

Membrane Technology
Prof. Kaustubha Mohanty
Department of Chemical Engineering
Indian Institute of Technology Guwahati

Lecture-15
Revision of Concepts and Fundamentals

Good morning students, this is lecture 15 under module 5. As you know, I told you, I think in the last class that till now we have discussed the basics of membrane what is the membrane what is the advantage, disadvantages, how transport takes place inside the membrane. Then we have also discussed the different material that is used for preparing membrane whether it is polymeric or whether it is ceramic.

They are properties that are advantages, disadvantages, all these things then we have proceeded and we have discussed how to prepare a membrane. So, by different techniques so, we have discussed this one how to prepare porous membrane and then we have also discussed how to prepare composite membranes by various techniques. Then we went and discussed the transporting membrane.

After that we have started specified 1st, we are going to start with basically, the different membrane and processes and detailed discussion about their things. And I just forgot to mention that we have also discussed about membrane and modules in detail. So, I have decided that it is better we have already covered 14 lectures almost half of the this one schedule lectures. So, let us just revise what we have discussed today. So, today's lecture is dedicated for the revision of concepts and fundamentals still we have till that we have whatever we have covered. So, let us begin so quickly we will see different content.

(Refer Slide Time: 01:59)

Membrane Separation Process

Membrane: It is a perm-selective barrier or interface between two phases that allows passage of certain things whereas stops others. These may be molecules, ions or small particles.

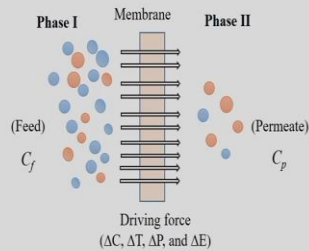


Figure: Schematic representation of two-phase system separated by a membrane

- **Phase I**, is usually considered as the feed (or upstream side phase),
- **Phase II**, is considered the permeate or downstream side.

Basically, as you understand membrane is of course a semi permeable perm selective barrier, and it is the interface between 2 phases that allows passage of certain things go through, whereas stops others. So, they know that these things may be they may be molecule they may be ions, maybe smaller particles and there is a driving force that does the separation in case of membrane and driving force can be of many types.

It can be either concentration difference, it can be temperature difference; it can be pressure depress or it can be electromotive force difference. So, usually the phase one is the feed phase which also acknowledge the upstream side and phase two is the downstream side or the permeate side. So, this is just a schematic of the usual membrane process.

(Refer Slide Time: 02:43)

- The performance of given membrane is determined by following two parameters:
(a) *selectivity*, and (b) *flow through* the membrane.
- The term flow through membrane is often termed as the **flux** or permeation rate.
- It can be denoted as the volume flowing through the membrane per unit area and time.
- The selectivity of a membrane towards a mixture is generally expressed by one of the two parameters:
(a) the retention, "*R*", and (b) the separation factor, "*α*".
- The retention is given by :

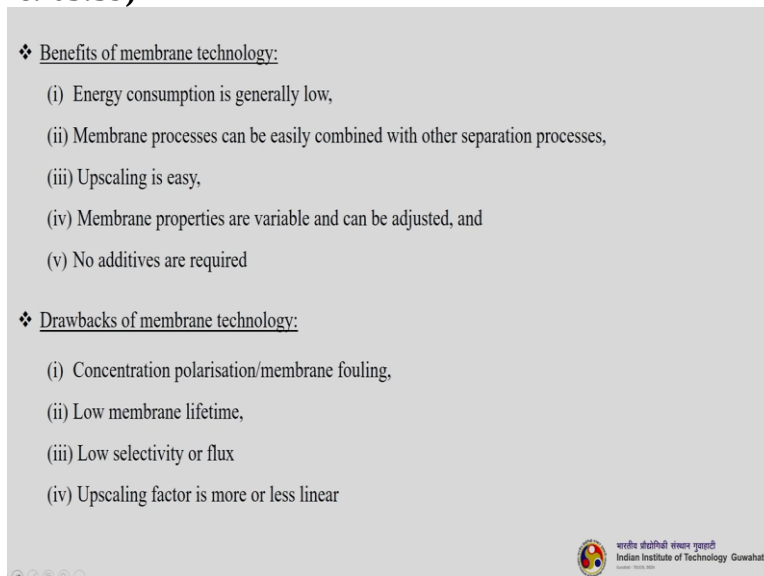
$$R = \frac{c_f - c_p}{c_f} = 1 - \frac{c_p}{c_f}$$

where, C_f is a solute concentration in the feed, and C_p is the solute concentration in the permeate.
- Since *R* is a dimensionless parameter, it does not depend on the units in which the concentration is expressed.
- The value of *R* varies from 100% (complete retention of solute) and 0% (solute or solvent pass through the membrane freely).

