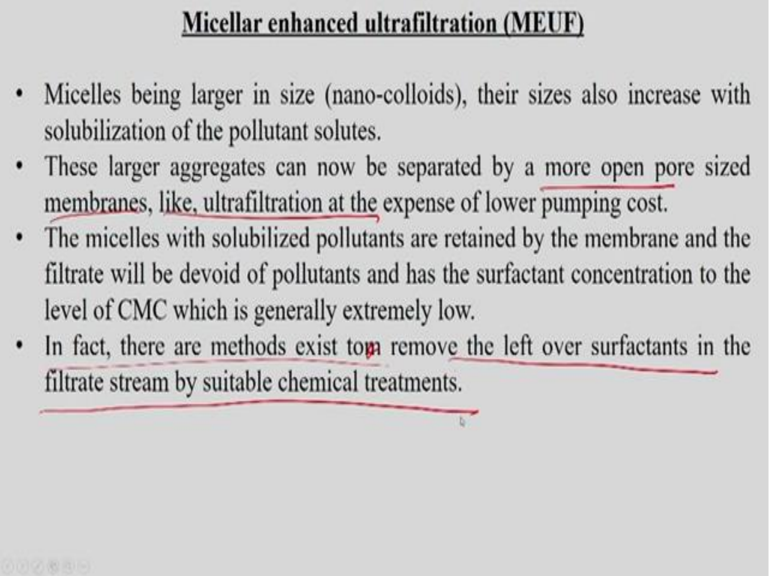
Micellar enhanced ultrafiltration (MEUF)

- In case of anionic micelles (SDS), the outer surface of the micelles are negatively charged and for cationic micelles (CPC), the outer surface of the micelles are positively charged.
- Now, in case of oppositely charged pollutants present in the system, they will be attached on the outer surface of anionic micelles of SDS.
- Anionic pollutants get attached to the cationic micelles of CPC, CTBr, etc., by electrostatic attraction.
- Therefore, for removal of cationic pollutants, anionic surfactants and for anionic pollutants, cationic surfactants should be used.
- If there are some non-ionic, organic pollutants present in the solution, they can be dissolved within the hydrophobic core of the micelles.
- Now, the transfer of the pollutants from the solution phase to the micelle phase is almost instantaneous.

So, in case of the enhanced surfacted SDS the outer surface of the micelles, are negatively charged and for the cationic surfact my micelle the outer surface actually of the micelles are positively charged. Now, in case of the oppositely charged pollutants present in the system, they will be attached on the outer surface of anionic micelles of SDS like this. The anionic pollutants get attached to the cationic micelles of CPC, CTBr or this by electrostatic attraction like this.

Therefore, for removal of cationic pollutants, anionic surfactant are required and for anionic pollutants, cationic surfactant are required. If there are some non-ionic organic pollutants present in the solution, they can be actually dissolved within the hydrophobic core of the micelles. So, that way also sometimes this non-ionic or some hydro carbon also are trap inside the core of the micelle. So, now the transfer of the pollutants from the solution phase to the micelle phase is almost instantaneous.

(Refer Slide Time: 30:07)



Micellar enhanced ultrafiltration (MEUF)

- Micelles being larger in size (nano-colloids), their sizes also increase with solubilization of the pollutant solutes.
- These larger aggregates can now be separated by a more open pore sized membranes, like, ultrafiltration at the expense of lower pumping cost.
- The micelles with solubilized pollutants are retained by the membrane and the filtrate will be devoid of pollutants and has the surfactant concentration to the level of CMC which is generally extremely low.
- In fact, there are methods exist to remove the left over surfactants in the filtrate stream by suitable chemical treatments.

And say micelles being larger in size, their sizes also increase with solubilisation of the pollutant solutes. These larger aggregates can now be separated by this one more open pore sized membranes, like this, using ultrafiltration that is the beauty of the system. So, in fact there are methods exist to remove the left over surfactant in the filtrate system by suitable chemical treatment also.

(Refer Slide Time: 30:37)

Mechanism of MEUF

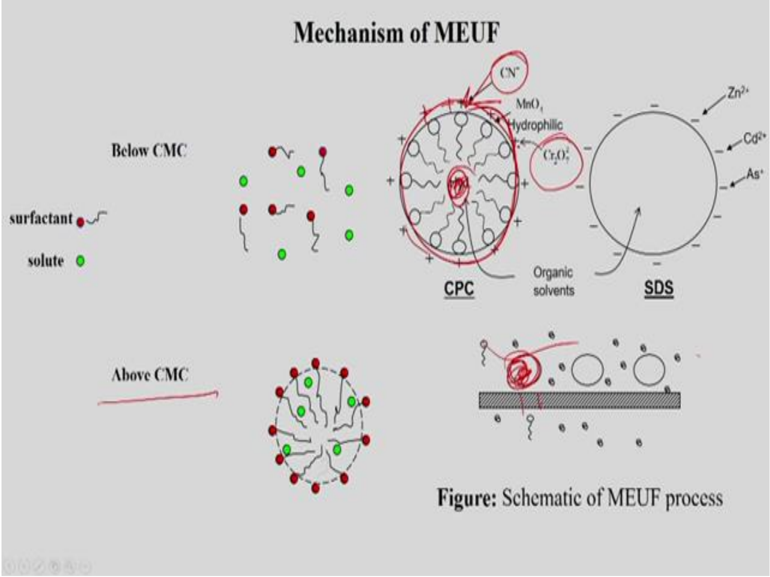
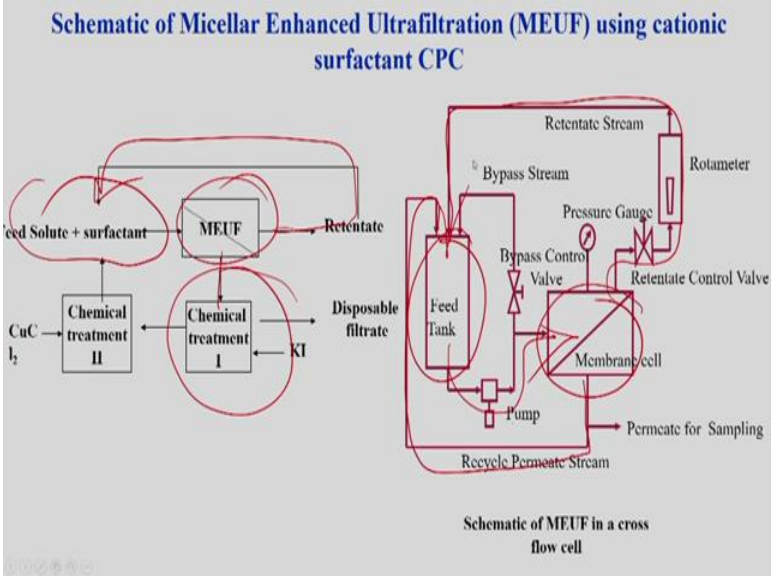


Figure: Schematic of MEUF process

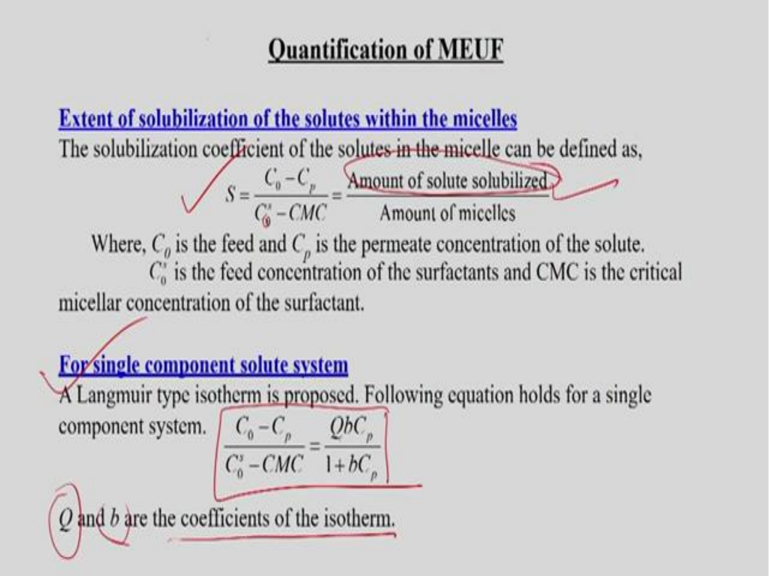
So, this is the mechanism of micelle, suppose this is the micelle and then suppose the cyanates will be trap here with the positive part of these outer surface and say chromate also will be trapped here and suppose this this sometime this hydrocarbon also will be trap inside this one or this one this, so solute particles will be trapped inside this micelle and then this will be separated using this (op) more open ultrafiltration membrane.

(Refer Slide Time: 31:10)



So, this is the schematic of the micellar enhanced ultrafiltration system using cationic surfactant CPC like this the feed solute and surfactant is added in the MEUF system then retentate will be recycle back to this system and then suing chemical treatment this again surfactant will be separated. And this is the schematic of the membrane separation process suppose feed is there it is entering into this membrane using this pump and then permeate actually is recycled back to the feed and whatever retentated is there it is again coming back to this feed tank.

(Refer Slide Time: 31:51)



Quantification of MEUF

Extent of solubilization of the solutes within the micelles

The solubilization coefficient of the solutes in the micelle can be defined as,

$$S = \frac{C_0 - C_p}{C_0^s - CMC} = \frac{\text{Amount of solute solubilized}}{\text{Amount of micelles}}$$

Where, C_0 is the feed and C_p is the permeate concentration of the solute. C_0^s is the feed concentration of the surfactants and CMC is the critical micellar concentration of the surfactant.

For single component solute system

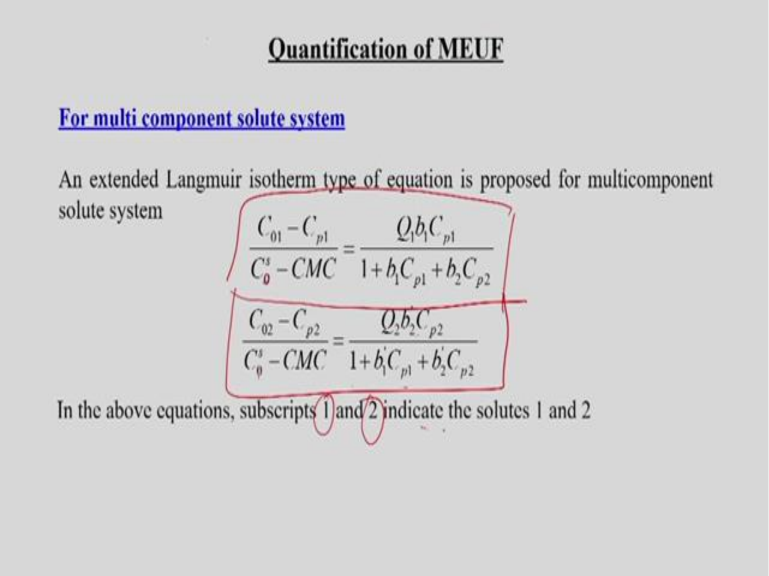
A Langmuir type isotherm is proposed. Following equation holds for a single component system. $\boxed{\frac{C_0 - C_p}{C_0^s - CMC} = \frac{QbC_p}{1 + bC_p}}$

Q and b are the coefficients of the isotherm.

Now, is a quantification of MUEF is done by this extent of solubilisation S is equal to C0 minus Cp by Cos minus CMC where this one is nothing but the amount of solute solubilized by amount of micelles. And for single component system we have:

$$\frac{C_0 - C_p}{C_0^s - CMC} = \frac{QbC_p}{1 + bC_p}$$

(Refer Slide Time: 32:27)



Quantification of MEUF

For multi component solute system

An extended Langmuir isotherm type of equation is proposed for multicomponent solute system

$$\frac{C_{01} - C_{p1}}{C_0^s - CMC} = \frac{Q_1 b_1 C_{p1}}{1 + b_1 C_{p1} + b_2 C_{p2}}$$

$$\frac{C_{02} - C_{p2}}{C_0^s - CMC} = \frac{Q_2 b_2 C_{p2}}{1 + b_1' C_{p1} + b_2' C_{p2}}$$

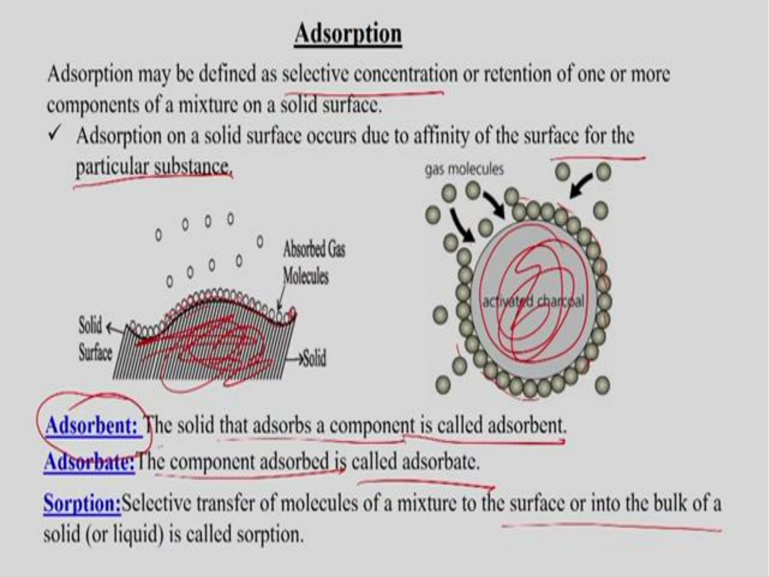
In the above equations, subscripts 1 and 2 indicate the solutes 1 and 2

And this extended Langmuir isotherm type this equation also is proposed for multicomponent solute system like:

$$\frac{C_{01} - C_{p1}}{C_0^s - CMC} = \frac{Q_1 b_1 C_{p1}}{1 + b_1 C_{p1} + b_2 C_{p2}}$$

$$\frac{C_{02} - C_{p2}}{C_0^s - CMC} = \frac{Q_2 b_2' C_{p2}}{1 + b_1' C_{p1} + b_2' C_{p2}}$$

(Refer Slide Time: 33:11)



Adsorption

Adsorption may be defined as selective concentration or retention of one or more components of a mixture on a solid surface.

✓ Adsorption on a solid surface occurs due to affinity of the surface for the particular substance.

Adsorbent: The solid that adsorbs a component is called adsorbent.

Adsorbate: The component adsorbed is called adsorbate.

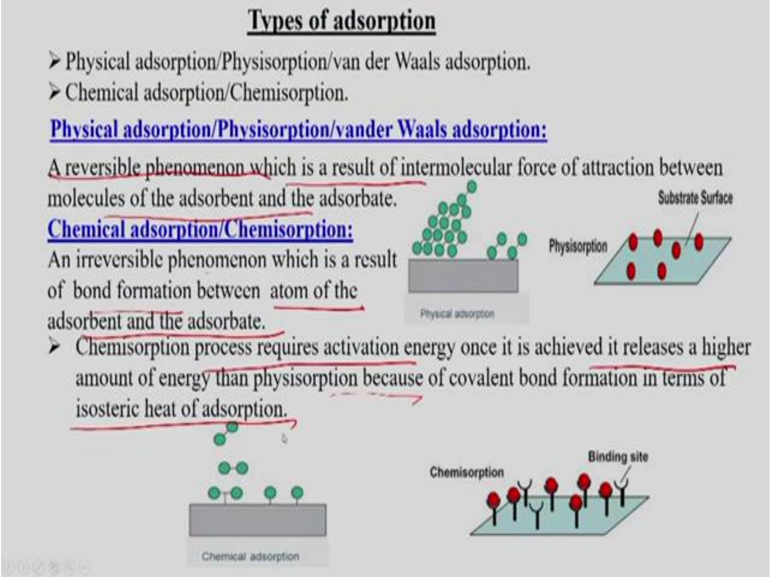
Sorption: Selective transfer of molecules of a mixture to the surface or into the bulk of a solid (or liquid) is called sorption.

And the 6th chapter is adsorption and Ion exchange. So, there adsorption process we explained that the see the surface phenomena, a adsorption may be define as the selective concentration or retention of one or more components of mixture on the solid surface. So, adsorption on a solid surface occurs due to the affinity of the surface for particular substance like this.

Suppose this is the solid substance and the expose surface is this one, this is the solid material the expo surface this and the absorbed gas molecules such the affinity on this surface then say this are actually stick on the outer surface of the solid material. Or this if we say activated charcoal then there also say suppose gas molecules will be absorbed on the outer surface of the active charcoal.

So, the term actually we this one learned adsorbent like the solid that adsorbs a component is called adsorbent. And adsorbate like this the component at adsorbed on the adsorbent that is called adsorbate. And the sorption process like this selective transfer of the molecules of the mixture to the surface or in the bulk of the solid is called sorption or sorption is the combination is the combination of adsorption and absorption, became in absorption in mass transfer operation one we have learned the see the bulk phenomena, now actually we have learned that adsorption is the surface phenomena. So, combination of this 2 is called sorption.

(Refer Slide Time: 34:45)



Types of adsorption

- Physical adsorption/Physisorption/van der Waals adsorption.
- Chemical adsorption/Chemisorption.

Physical adsorption/Physisorption/vander Waals adsorption:

A reversible phenomenon which is a result of intermolecular force of attraction between molecules of the adsorbent and the adsorbate.

Chemical adsorption/Chemisorption:

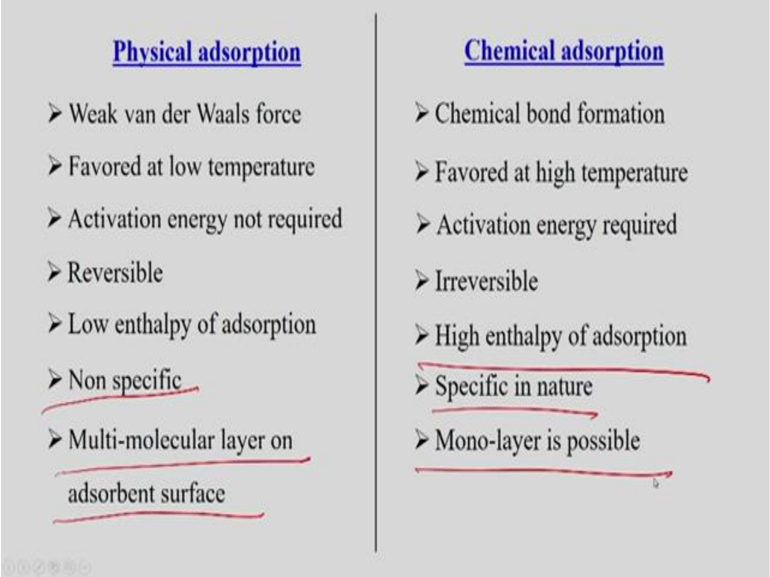
An irreversible phenomenon which is a result of bond formation between atom of the adsorbent and the adsorbate.

- Chemisorption process requires activation energy once it is achieved it releases a higher amount of energy than physisorption because of covalent bond formation in terms of isosteric heat of adsorption.

Now the types of adsorption we have learned that physical adsorption or physisorption and chemical adsorption. Physical adsorption process actually a reversible phenomenon which is the result of this intermolecular force of attraction between these molecules of the adsorbent and the adsorbate. And for chemical adsorption or chemisorption, and irreversible phenomenon the which is the result of this bond formation between this atom of the adsorbent and the adsorbate.

So, physical adsorption is the physical phenomenon and chemical adsorption means the formation of the different chemical bond. So, chemisorption process actually requires activation energy once it is achieved it releases a higher amount of energy than physisorption process because the covalent bond formation in terms of the isosteric heat of adsorption process.

(Refer Slide Time: 35:39)



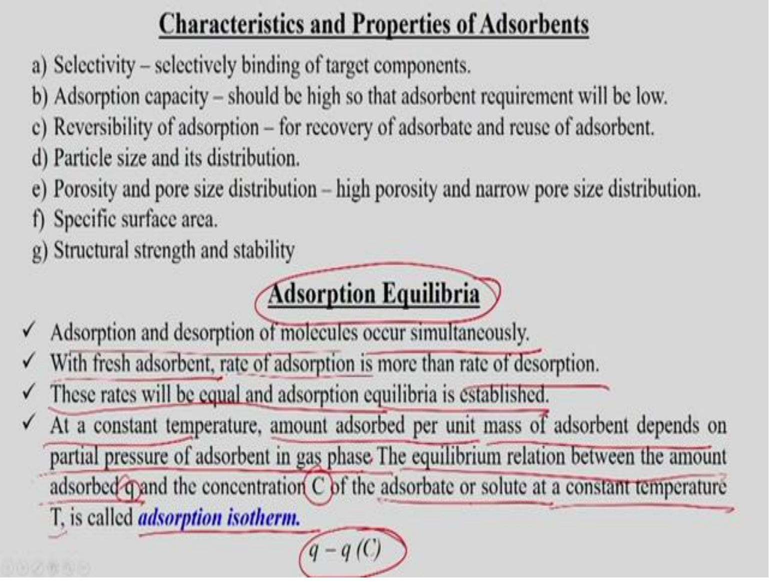
Physical adsorption	Chemical adsorption
➢ Weak van der Waals force	➢ Chemical bond formation
➢ Favored at low temperature	➢ Favored at high temperature
➢ Activation energy not required	➢ Activation energy required
➢ Reversible	➢ Irreversible
➢ Low enthalpy of adsorption	➢ High enthalpy of adsorption
➢ Non specific	➢ Specific in nature
➢ Multi-molecular layer on adsorbent surface	➢ Mono-layer is possible

And then we this one demarcated this between physical adsorption and chemical adsorption by this different evidences like this, weak van der Waals force of attraction is there for physical adsorption but for chemical adsorption chemical bond are formed for physical adsorption it favoured this one it favoured at low temperature but chemical adsorption favoured at high temperature.

Activation energy is not required at all, it is a simply this addition of the solvent this targets component on the adsorbent surface but activation energy is required and physical adsorption process is high reversible but chemical adsorption process is irreversible in nature and low enthalpy of the adsorption is there for physical adsorption process but high enthalpy of the adsorption is there for chemical adsorption process.

It is a non-specific but it is at the specific at nature and multi molecular layer on the adsorbent surface is observed but it is a mono layer is possible. Because reaction is taking place then that active surface is exhausted.

(Refer Slide Time: 36:54)



Characteristics and Properties of Adsorbents

a) Selectivity – selectively binding of target components.
b) Adsorption capacity – should be high so that adsorbent requirement will be low.
c) Reversibility of adsorption – for recovery of adsorbate and reuse of adsorbent.
d) Particle size and its distribution.
e) Porosity and pore size distribution – high porosity and narrow pore size distribution.
f) Specific surface area.
g) Structural strength and stability

Adsorption Equilibria

- ✓ Adsorption and desorption of molecules occur simultaneously.
- ✓ With fresh adsorbent, rate of adsorption is more than rate of desorption.
- ✓ These rates will be equal and adsorption equilibria is established.
- ✓ At a constant temperature, amount adsorbed per unit mass of adsorbent depends on partial pressure of adsorbent in gas phase The equilibrium relation between the amount adsorbed q and the concentration C of the adsorbate or solute at a constant temperature T, is called ***adsorption isotherm.***

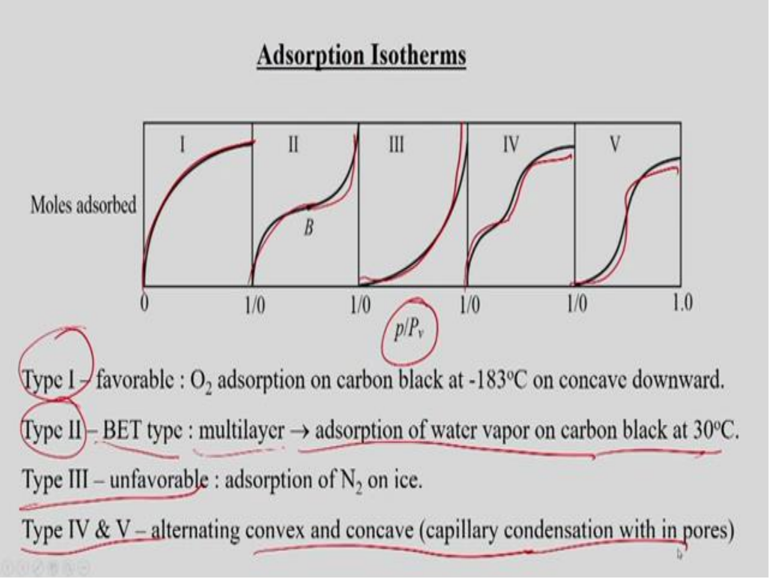
$$q - q\,(C)$$

And characteristic and the properties of the adsorbent are like this selectivity then adsorption capacity, then reversibility, then particle size and its distribution, then porosity and pore size distribution, then specific surface and structural strength of the and the stability also.