So, the performance of given membrane is determined by following 2 parameters selectivity and flow through. So, you know the term flow through means it is nothing but the flux or the permeation rate. So, it can be denoted as the volume flowing through the membrane per unit area and unit time. So, the selectivity of the membrane can be defined by 2 base one is retention, that is R or rejection and then there is separation factor α . So, retention is much more important respect to a membrane.

So, retention or rejection can be defined as $C_f - C_p / C_f$, or $1 - C_p / C_f$ where C_f is a solute concentration in the feed, C_p is the solute concentration in the permeate R is a dimensionless parameter, it does not depend on the units in which the concentration is expressed. The value of R varies from 100% means that is complete retention of the solute to 0% solute or solvent pass through the membrane freely there is no retention.

(Refer Slide Time: 03:39)



❖ Benefits of membrane technology:

- (i) Energy consumption is generally low,
- (ii) Membrane processes can be easily combined with other separation processes,
- (iii) Upscaling is easy,
- (iv) Membrane properties are variable and can be adjusted, and
- (v) No additives are required

❖ Drawbacks of membrane technology:

- (i) Concentration polarisation/membrane fouling,
- (ii) Low membrane lifetime,
- (iii) Low selectivity or flux
- (iv) Upscaling factor is more or less linear

Logo: Indian Institute of Technology Guwahati

There are many benefits or advantages of membrane separation. The first and foremost important is of course, the energy consumption is low. Then membrane processes can be easily combined with separation processes, this is called hybrid processes basically. So, in our subsequent discussions will discuss how membrane has been clubbed with distillation process at to make hybrid processes.

As you know this up scaling is also easy membrane properties are variable and can be adjusted. So, in many classes I have already told that membrane a particular membrane can be tailor made just like a tailor stitches our suit or this one shirt or pant whatever it is similar

way, we can make a membrane, which is selectively applicable for a particular target pollutant. You can say pollutant or molecular solute, whatever it is.

So, let us say I am targeting the separation of a particular pollutant, I am just giving an example of a (O) (04:35) which is present along with other pollutants, but I am targeting that one because that is more toxic. Others can be removed by other techniques. A constant does not also depend whether concentration is higher concentration is low. So I can make a membrane which will selectively but either written this particular pollutant or it can be permeated to the downstream side.

So this is what is the meaning of the tailor making actually, and you do not need any additives in a membrane separation just like us, we need to extract and in allele or we need another solvent to break edge it drops in case of dislesson columns, but nevertheless there are certain drawbacks. The first important drawback is of course, the concentration, polarization and membrane and fouling.

so I am not going to discuss again on all these things, today's lecture is devoted to that just brief discussion about and revising the concepts and we know what is concentration polarization just again I am just telling you let us say this is the membrane. So, the solutes are getting deposited on the surface of the membrane initially. Then again the deposition layer increases slowly the thickness increases.

After a certain time what will happen this will become a cake under the pressure it will become cake or we can say it gel so what is the meaning of this? So, in this gel or cackler is getting built up. So, it will be 2 things first is that a flux will decrease very drastically, that is because it is providing a huge resistance and resistance to the flow either this way or this way does not matter (O) (06:13). So, flux versus time and then second thing is that it will also a result in fouling.

So, fouling can be external fouling it can be internal fouling internal fouling with the fouling getting trapped inside the pores of the membrane. So, by all these things, the membrane lifetime is getting reduced and selectivity of flux is a concentration independent a concentration polarization and of fouling independent, nothing as it is very clear from this

picture. So, selectivity or flux decreases with progress in time and up scaling factor is very, very linear.

(Refer Slide Time: 06:46)

- The major membrane separation processes are:

Name of process	Driving force	Separation size range
Microfiltration	Pressure gradient	10 - 0.1 μm
Ultrafiltration	Pressure gradient	< 0.1 μm - 5 nm
Reverse osmosis	Pressure gradient	< 5 nm
Electrodialysis	Electric field gradient	< 5 nm
Dialysis	Concentration gradient	< 5 nm

- The membrane has the ability to transport one component more readily than others because of differences in physical and/ or chemical properties between the membrane and the permeating components.