Then we discussed about the adsorption equilibrium like this adsorption and desorption of the molecules occurs simultaneously, then with fresh adsorbent rate of adsorption is more than rate of the desorption process. These rates actually will be equal and adsorption equilibrium actually is stablished. So, at a constant temperature, amount adsorbed per unit mass of the adsorbent depends on the partial pressure of the adsorbent in gas phase.

And the equilibrium relation between the amount of adsorbed that is q and the concentration C of the adsorbate or the solute at a constant temperature T actually is called adsorption isotherm that is q is the function of concentration.

(Refer Slide Time: 37:53)



Adsorption Isotherms

Type I – favorable : O_2 adsorption on carbon black at -183°C on concave downward.

Type II – BET type : multilayer → adsorption of water vapor on carbon black at 30°C.

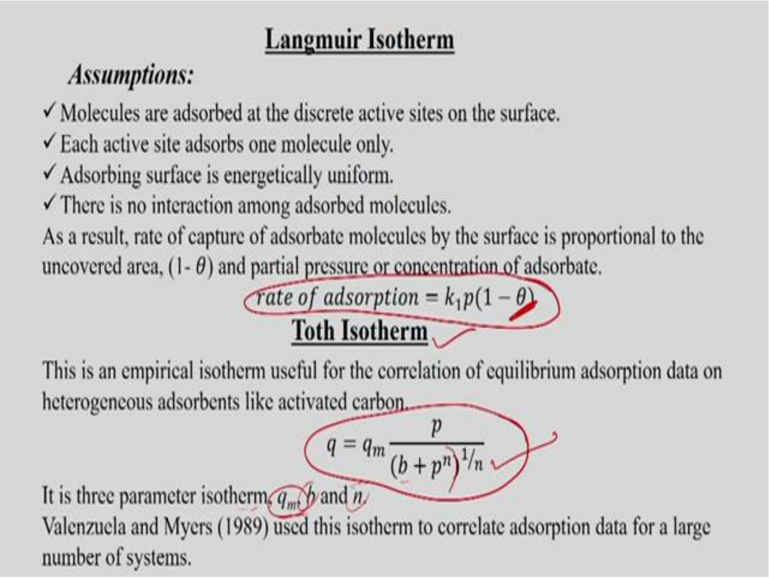
Type III – unfavorable : adsorption of N_2 on ice.

Type IV & V – alternating convex and concave (capillary condensation with in pores)

Now, you say we learned also hat types of isotherms are different 5 types like this 5 type, type a is favourable hence with P by Pv this moulds absorb actually is increasing constantly. Type b actually BET type B is multilayer in the beginning it is increasing but this rate actually is decreasing after that, like adsorption of the water vapour on the carbon black at 30 degree Celsius.

Type 3 that is unfavourable that is exponential it is increasing, like type 4 and 5 actually alternating this convex and concave like this. Convex concave like this one, so this are capillary condensation with in the pores like this.

(Refer Slide Time: 38:42)



Langmuir Isotherm

Assumptions:

✓ Molecules are adsorbed at the discrete active sites on the surface.
✓ Each active site adsorbs one molecule only.
✓ Adsorbing surface is energetically uniform.
✓ There is no interaction among adsorbed molecules.

As a result, rate of capture of adsorbate molecules by the surface is proportional to the uncovered area, $(1-\theta)$ and partial pressure or concentration of adsorbate.

$$rate\ of\ adsorption = k_1 p(1-\theta)$$

Toth Isotherm

This is an empirical isotherm useful for the correlation of equilibrium adsorption data on heterogeneous adsorbents like activated carbon.

$$q = q_m \frac{p}{(b+p^n)^{1/n}}$$

It is three parameter isotherm, q_m, b and n.

Valenzuela and Myers (1989) used this isotherm to correlate adsorption data for a large number of systems.

Now, we discussed about the Langmuir Isotherm, there actually:

$$rate\ of\ desorption = k_2\theta,$$

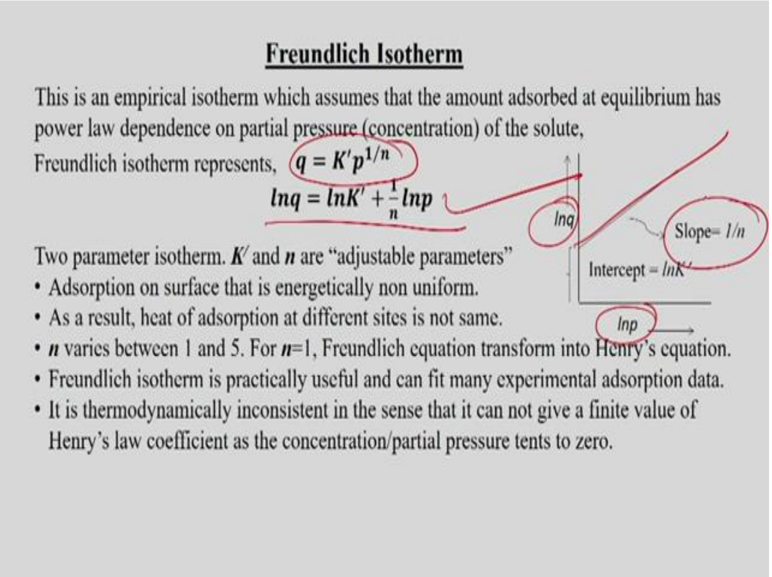
where θ is the how much amount of the available space.

And for Toth Isotherm we have discussed about,

$$q = q_m \frac{p}{(b + p^n)^{1/n}}$$

It is three parameter isotherm, q_m, b and n.

(Refer Slide Time: 39:17)



Freundlich Isotherm

This is an empirical isotherm which assumes that the amount adsorbed at equilibrium has power law dependence on partial pressure (concentration) of the solute,

Freundlich isotherm represents, $q = K'p^{1/n}$

$$lnq = lnK' + \frac{1}{n}lnp$$

Two parameter isotherm. K' and n are "adjustable parameters"

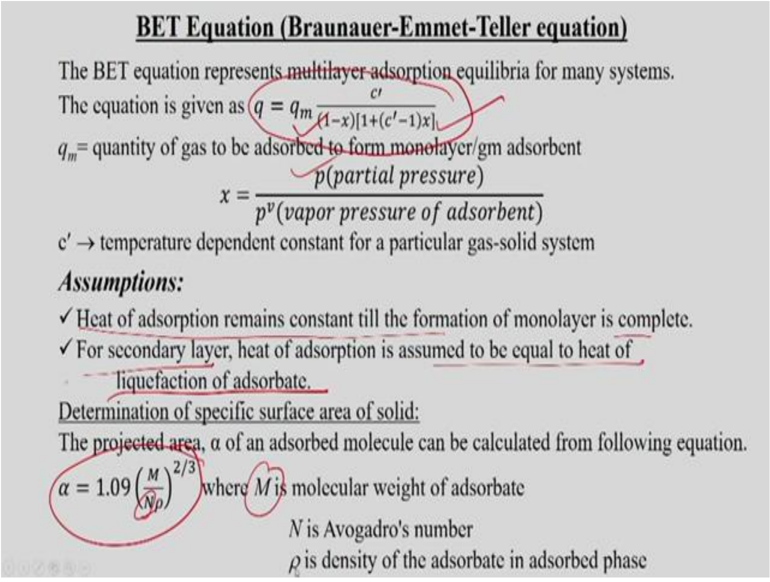
- Adsorption on surface that is energetically non uniform.
- As a result, heat of adsorption at different sites is not same.
- n varies between 1 and 5. For n=1, Freundlich equation transform into Henry's equation.
- Freundlich isotherm is practically useful and can fit many experimental adsorption data.
- It is thermodynamically inconsistent in the sense that it can not give a finite value of Henry's law coefficient as the concentration/partial pressure tents to zero.

And then we discussed about this Freundlich Isotherm like:

$$\boldsymbol{q = K'p^{1/n}}$$

$$\boldsymbol{lnq = lnK' + \frac{1}{n}lnp}$$

(Refer Slide Time: 39:43)



BET Equation (Braunauer-Emmet-Teller equation)

The BET equation represents multilayer adsorption equilibria for many systems.

The equation is given as $q = q_m \frac{c'}{(1-x)[1+(c'-1)x]}$

q_m= quantity of gas to be adsorbed to form monolayer/gm adsorbent

$$x = \frac{p(partial\ pressure)}{p^v(vapor\ pressure\ of\ adsorbent)}$$

c′ → temperature dependent constant for a particular gas-solid system

Assumptions:

✓ Heat of adsorption remains constant till the formation of monolayer is complete.

✓ For secondary layer, heat of adsorption is assumed to be equal to heat of liquefaction of adsorbate.

Determination of specific surface area of solid:

The projected area, α of an adsorbed molecule can be calculated from following equation.

$\alpha = 1.09\left(\frac{M}{N\rho}\right)^{2/3}$ where M is molecular weight of adsorbate

N is Avogadro's number

ρ is density of the adsorbate in adsorbed phase

And then we learned about this BET Isotherm or this is the multilayer adsorption where we learned he details about:

The BET equation represents multilayer adsorption equilibria for many systems. The equation is given as

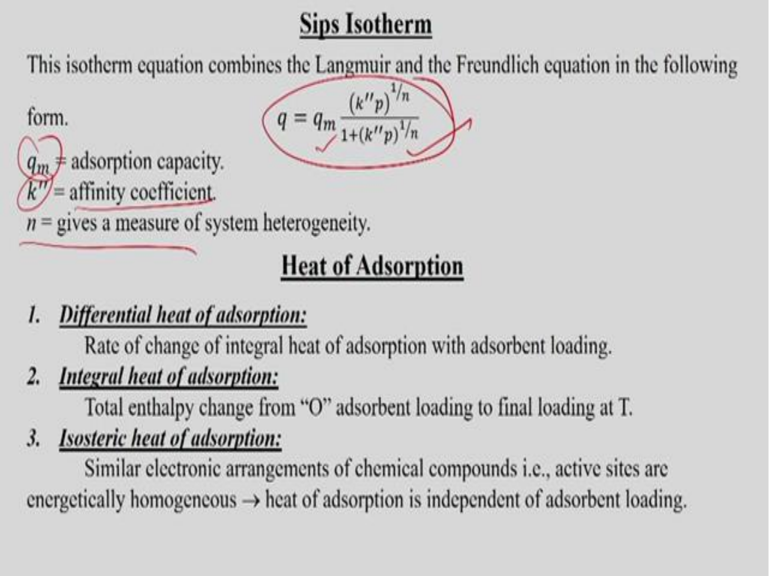
$$q = q_m \frac{c'}{(1-x)[1+(c'-1)x]}$$

q_m= quantity of gas to be adsorbed to form monolayer/gm adsorbent

$$x = \frac{p(partial\ pressure)}{p^v(vapor\ pressure\ of\ adsorbent)}$$

c′ → temperature dependent constant for a particular gas-solid system

(Refer Slide Time: 40:39)



Sips Isotherm

This isotherm equation combines the Langmuir and the Freundlich equation in the following form.

$$q = q_m \frac{(k''p)^{1/n}}{1+(k''p)^{1/n}}$$

q_m = adsorption capacity.

k'' = affinity coefficient.

n = gives a measure of system heterogeneity.

Heat of Adsorption

1. ***Differential heat of adsorption:***
   Rate of change of integral heat of adsorption with adsorbent loading.
2. ***Integral heat of adsorption:***
   Total enthalpy change from "O" adsorbent loading to final loading at T.
3. ***Isosteric heat of adsorption:***
   Similar electronic arrangements of chemical compounds i.e., active sites are energetically homogeneous → heat of adsorption is independent of adsorbent loading.

And Sips Isotherm

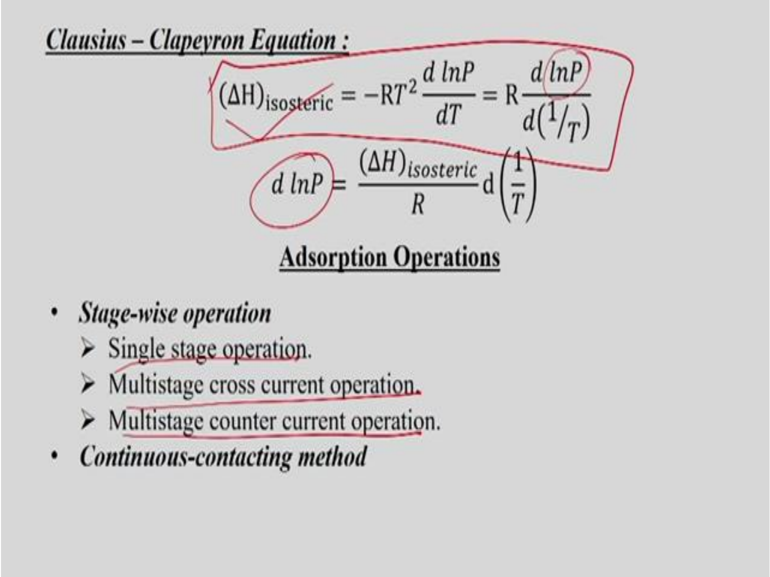
$$q = q_m \frac{(k''p)^{1/n}}{1+(k''p)^{1/n}}$$

q_m = adsorption capacity.

k'' = affinity coefficient.

n = gives a measure of system heterogeneity.

(Refer Slide Time: 41:09)



Clausius – Clapeyron Equation :

$$(\Delta \mathrm{H})_{\text{isosteric}} = -\mathrm{R}T^2 \frac{d\,lnP}{dT} = \mathrm{R}\frac{d\,lnP}{d(^1/_T)}$$

$$d\,lnP = \frac{(\Delta H)_{isosteric}}{R}\,\mathrm{d}\left(\frac{1}{T}\right)$$

Adsorption Operations

- ***Stage-wise operation***
  - Single stage operation.
  - Multistage cross current operation.
  - Multistage counter current operation.
- ***Continuous-contacting method***

And we discussed about this Heat of Adsorption values:

Exothermic process : ΔG = ΔH - TΔS (ΔG is -ve)

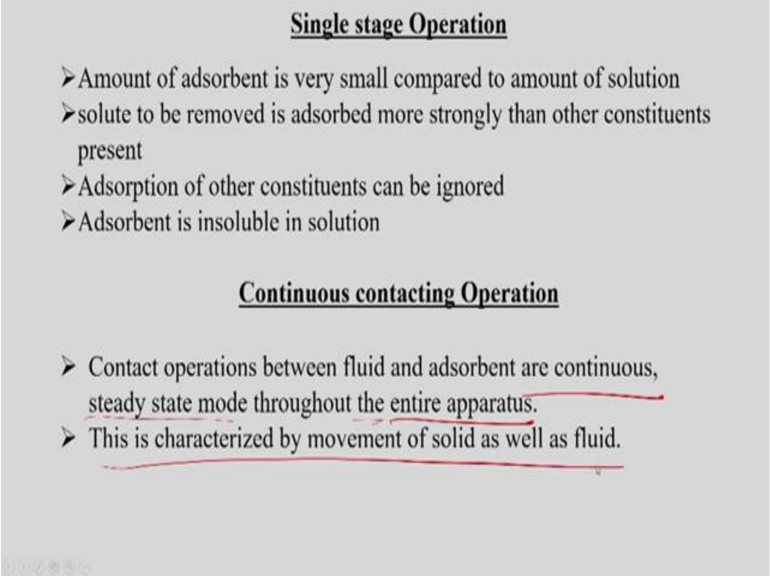
Clausius – Clapeyron Equation :

$$(\Delta \mathrm{H})_{\text{isosteric}} = -\mathrm{R}T^2 \frac{d\,lnP}{dT}$$

$$= \mathrm{R}\frac{d\,lnP}{d(^1/_T)}$$

$$d\,lnP = \frac{(\Delta H)_{isosteric}}{R}\,\mathrm{d}\left(\frac{1}{T}\right)$$

(Refer Slide Time: 41:56)



Single stage Operation

- Amount of adsorbent is very small compared to amount of solution
- solute to be removed is adsorbed more strongly than other constituents present
- Adsorption of other constituents can be ignored
- Adsorbent is insoluble in solution

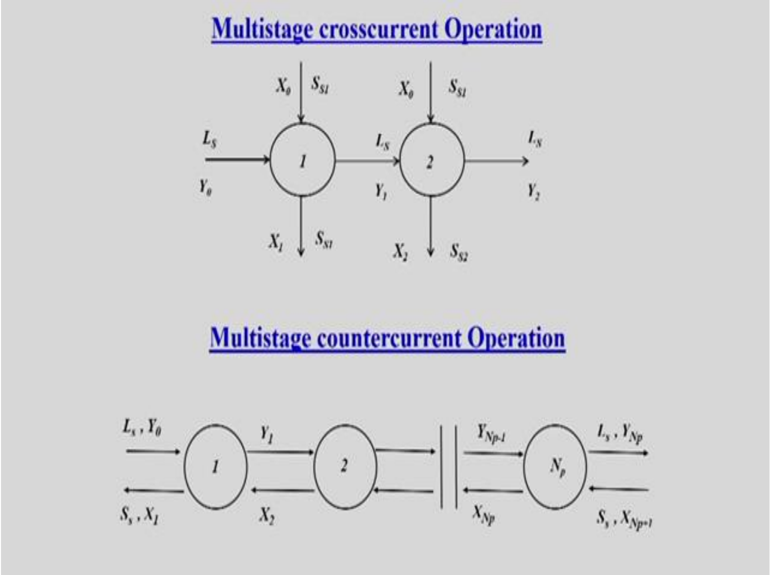
Continuous contacting Operation

- Contact operations between fluid and adsorbent are continuous, steady state mode throughout the entire apparatus.
- This is characterized by movement of solid as well as fluid.

Then in single stage operation we discussed about this amount of adsorbent is very small compared to amount of the solution. And then solute to be removed is adsorbed more strongly than other constituents present and that is the target also and adsorption of other can be ignored and adsorbent is insoluble in the solution.

For continuous contacting operation like this contact operation between the fluid and adsorbent actually are continuous. And we can this steady state mode throughout the entire apparatus. And this is characterized by movement of the solid as well as this fluid.

(Refer Slide Time: 42:37)

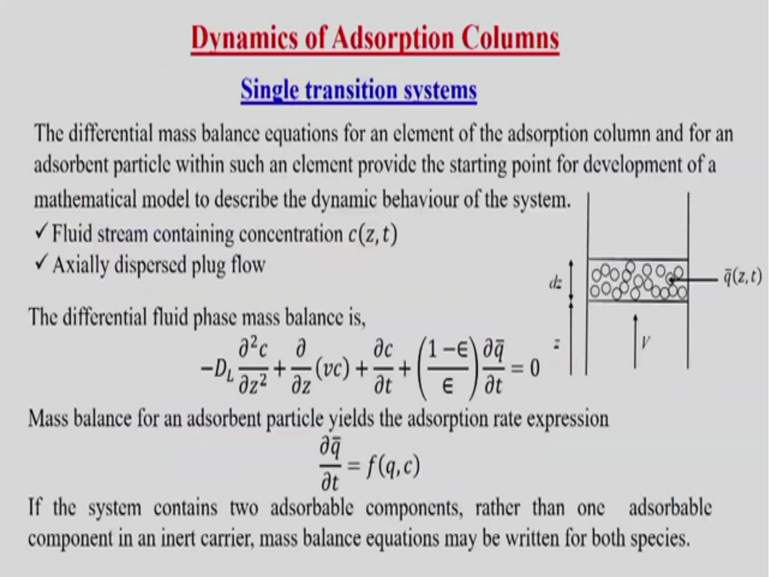


Multistage crosscurrent Operation

Multistage countercurrent Operation

And then say multistage crosscurrent operation, it is similar to that of whatever we have discussed in case of this extraction leaching for multilayer, counter current operation also this is equivalent to that we have already discussed in leaching extraction.

(Refer Slide Time: 42:56)



Dynamics of Adsorption Columns

Single transition systems

The differential mass balance equations for an element of the adsorption column and for an adsorbent particle within such an element provide the starting point for development of a mathematical model to describe the dynamic behaviour of the system.

- ✓ Fluid stream containing concentration $c(z,t)$
- ✓ Axially dispersed plug flow

The differential fluid phase mass balance is,

$$-D_L\frac{\partial^2 c}{\partial z^2}+\frac{\partial}{\partial z}(vc)+\frac{\partial c}{\partial t}+\left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}}{\partial t}=0$$

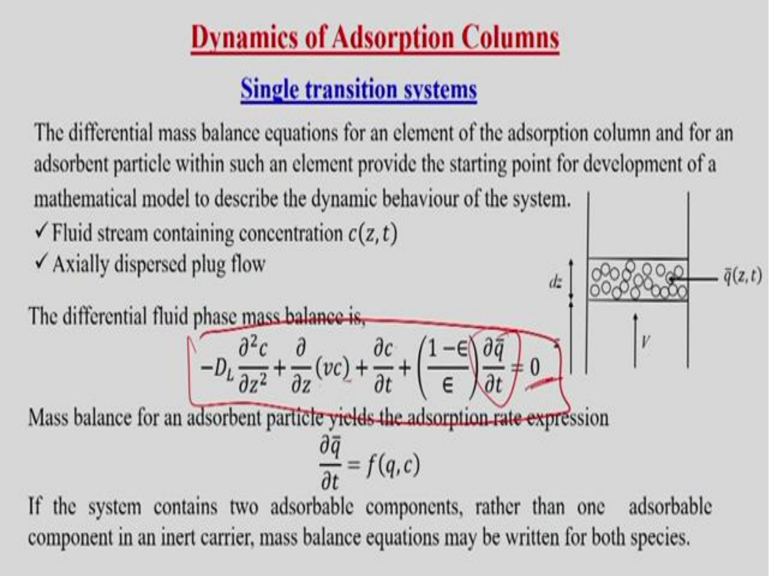
Mass balance for an adsorbent particle yields the adsorption rate expression

$$\frac{\partial \bar{q}}{\partial t}=f(q,c)$$

If the system contains two adsorbable components, rather than one adsorbable component in an inert carrier, mass balance equations may be written for both species.

And then classification of the adsorption system like this single transition system, then we have discussed about the 2 transition system, then we have discussed about the multiple transition system.

(Refer Slide Time: 43:08)



Dynamics of Adsorption Columns

Single transition systems

The differential mass balance equations for an element of the adsorption column and for an adsorbent particle within such an element provide the starting point for development of a mathematical model to describe the dynamic behaviour of the system.