So, major measure membrane separation processes are, microfiltration and ultrafiltration and reverse osmosis, electro dialysis and dialysis you can see in the first 3, so what is (06:58) RO, the driving force is pressure gradient, it says Δp we can see as you come from microfiltration to ultrafiltration, the size decreases the size of the solutes that it will separate basically decreases.

So, 10 to 0.1 micron in microfiltration 0.1 micron to 5 nanometer in ultrafiltration and less than 5 nanometer in RO, then we have electro dialysis in which electric do field gradient is the driving force less than 5 nanometer and dialysis that is concentration gradient less than 5 nanometer. So, membrane has the ability to transport one component more readily than others because of the differences in physical chemical properties between the membranes.

And as well as the permeating component. So, let us again understand that it is not the properties of the solute along that is deciding the permeation or separation but the membrane properties also plays a big role.

(Refer Slide Time: 07:53)

Diagram illustrating three types of membrane separation processes:

- Liquid-Liquid:** Driving force acts on a liquid feed (Phase I) to separate it into two liquid streams (Phase II).
- Liquid-Gas:** Driving force acts on a liquid feed (Phase I) to separate it into a liquid stream (Phase II) and a gas stream (Phase II).
- Gas-Gas:** Driving force acts on a gas feed (Phase I) to separate it into two gas streams (Phase II).

• In membrane processes, the driving force can be gradient in pressure, concentration, electrical potential, or temperature.

• Other than the driving force, the membrane itself plays a major role determining the selectivity, and flux.

• The nature of membrane determines the type of application, ranging from the separation of microscopic particles to the separation of molecules of an identical shape and/or size.

Indian Institute of Technology Guwahati

So, we can have different types of separation in membrane. So, you can have a liquid separation we can have a liquid gas separation we can have a gas separation so in the membrane processes the driving force can be gradient in pressure concentration electrical potential or temperature, other than driving force membrane itself plays a major role in determining the selectivity and flux the membrane material basically. So, nature of the membrane determines the type of application ranging from the separation of microscopic particles to the separation of molecules of an identical shape and or size.

(Refer Slide Time: 08:24)

- Transport through the membrane takes place as a result of driving force acting on the components in the feed.
- The permeation rate through membrane is directly proportional to the driving force.
- The flux-force relationship can be described using a phenomenological equation, given by:

$$J = -A \frac{dX}{dx}$$

where, A is phenomenological coefficient and $\frac{dX}{dx}$ is the driving force expressed as the gradient of X (temperature, concentration, and pressure) along a coordinate x perpendicular to the transport barrier.

- For a pure component permeating through a membrane, it is possible to employ linear relations to describe transport. However, when two or more components permeate simultaneously, such relations cannot be generally employed since the coupling phenomenon may occur in the fluxes and forces.

Indian Institute of Technology Guwahati

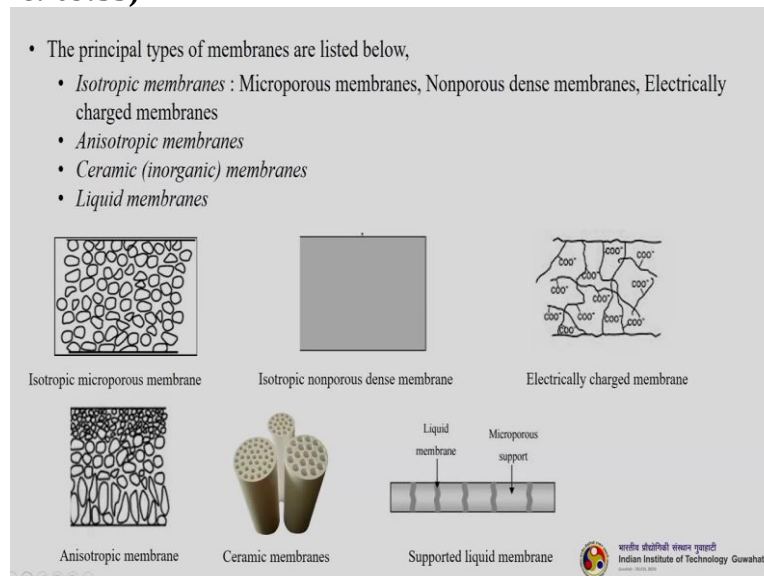
Let us understand the transport. So, transport to the membrane takes place as a result of driving force acting on the components in the feed permeation rate through membrane is directly proportional to the driving force. So, the flux force relationship is this. So, $J = - A \frac{dX}{dx}$. So, A is the phenomenological coefficient and $\frac{dX}{dx}$ is the driving force expressed as

the gradient of x , x can be X , x can be either temperature it can be concentration it can be pressure and along the coordinate x which is perpendicular to the transport barrier.