✓ Fluid stream containing concentration $c(z,t)$
✓ Axially dispersed plug flow

The differential fluid phase mass balance is,

$$-D_L\frac{\partial^2 c}{\partial z^2}+\frac{\partial}{\partial z}(vc)+\frac{\partial c}{\partial t}+\left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}}{\partial t}=0$$

Mass balance for an adsorbent particle yields the adsorption rate expression

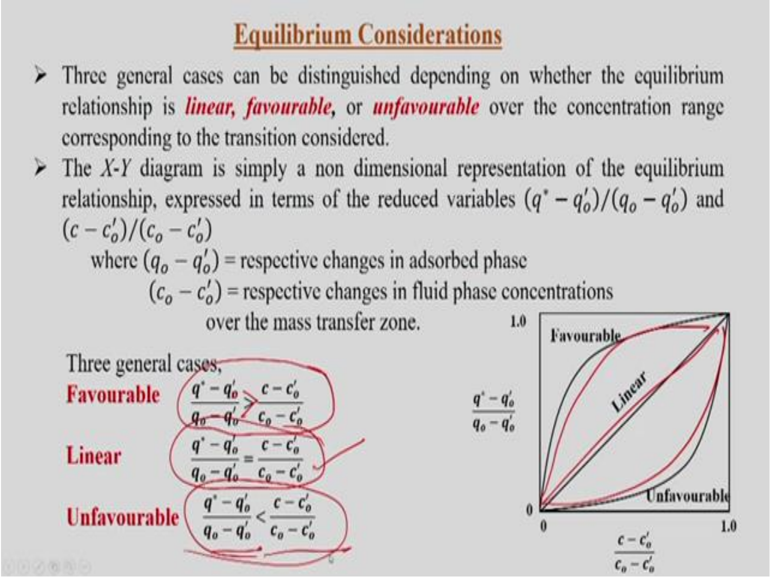
$$\frac{\partial \bar{q}}{\partial t}=f(q,c)$$

If the system contains two adsorbable components, rather than one adsorbable component in an inert carrier, mass balance equations may be written for both species.

And we have discussed in detail about the dynamic of the adsorption column and like the single transition system that differential form is like:

$$-D_L\frac{\partial^2 c}{\partial z^2}+\frac{\partial}{\partial z}(vc)+\frac{\partial c}{\partial t}+\left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}}{\partial t}=0$$

(Refer Slide Time: 43:34)



Equilibrium Considerations

- Three general cases can be distinguished depending on whether the equilibrium relationship is ***linear, favourable***, or ***unfavourable*** over the concentration range corresponding to the transition considered.
- The *X-Y* diagram is simply a non dimensional representation of the equilibrium relationship, expressed in terms of the reduced variables $(q^* - q_o')/(q_o - q_o')$ and $(c - c_o')/(c_o - c_o')$

  where $(q_o - q_o')$ = respective changes in adsorbed phase

  $(c_o - c_o')$ = respective changes in fluid phase concentrations over the mass transfer zone.

Three general cases,

Favourable $\frac{q^* - q_o'}{q_o - q_o'} > \frac{c - c_o'}{c_o - c_o'}$

Linear $\frac{q^* - q_o'}{q_o - q_o'} = \frac{c - c_o'}{c_o - c_o'}$

Unfavourable $\frac{q^* - q_o'}{q_o - q_o'} < \frac{c - c_o'}{c_o - c_o'}$

For this one:

Favorable

$$\frac{q^* - q_o'}{q_o - q_o'} > \frac{c - c_o'}{c_o - c_o'}$$

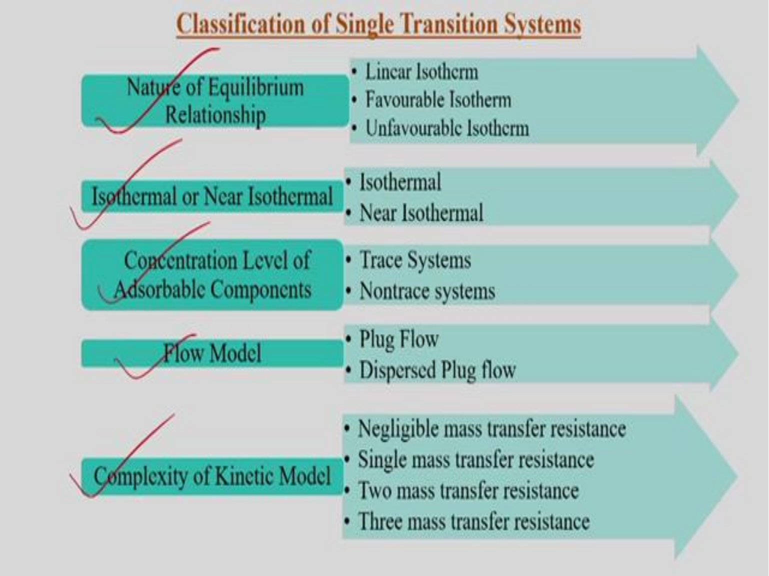
Linear

$$\frac{q^* - q_o'}{q_o - q_o'} = \frac{c - c_o'}{c_o - c_o'}$$

Unfavorable

$$\frac{q^* - q_o'}{q_o - q_o'} < \frac{c - c_o'}{c_o - c_o'}$$

(Refer Slide Time: 44:23)



Classification of Single Transition Systems

Nature of Equilibrium Relationship
- Linear Isotherm
- Favourable Isotherm
- Unfavourable Isotherm

Isothermal or Near Isothermal
- Isothermal
- Near Isothermal

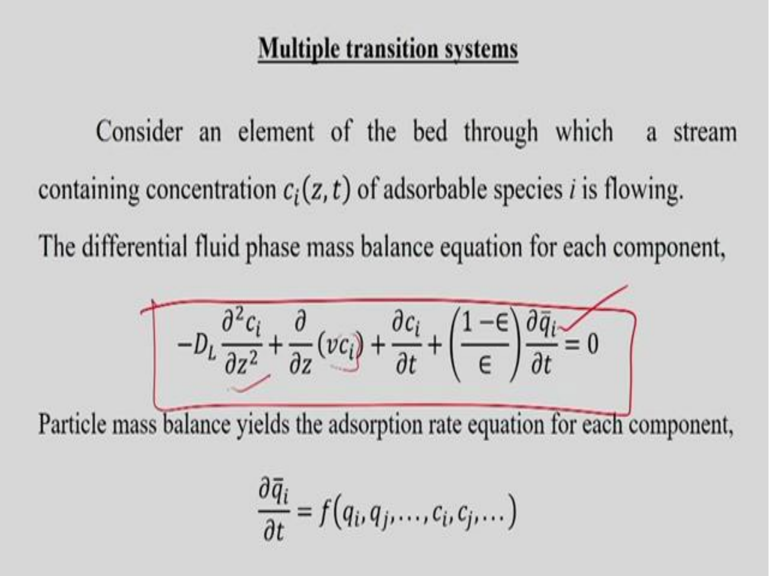
Concentration Level of Adsorbable Components
- Trace Systems
- Nontrace systems

Flow Model
- Plug Flow
- Dispersed Plug flow

Complexity of Kinetic Model
- Negligible mass transfer resistance
- Single mass transfer resistance
- Two mass transfer resistance
- Three mass transfer resistance

And the classification of the single transition system like this nature of the equilibrium relationship, then isothermal or near isothermal, then concentration level of this adsorbable components, then flow model, then complexity of the kinetic model we discussed in detail.

(Refer Slide Time: 44:45)



Multiple transition systems

Consider an element of the bed through which a stream containing concentration $c_i(z,t)$ of adsorbable species i is flowing.

The differential fluid phase mass balance equation for each component,

$$\boxed{-D_L\frac{\partial^2 c_i}{\partial z^2}+\frac{\partial}{\partial z}(vc_i)+\frac{\partial c_i}{\partial t}+\left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}_i}{\partial t}=0}$$

Particle mass balance yields the adsorption rate equation for each component,

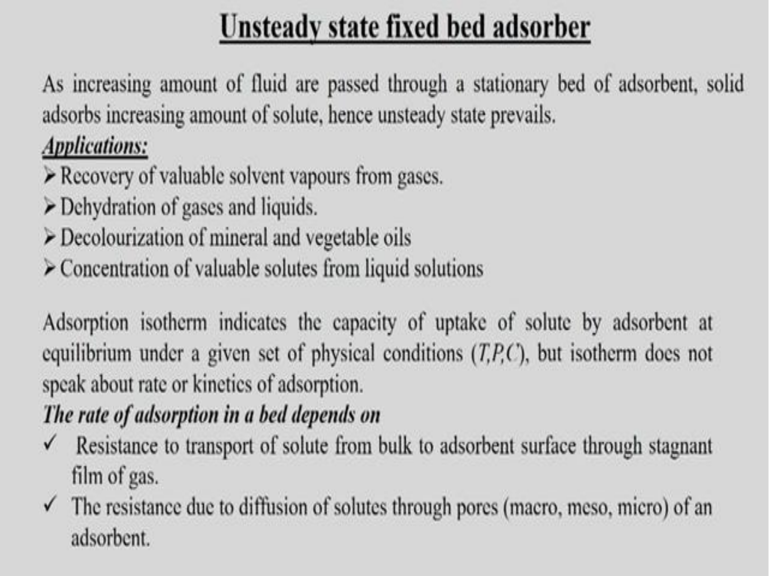
$$\frac{\partial \bar{q}_i}{\partial t}=f(q_i,q_j,\ldots,c_i,c_j,\ldots)$$

And then multiple transition systems also there we have done this component balanced like:

$$-D_L\frac{\partial^2 c_i}{\partial z^2}+\frac{\partial}{\partial z}(vc_i)+\frac{\partial c_i}{\partial t}+\left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}_i}{\partial t}=0$$

$$\frac{\partial \bar{q}_i}{\partial t}=f(q_i,q_j,.\,.\,.,c_i,c_j,.\,.\,.)$$

(Refer Slide Time: 45:08)



Unsteady state fixed bed adsorber

As increasing amount of fluid are passed through a stationary bed of adsorbent, solid adsorbs increasing amount of solute, hence unsteady state prevails.

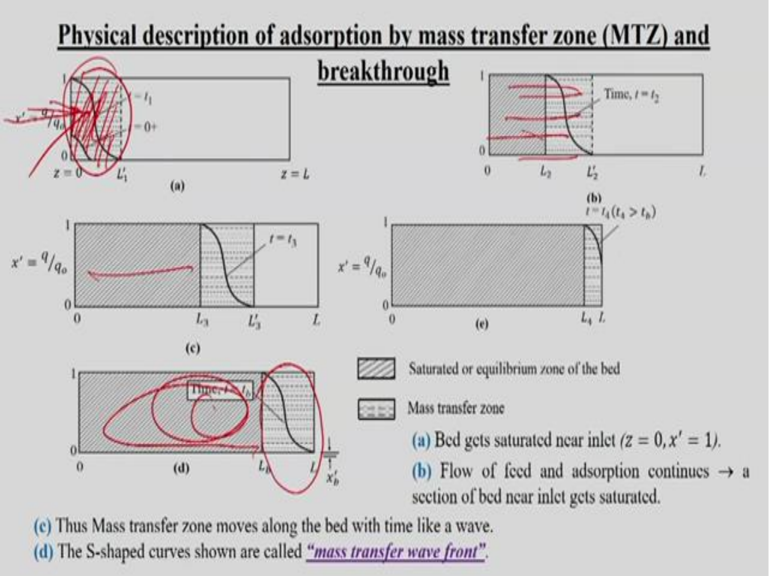
Applications:

- Recovery of valuable solvent vapours from gases.
- Dehydration of gases and liquids.
- Decolourization of mineral and vegetable oils
- Concentration of valuable solutes from liquid solutions

Adsorption isotherm indicates the capacity of uptake of solute by adsorbent at equilibrium under a given set of physical conditions (*T,P,C*), but isotherm does not speak about rate or kinetics of adsorption.

The rate of adsorption in a bed depends on

- ✓ Resistance to transport of solute from bulk to adsorbent surface through stagnant film of gas.
- ✓ The resistance due to diffusion of solutes through pores (macro, meso, micro) of an adsorbent.



Physical description of adsorption by mass transfer zone (MTZ) and breakthrough

▨ Saturated or equilibrium zone of the bed

▤ Mass transfer zone

(a) Bed gets saturated near inlet ($z = 0, x' = 1$).

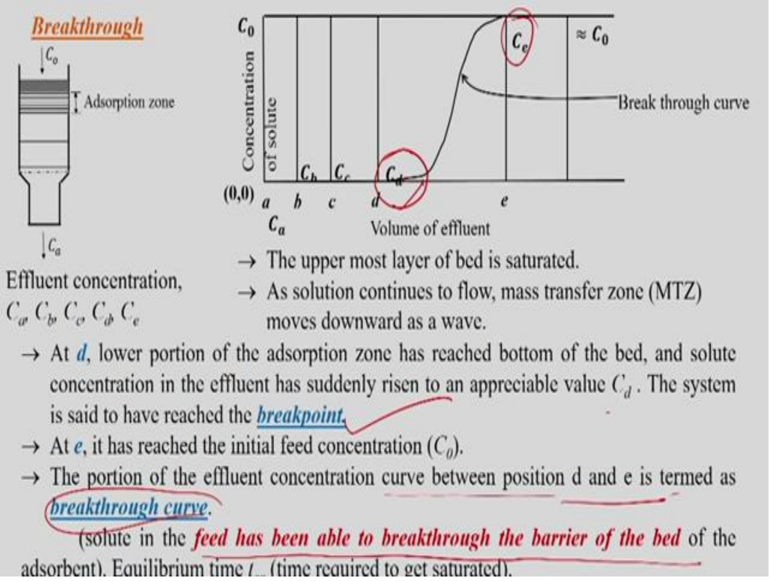
(b) Flow of feed and adsorption continues → a section of bed near inlet gets saturated.

(c) Thus Mass transfer zone moves along the bed with time like a wave.

(d) The S-shaped curves shown are called ***"mass transfer wave front"***.

Then we discussed about the unsteady state fixed bed adsorber, so suppose this bed is fixed and then suppose the adsorbent is there and suppose the adsorbate is entering then suppose some portions are now saturated and then with time the saturation zone actually will go on increasing and say with time one time will be reaching there, see this almost enter part is saturated and then we have this mass transfer zone actually the remaining part. And it is actually moving like this the S shaped curve zone is called this mass transfer wave front.

(Refer Slide Time: 45:43)



Breakthrough

Effluent concentration, C_a, C_b, C_c, C_d, C_e

→ The upper most layer of bed is saturated.

→ As solution continues to flow, mass transfer zone (MTZ) moves downward as a wave.

→ At *d*, lower portion of the adsorption zone has reached bottom of the bed, and solute concentration in the effluent has suddenly risen to an appreciable value C_d. The system is said to have reached the ***breakpoint***.

→ At *e*, it has reached the initial feed concentration (C_0).

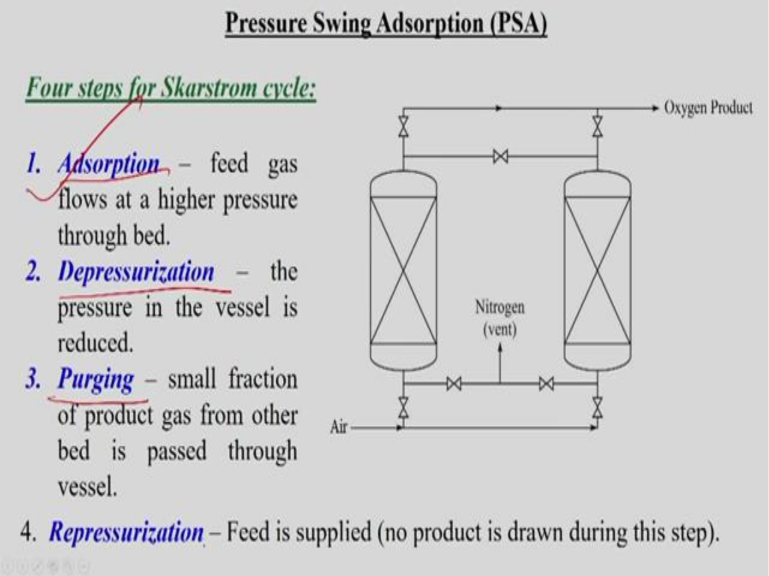
→ The portion of the effluent concentration curve between position d and e is termed as ***breakthrough curve***.

(solute in the ***feed has been able to breakthrough the barrier of the bed*** of the adsorbent). Equilibrium time t (time required to get saturated).

And this breakthrough like this whenever we say this one whenever this this concentration of the solute in the effluent actually we will suit up from Cd to Ce, this one at point d the lower portion of the adsorption zone has reach bottom of this bed. And this solute concentration in the effluent has suddenly risen to the appreciable value Cd.

The system is said to have the reached the breakpoint actually. And the portion of the influent concentration curve between this d and e is called breakthrough curve. Means the solute in the feed has been able to break through the barrier of the bed of the adsorbent, so equilibrium time t actually is required to get the get saturated.

(Refer Slide Time: 46:39)



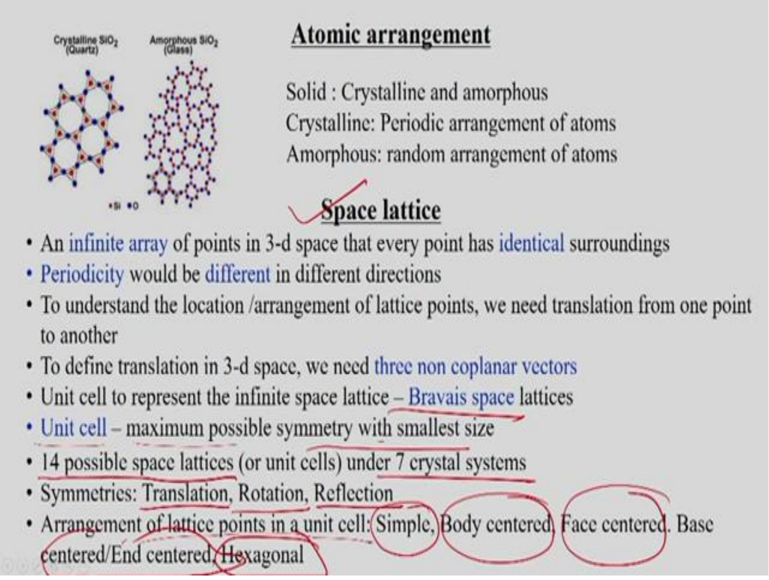
Pressure Swing Adsorption (PSA)

Four steps for Skarstrom cycle:

1. ***Adsorption*** – feed gas flows at a higher pressure through bed.
2. ***Depressurization*** – the pressure in the vessel is reduced.
3. ***Purging*** – small fraction of product gas from other bed is passed through vessel.
4. ***Repressurization*** – Feed is supplied (no product is drawn during this step).

And then we discussed about the pressure swing adsorption process, then adsorption, then depressurization, then purging and then this one repressurization also we have discussed this one.

(Refer Slide Time: 47:00)



Atomic arrangement

Solid : Crystalline and amorphous
Crystalline: Periodic arrangement of atoms
Amorphous: random arrangement of atoms

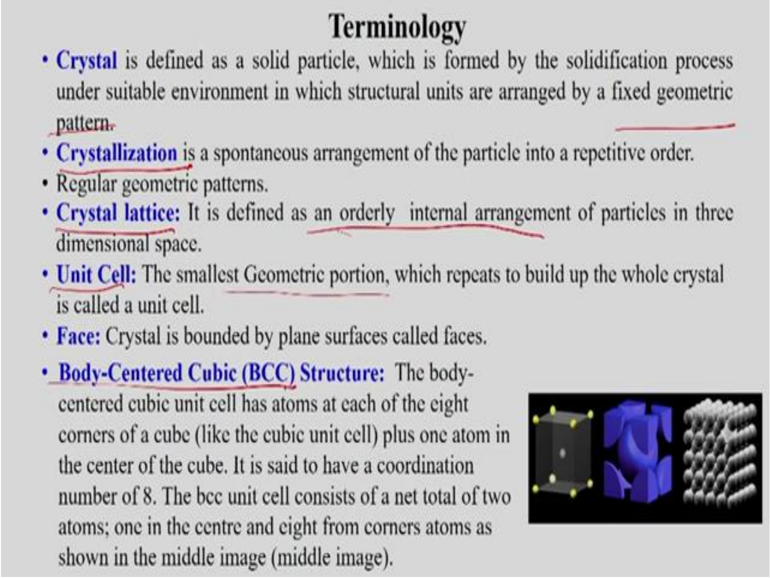
Space lattice

- An infinite array of points in 3-d space that every point has identical surroundings
- Periodicity would be different in different directions
- To understand the location /arrangement of lattice points, we need translation from one point to another
- To define translation in 3-d space, we need three non coplanar vectors
- Unit cell to represent the infinite space lattice – Bravais space lattices
- Unit cell – maximum possible symmetry with smallest size
- 14 possible space lattices (or unit cells) under 7 crystal systems
- Symmetries: Translation, Rotation, Reflection
- Arrangement of lattice points in a unit cell: Simple, Body centered, Face centered. Base centered/End centered, Hexagonal

And the last chapter that we discussed that is small chapter like this crystallization process. And for that we discussed in the beginning like the atomic arrangement, then the space lattice is like this, 7 crystal systems, then we discussed about the Bravais space lattices like unit cell, maximum possible symmetry with the smallest size, then 14 possible space lattices or under the 7 crystal systems.

Like symmetries are like translation, then rotational and reflectional symmetries must be there in the system. Then arrangement of the lattice points in unit cell like this simple system, then body centred system, then face centered system like this base centred systems or end centered system or hexagonal system.

(Refer Slide Time: 47:48)

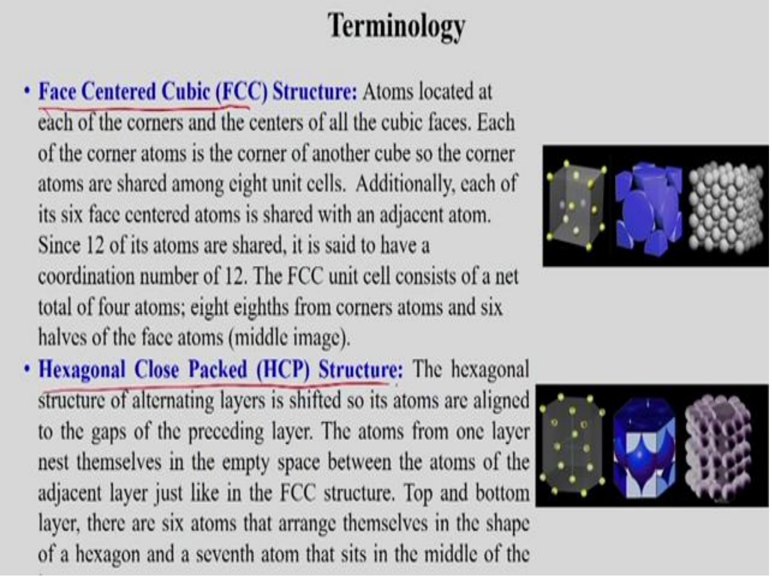


Terminology

- **Crystal** is defined as a solid particle, which is formed by the solidification process under suitable environment in which structural units are arranged by a fixed geometric pattern.
- **Crystallization** is a spontaneous arrangement of the particle into a repetitive order.
- Regular geometric patterns.
- **Crystal lattice:** It is defined as an orderly internal arrangement of particles in three dimensional space.
- **Unit Cell:** The smallest Geometric portion, which repeats to build up the whole crystal is called a unit cell.
- **Face:** Crystal is bounded by plane surfaces called faces.
- **Body-Centered Cubic (BCC) Structure:** The body-centered cubic unit cell has atoms at each of the eight corners of a cube (like the cubic unit cell) plus one atom in the center of the cube. It is said to have a coordination number of 8. The bcc unit cell consists of a net total of two atoms; one in the centre and eight from corners atoms as shown in the middle image (middle image).

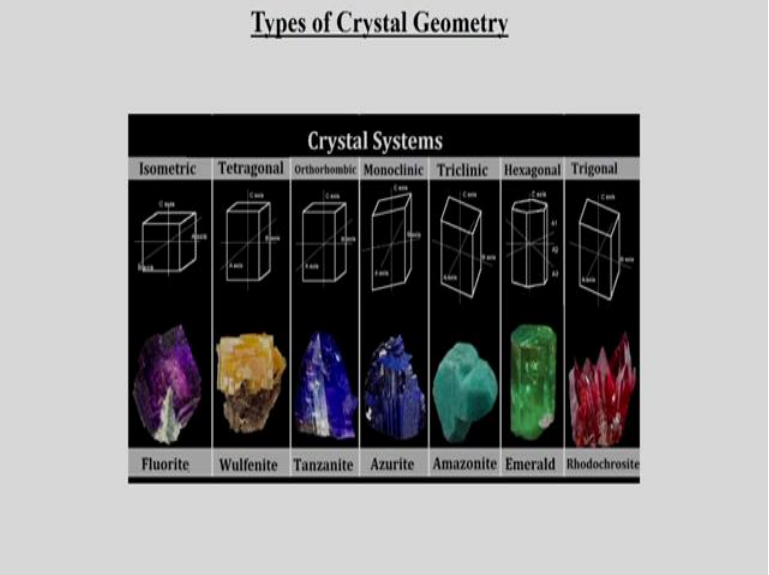
So, there this terminology is like crystal that is defined as the solid particle, which is formed by the solidification process under suitable environment in which the structural unit are arranged by the fixed geometric pattern. Like then crystallization this process, the crystal lattice we can this defined as the an orderly internal arrangement, then unit cell the smallest geometric portion, which repeats to build up the whole crystal is called the unit cell. Then we have this body centered cubic crystal.