Now, for a pure component permeating through a membrane it is possible to employ linear relation to describe the transport. However, when 2 or more components permeate simultaneously, such relations cannot be generally employed since the coupling phenomena occur in the fluxes and forces. If you can recall the lecture on transport membrane in which we have discussed non equilibrium.

This one thermodynamics in which you have discussed about the L_1 L_2 and different coefficient like the main coefficient and coupling coefficient L_{11} L_{22} and L_{12} L_{21} . So, I hope you will recall those. So, in today's lecture it is not possible to describe everything.

(Refer Slide Time: 09:33)



But let us see what are the different types of membrane that are available commercially. So, basically we can group into isotropic membranes and isotropic ceramic or inorganic membranes and liquid membranes. So, isotropic membranes are basically micro porous membrane they can be non porous membrane also electrically charged membrane. So, in isotropic micro porous membrane you can see the membrane pore size of more or less homogeneously distributor.

You can see in this and we have non porous dense membrane with something looks like this. So, this is also isotropic it is homogeneous nature, very small force usually may be present, but they are not visible or cannot be seen and electrically charged membranes that also comes

under isotopic membranes. So different types of tectonic groups are aligning groups are fused along with the membrane and matron switch to make it as either a ceramic membrane or inorganic membrane or we can have a bipolar membrane.

And so, were both cation and anion are present then let us go for anisotropic membrane. So, the structure is like this you can see the 2 distinct layers here. This is one layer and this is another layer. So, here the pore size is small and here the pore size is bigger. So, this is actually providing so, basically you can see that 2 different porous membranes are fused together. So, the bottom person, this one is providing the support, where is the top percent portion and this one is doing this separation.

So, all the separation is achieved by the top layer. So, thickness up top layer plays a very big role then we have ceramic membrane. So, this is an example of tubular ceramic membranes, ceramic membranes can be prepared by various materials. Then we have liquid membrane will be discussing in one class the liquid membrane concepts. So, you just can understand that liquid membrane is something in which the membrane itself is a liquid.

Now, to enhance the membrane stability, liquid membrane material has been impregnated inside the solid porous membrane. So, this is a solid porous membrane and micro usually micro pores support microfiltration and support in use the pores are getting filled with liquid membrane and then the separation will be done by the liquid membrane. The micro porous membrane is only providing the mechanical support.

(Refer Slide Time: 11:44)

Membrane Processes Classifications

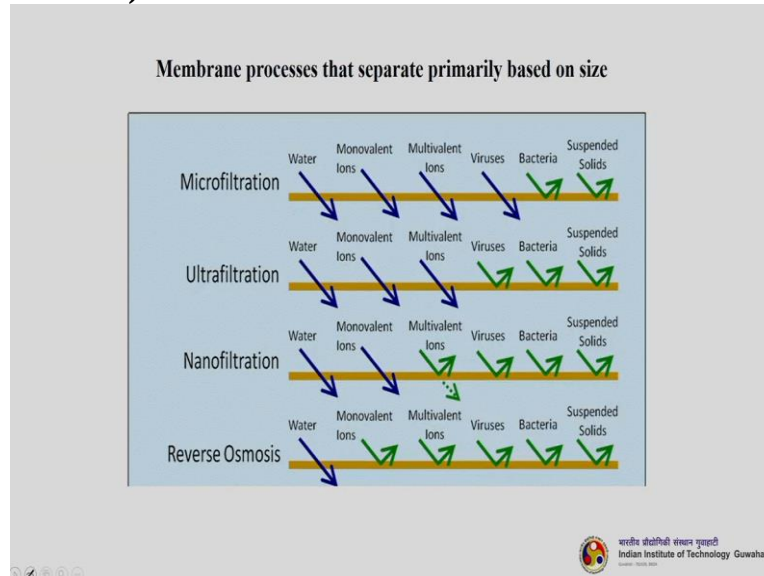
Though the earlier slide gave a general classification, in a better way we can classify the membranes processes as given below,

- ☐ Based on material
- ☐ Based on membrane structure and morphology
- ☐ Based on operational modes
- ☐ Based on charges
- ☐ Based on driving forces

 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
Indian Institute of Technology Guwahati

So, if we talk about membrane processes classification, we have already discussed about this. So, we can classify membrane based on material, based on membrane structure and morphology based on operational modes based on charges and based on driving forces.

(Refer Slide Time: 11:59)



So, let us now see that actually, what is the basic difference between microfiltration ultrafiltration and Nano filtration reverse osmosis or 4 distinct presser driven membrane and processes. So, you can see microfiltration everything here is getting to the permeate side, including the particles whether it is bacterial and suspended solids will be returned. So, please remember, as we come down from microfiltration and to ultrafiltration into Nano filtration into reverse osmosis, the size of the pore decreases.

So, pore size is decreasing as we come down from microfiltration to ultrafiltration that means what smaller and smaller molecules will start returning. So, let us see ultrafiltration you can see virus, he will also be a return here, but virus was not getting returned in the microfiltration because by the virtue of the size, when you come to Nano filtration multivalent I am also get returned few may pass through because of the sizes again. And reverse osmosis will return everything.

It will only allow the presses of the solvent water. So, this slide just gives us an idea about the different applications that can be achieved using the pore distinct president processes, microfiltration and ultrafiltration Nano filtration and reverse osmosis.

(Refer Slide Time: 13:18)

Polymers used in membrane preparation

➤ Porous membrane

- Porous membrane contains fixed pores, in the range of 0.1-10 μm for microfiltration and 2-100 μm for ultrafiltration.
- The selectivity is determined by the dimensions of the pores but the choice of material affects the phenomenon such as adsorption, and chemical stability under actual conditions.
- The main problem in microfiltration and ultrafiltration membrane is flux decline. Therefore, the choice of membrane material for such process is based on prevention of fouling and cleaning procedure after it is fouled.
- Frequently used polymers used in microfiltration membrane are: Polycarbonate, polyvinylidene fluoride, polytetrafluoroethylene, polypropylene, polyamide, polysulfone, polyether-imide.



So, let us talk a little about the material that is being used to prepare the membranes. So, the first and porous is of course polymers before that in the porous membrane actually porous membrane contains fixed pores in the range of 0.1 to 10 micron for microfiltration and 2 to 100 micron for ultrafiltration. The selectivity is determined by the dimensions of the pores, but the choices of material affect the phenomenon.

Such as adsorption and chemical stability under actual conditions, the main problem in microfiltration and ultrafiltration and membrane is flux decline this we have discussed many times. So, therefore, again we will be discussing we will discuss microfiltration and ultrafiltration in detail is a processes basically, so, therefore the choice of membrane material for such processes based on prevention of fouling and cleaning procedure after it is fouled, you do anything membrane will be fouled.

So, you have to take care in such a way that if you choose a membrane material properly, that it is a less foul able material and easily cleanable that is it is always better for a microfiltration and ultrafiltration system. So frequently used polymers used in microfiltration and membrane or polycarbonate, polyvinylidene fluoride, polytetrafluoroethylene, polypropylene, polysulfone and polyether imide and I just forgot to mention PES is a variety of this polyether sulfur.

(Refer Slide Time: 14:34)

Polymers used in membrane preparation

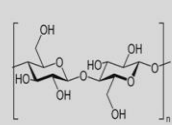
➤ Non-porous membranes

- Non-porous membranes are primarily used for gas (vapour) separation, and pervaporation.
- The choice of material is determined by the type of application, and the polymer type can range from an elastomer to glassy material.

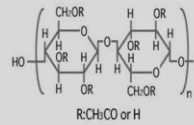
So, for non porous membranes are primarily used for gas separation and pervaporation the choice of material is determined by the type of application and the polymer type can range from elastomer to glassy material.

(Refer Slide Time: 14:47)

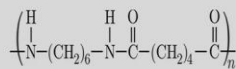
Polymers used in membrane preparation



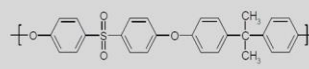
Cellulose



Cellulose Acetate



Polyamides



Polysulfones

These are the materials which are being used for making polymer membranes cellulose we have cellulose acetate which is be cellulous the most abundantly available methylene north. From the planet sources basically than cellulose acetate is being developed from cellulous by tries to lessen reaction. Then we have polyamide we have polysulfones.