(Refer Slide Time: 48:21)



Terminology

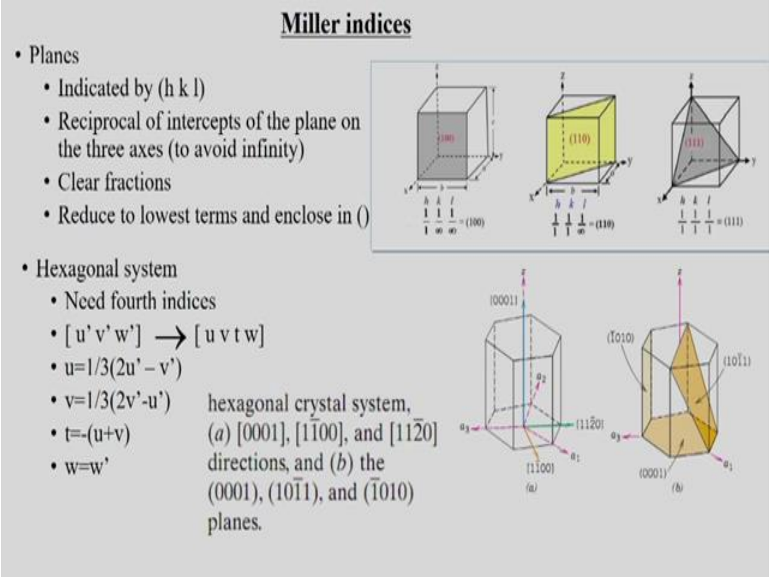
- **Face Centered Cubic (FCC) Structure:** Atoms located at each of the corners and the centers of all the cubic faces. Each of the corner atoms is the corner of another cube so the corner atoms are shared among eight unit cells. Additionally, each of its six face centered atoms is shared with an adjacent atom. Since 12 of its atoms are shared, it is said to have a coordination number of 12. The FCC unit cell consists of a net total of four atoms; eight eighths from corners atoms and six halves of the face atoms (middle image).
- **Hexagonal Close Packed (HCP) Structure:** The hexagonal structure of alternating layers is shifted so its atoms are aligned to the gaps of the preceding layer. The atoms from one layer nest themselves in the empty space between the atoms of the adjacent layer just like in the FCC structure. Top and bottom layer, there are six atoms that arrange themselves in the shape of a hexagon and a seventh atom that sits in the middle of the



Types of Crystal Geometry

Then we have this face centered cubic crystal and this hexagonal closed packing. Like different 7 crystal system like this isometric then tetragonal, then orthorhombic, then monoclinic, triclinic, hexagonal, then trigonal.

(Refer Slide Time: 48:41)



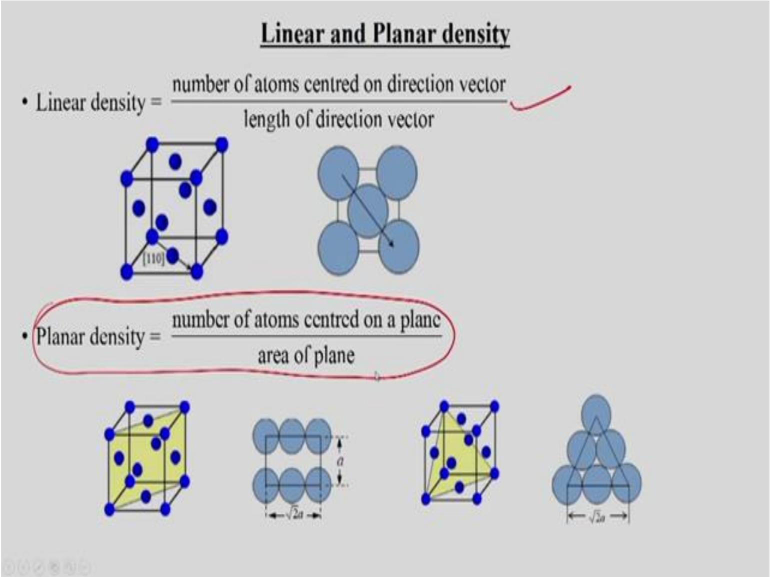
Miller indices

- Planes
  - Indicated by (h k l)
  - Reciprocal of intercepts of the plane on the three axes (to avoid infinity)
  - Clear fractions
  - Reduce to lowest terms and enclose in ()
- Hexagonal system
  - Need fourth indices
  - [u' v' w'] ⟶ [u v t w]
  - u=1/3(2u' – v')
  - v=1/3(2v'-u')
  - t=-(u+v)
  - w=w'

hexagonal crystal system, (*a*) [0001], $[1\bar{1}00]$, and $[11\bar{2}0]$ directions, and (*b*) the (0001), $(10\bar{1}1)$, and $(\bar{1}010)$ planes.

With the different example. And miller indices also that is indicated by h k l, in this x y z in 3 directions using this these indices we are able to designate particular hexagonal crystal system.

(Refer Slide Time: 49:00)

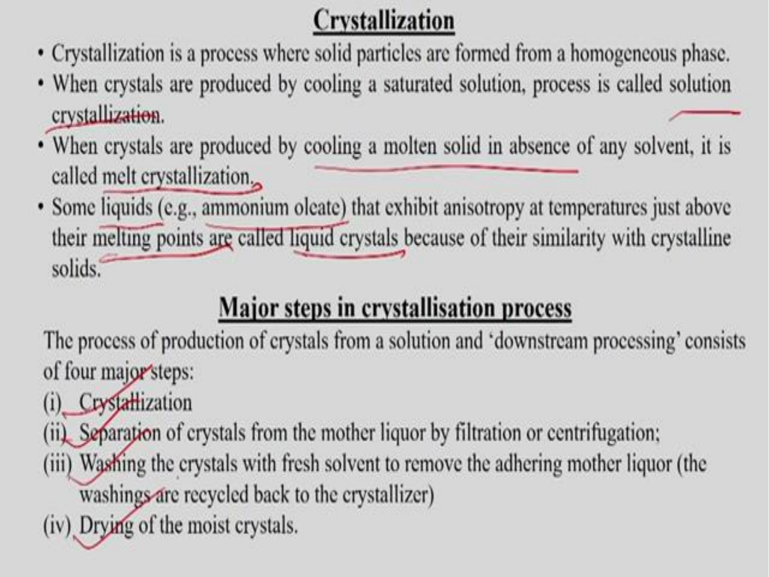


Linear and Planar density

- Linear density = $\frac{\text{number of atoms centred on direction vector}}{\text{length of direction vector}}$
- Planar density = $\frac{\text{number of atoms centred on a plane}}{\text{area of plane}}$

 And then we have discussed about the linear density like number of the atoms centred on the direction velocity direction vector divided by the length of the direction vector and in case of the planar density we described about this number of atom to centred on a plane divided by area of the plane.

(Refer Slide Time: 49:22)



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.

Major steps in crystallisation process

The process of production of crystals from a solution and 'downstream processing' consists of four major steps:

(i) Crystallization

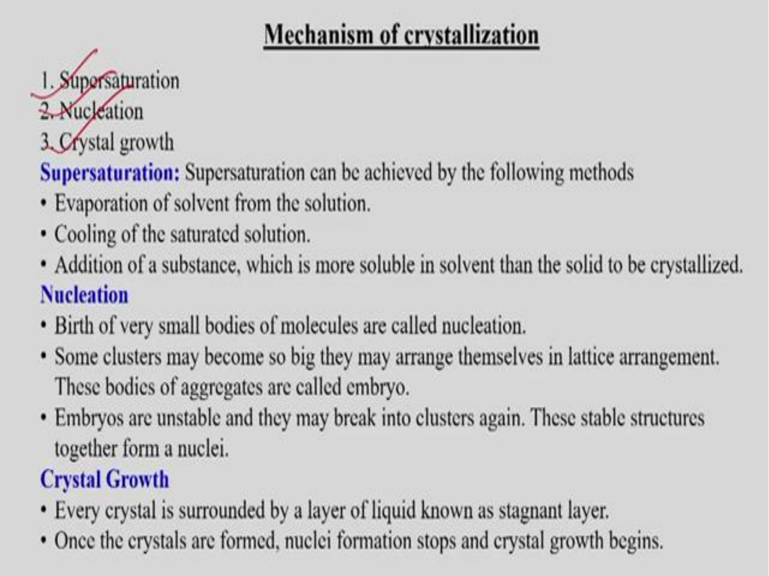
(ii) Separation of crystals from the mother liquor by filtration or centrifugation;

(iii) Washing the crystals with fresh solvent to remove the adhering mother liquor (the washings are recycled back to the crystallizer)

(iv) Drying of the moist crystals.

And in the crystallization process we have discussed about the when the crystal are produced by cooling saturated solution process is called solution crystallization. When crystals are produced by cooling this molten solid in absence of any solvent it is called this melt crystallization. Some liquids like this ammonium olcate et cetera exhibits this anisotropy at temperature just above this their melting points are called liquid crystals or lc. So, major steps in the crystallization process are like crystallization, then separation of the crystals, then washing of the crystals, then drying of the crystal, this one moist crystal.

(Refer Slide Time: 50:04)



Mechanism of crystallization

1. Supersaturation
2. Nucleation
3. Crystal growth

Supersaturation: Supersaturation can be achieved by the following methods

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

Nucleation

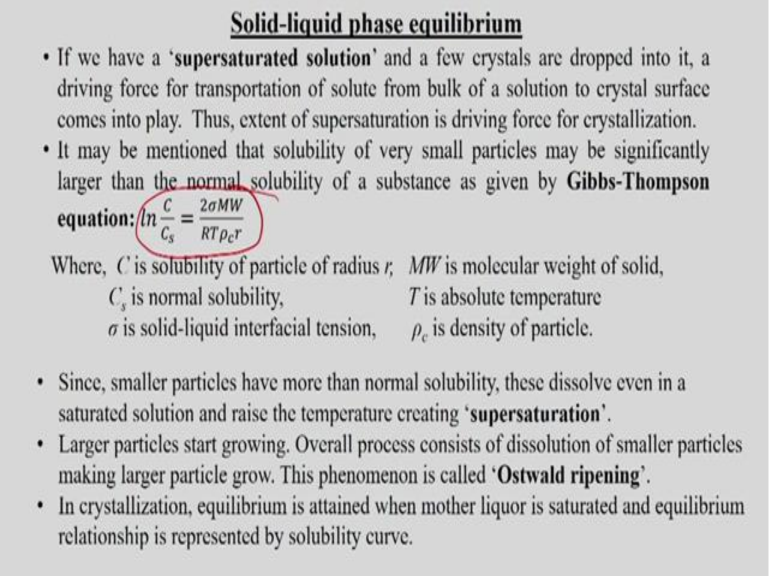
- Birth of very small bodies of molecules are called nucleation.
- Some clusters may become so big they may arrange themselves in lattice arrangement. These bodies of aggregates are called embryo.
- Embryos are unstable and they may break into clusters again. These stable structures together form a nuclei.

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.

And the mechanism of the crystallization we discussed about the super saturation, then nucleation and then crystal growth.