(Refer Slide Time: 15:09)

- Polymeric membranes have **low mechanical stability** and **fouling problems**.
- On the other hand, **inorganic membranes** possess better properties such as
High chemical,
Thermal and
Mechanical stabilities
- Inorganic membranes also, suitable for use in harsh conditions such as
Corrosive and
High temperature environments.

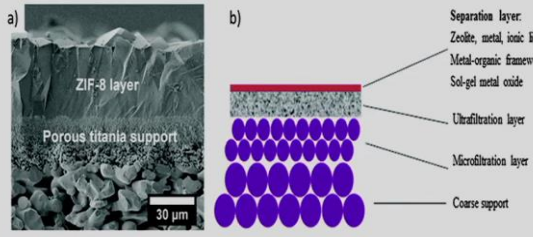
Hence, compared to polymeric, inorganic membranes have more advantages.

- Inorganic membranes refer to membranes made of materials such as:
 - **Ceramic, Carbon, Silica, Zeolite, Various oxides** (alumina, titania, zirconia) and
 - **Metals** such as **Palladium, Silver** and their alloys.


 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
 Indian Institute of Technology Guwahati
 Guwahati - 781 005, India

And there are other materials have just skipped it. So, polymeric membranes have low mechanical stability and fouling problems. So, on the other hand inorganic membrane possess better properties such as high chemical, thermal and mechanical stability, so, inorganic membranes also suitable for harsh conditions such as corrosive environments and high temperature applications. Hence, compared to polymeric, inorganic membranes have more advantages. So, the inorganic materials that are being used for preparation membrane of ceramic carbon silica zeolite various oxides metals such as palladium silver and their alloys.

(Refer Slide Time: 15:44)



(a) A metal-organic framework (MOF) type ZIF-8 layer on an asymmetric graded titania support, (b) principle of a supported membrane: the μm -thick separation layer is deposited on a macroporous ceramic or metallic support. To reduce the pressure drop across the support, *i.e.* to minimize the flow resistance, usually asymmetric (graded) supports with hierarchical cross section are used.

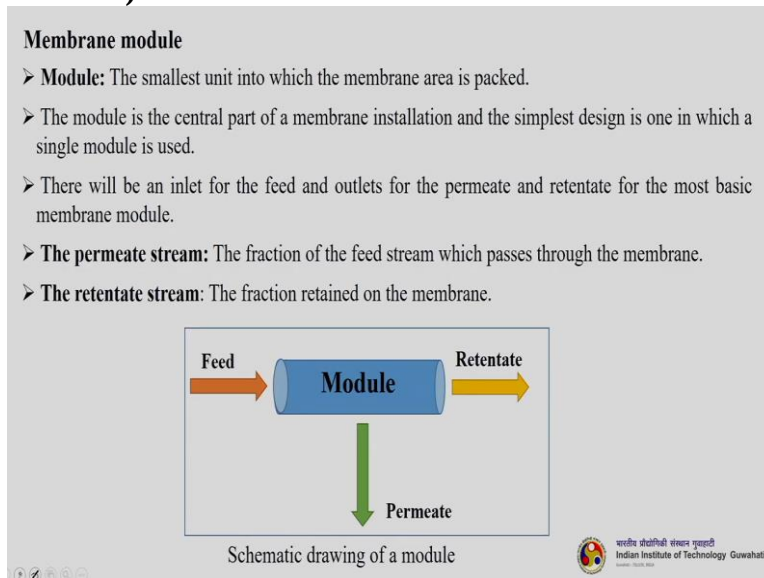

 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
 Indian Institute of Technology Guwahati
 Guwahati - 781 005, India

So, you can see this is a composite membrane basically. So, here you can see there are 3 distinct layers, one is this red one and other is this one another is this one. So, the first one is the separation layer that is doing the separation. Do not think that always a composite

membrane or an isotropic membrane and will have only 2 layers, it is not like that mostly it can have 3 layers it can have more than that also, but usually not more than 3 layers.

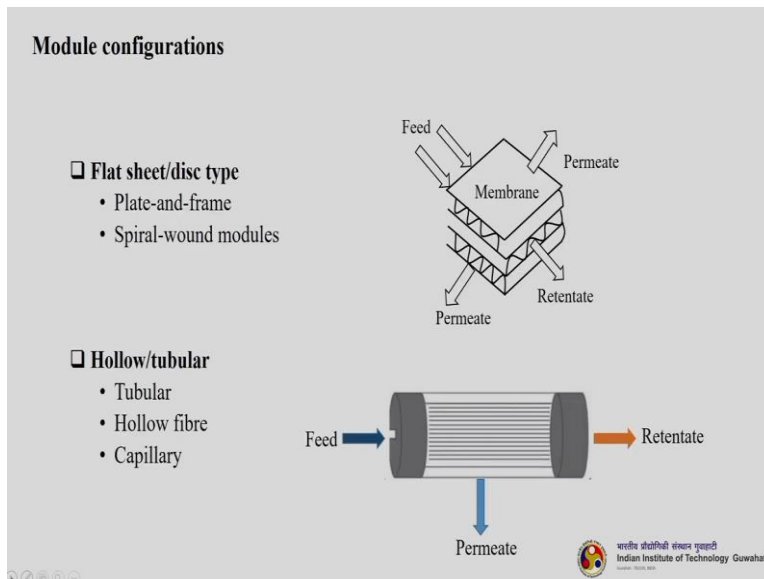
So, in this particular case in this application, you can see the distinct layers, this is the first one the separation is being done, this is the second layer and this is the micro porous layer, 3rd layer the titania support. So, the first one is separation layer, which is used by the sol gel methods. The second layer is a distinct ultrafiltration layer and the 3rd one this one which is providing the support is the microfiltration layer and below that we have coarse layer.

(Refer Slide Time: 16:38)



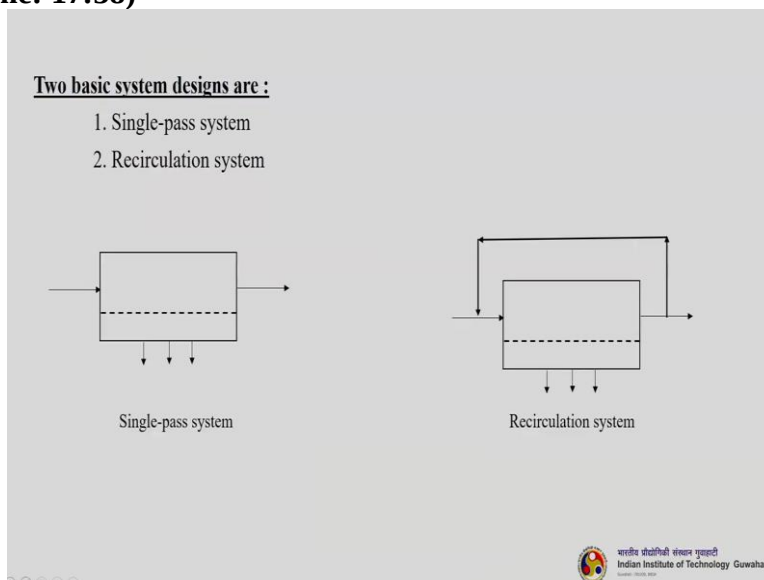
So, then let us discuss about membrane module. So, the module is what so module is something that is actually holding the membrane; it is the smallest in unit into which the membrane area is packed. So, the module is the central part of the membrane installation, and the simplest design is one in which a single module is used. There will be an inlet for the feed and outlets for the permeate. And retentate for the most basic membrane module, the permeate stream the fraction of the feed team which passes through the membrane. The retentate stream the fraction retained on the membrane.

(Refer Slide Time: 17:08)



So, we have different types of module configurations flat sheet and disc type, hollow tubular type. So, in plate we can have a flattened flame type of module. So, you can have a spiral wound modules. So, you can have a hollow fibre or tubular module. So, this is a hollow fibre system, we have capillary module we have tubular module. So, this also have discussed in detail so I am just quickly going through little basics so that you can recall what we have discussed.

(Refer Slide Time: 17:38)



So, we have 2 basic system designs of the membrane. So the first one is single pass system in vice a feed is coming, we get a retentate and we get a permeate. So this is single pass system and there is a recirculation system. So feed is coming here. We get permeate here. We get retentate here and part of retentate that we can say a desk that is getting recycle and mixed

with feeds. So, this is being done for specific applications switch to maintain the feed concentration.