(Refer Slide Time: 50:13)



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:** $ln\frac{C}{C_s} = \frac{2\sigma MW}{RT\rho_C r}$

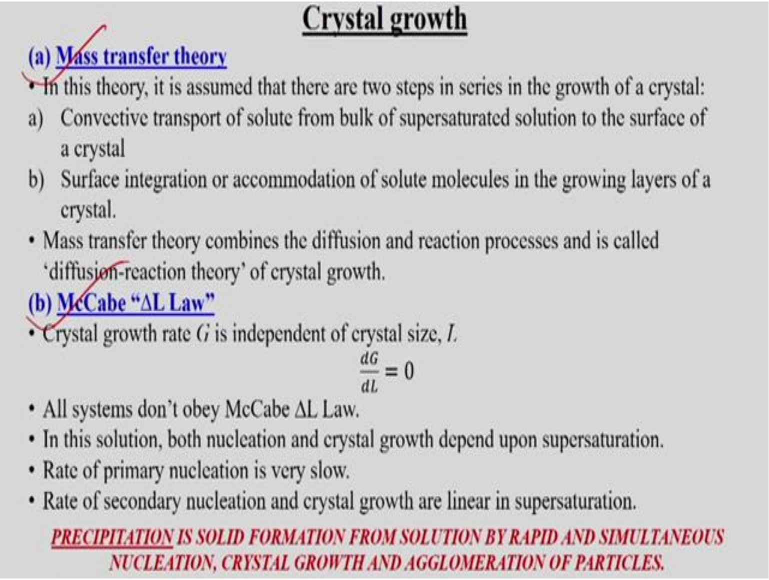
Where, C is solubility of particle of radius r, MW is molecular weight of solid,
C_s is normal solubility, T is absolute temperature
σ is solid-liquid interfacial tension, ρ_c is density of particle.

- 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.

Then say we have discussed about the Gibbs Thompson equation this ln C by Cs is equal to 2 sigma into MW by RT into rho c into r, where C is the solubility of the particle radius r, then Cs is equal to normal solubility, sigma is equal to solid liquid interfacial tension, MW is equal to molecular weight, T is the temperature and rho c is the density of the particle. Since these smaller particles have more than normal solubility, these dissolve even in a saturated solution and raise the temperature creating super saturation.

And say the larger particles start growing actually overall process consist of this dissolution of the smaller particles making the larger particles grow. This phenomenon is called Ostwald ripening.

(Refer Slide Time: 51:06)



Crystal growth

(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.

(b) McCabe "ΔL Law"

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

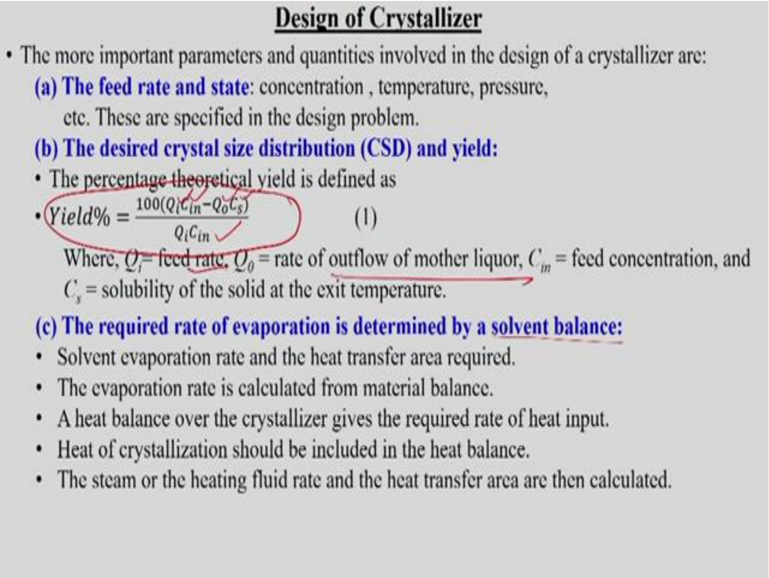
$$\frac{dG}{dL} = 0$$

- 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.

And then so we discussed about the crystal growth like using this mass transfer theory is the MeCabe delta L law and we this one explained that the precipitation is solid formation from the solution by rapid and simultaneous nucleation crystal growth and agglomeration of the particles.

(Refer Slide Time: 51:32)



Design of Crystallizer

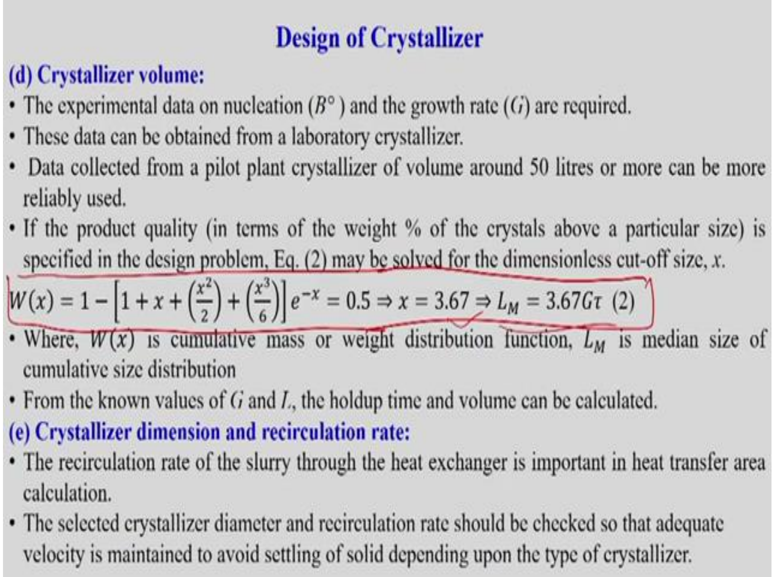
- The more important parameters and quantities involved in the design of a crystallizer are:
  - **(a) The feed rate and state**: concentration , temperature, pressure, etc. These are specified in the design problem.
  - **(b) The desired crystal size distribution (CSD) and yield:**
  - The percentage theoretical yield is defined as
  - $Yield\% = \frac{100(Q_i C_{in} - Q_0 C_s)}{Q_i C_{in}}$ (1)

    Where, Q_i = feed rate, Q_0 = rate of outflow of mother liquor, C_{in} = feed concentration, and C_s = solubility of the solid at the exit temperature.
  - **(c) The required rate of evaporation is determined by a solvent balance:**
  - Solvent evaporation rate and the heat transfer area required.
  - The evaporation rate is calculated from material balance.
  - A heat balance over the crystallizer gives the required rate of heat input.
  - Heat of crystallization should be included in the heat balance.
  - The steam or the heating fluid rate and the heat transfer area are then calculated.

And we discussed about the design of the crystallizer, by this on the feed rate and the state by the desired crystal size distribution and the yield like this yield as calculated like this 100 into Qi into Cin minus Q into Cs divided by Qi into Cin, where Q is equal to feed rate and Q is equal to rate of the outflow of the mother liquor.

And then required rate of the evaporation is determined by the solvent balance so during this crystal crystallizer design we consider that with some amount of the evaporation and with without evaporation also.

(Refer Slide Time: 52:17)



Design of Crystallizer

(d) Crystallizer volume:

- The experimental data on nucleation (B°) and the growth rate (G) are required.
- These data can be obtained from a laboratory crystallizer.
- Data collected from a pilot plant crystallizer of volume around 50 litres or more can be more reliably used.
- If the product quality (in terms of the weight % of the crystals above a particular size) is specified in the design problem, Eq. (2) may be solved for the dimensionless cut-off size, x.

$$W(x) = 1 - \left[1 + x + \left(\frac{x^2}{2}\right) + \left(\frac{x^3}{6}\right)\right] e^{-x} = 0.5 \Rightarrow x = 3.67 \Rightarrow L_M = 3.67G\tau \quad (2)$$

- Where, $W(x)$ is cumulative mass or weight distribution function, L_M is median size of cumulative size distribution
- From the known values of G and L, the holdup time and volume can be calculated.

(e) Crystallizer dimension and recirculation rate:

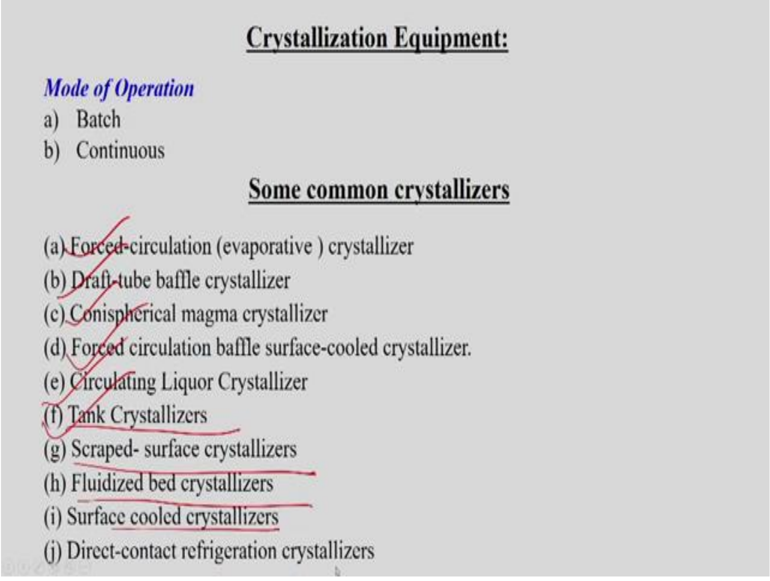
- The recirculation rate of the slurry through the heat exchanger is important in heat transfer area calculation.
- The selected crystallizer diameter and recirculation rate should be checked so that adequate velocity is maintained to avoid settling of solid depending upon the type of crystallizer.

Like then crystal volume actually is designed by this equation:

$$W(x) = 1 - \left[1 + x + \left(\frac{x^2}{2}\right) + \left(\frac{x^3}{6}\right)\right] e^{-x} = 0.5 \Rightarrow x = 3.67 \Rightarrow L_M = 3.67G\tau \quad (2)$$

And then we have done the crystallization dimension and recirculation rate also.

(Refer Slide Time: 52:58)



Crystallization Equipment:

Mode of Operation

a) Batch
b) Continuous

Some common crystallizers

(a) Forced-circulation (evaporative) crystallizer
(b) Draft-tube baffle crystallizer
(c) Conispherical magma crystallizer
(d) Forced circulation baffle surface-cooled crystallizer.
(e) Circulating Liquor Crystallizer
(f) Tank Crystallizers
(g) Scraped- surface crystallizers
(h) Fluidized bed crystallizers
(i) Surface cooled crystallizers
(j) Direct-contact refrigeration crystallizers

And some equipment for crystallization are of like batch and continuous, some common crystallizer are like forced circulation, then draft tube, then conispherical, forced circulation baffle surface cooling crystallizer, then circulating liquid crystallizer, then tank crystallizer it is used like scraped surface crystallizer, fluidized bed, then surface cooled and direct contact refrigeration crystallizer also.

(Refer Slide Time: 53:27)

References

1. R. E. Treybal "Mass Transfer Operations", McGraw –Hill International Edition, 3rd Ed., 1981.
2. W. L. McCabe, J. Smith and P. Harriot, "Unit Operations of Chemical Engineering", 6th Ed., McGraw – Hill International Edition, 2001.
3. B.K. Dutta, "Principles of Mass Transfer and Separation Processes", 1st Ed., PHI, 2012.
4. D.M. Ruthven, "Principles of Adsorption & Adsorption Processes", John Wiley & Sons, 1984
5. K. Li, A.G. Fane, W.S. Winston Ho, T. Matsura, "Advanced Membrane Technology and Applications", John Wiley & Sons, 2008

So, the references are huge:

1. R. E. Treybal "Mass Transfer Operations", McGraw –Hill International Edition, 3rd Ed., 1981.

2. W. L. McCabe, J. Smith and P. Harriot, "Unit Operations of Chemical Engineering", 6th Ed., McGraw – Hill International Edition, 2001.

3. B.K. Dutta, Principles of Mass transfer and separation processes, 1st Ed., PHI, 2012.

4. D M Ruthven, "Principles of adsorption and adsorption processes" by John Wiley and sons of1984

5. K Li, A G Fane, W S Winston Ho and T Matsura, "Advanced membrane technology and application" by John Wiley and sons 2008

And. thank you very much for your kind this one patients and good luck for the examination, if you have any suggestions feedback I will be happy to receive.