(Refer Slide Time: 18:07)

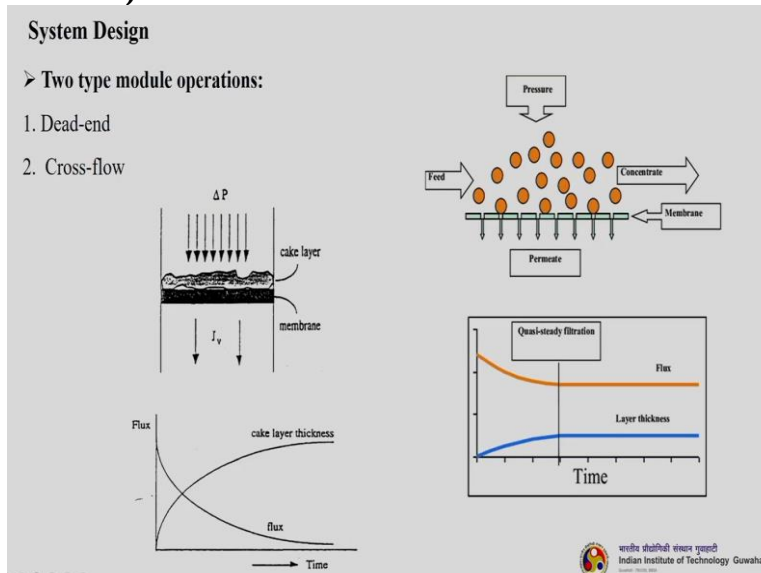
The choice of module configuration, as well as the arrangement of the modules in a system depends on:

- Economic considerations (cost is most important)
- Type of separation problem
- Ease of cleaning
- Ease of maintenance and operation
- Ease of compactness of the system
- Scale and the possibility of membrane replacement



So, choice of module configuration as well as the arrangement of the module in a system depends on several features several characteristics features or parameters. So, that we can the first one is of course the cost, the cost is most important thing, second is type of separation problem. So, ease of cleaning ease of maintenance and operation ease of compactness of the system scale and the possibility of the membrane replacement.

(Refer Slide Time: 18:31)



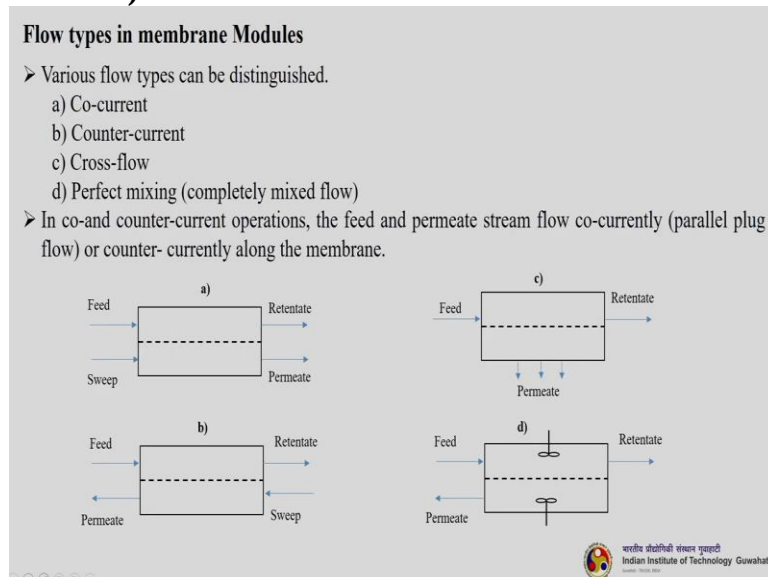
We can have 2 different types of module operations. So, we can have a dead end operation we can have a cross flow operation is the dead end operation. So, you can see this is your membrane on which of course, this concentration polarization and cake layer is getting

deposited, your permeate is coming here you are applying pressure. So, your feed is fixed volume. So, whatever you have given then you are pressurized the system.

So, the feed volume is continuously decreasing and permeates and getting out here. So you can permeate so your feed and then be getting retentated on this surface of the. So, what is happening you see the flux profile flux there is a drastic fall of flux here, because it is a dead end filtration system and cake layer thickness in this is also it is almost complementary to each other the way the flux is decreasing the in the same way that cake layer thickness is increasing.

Now, another one is the cross flow system. So, here the feed is flowing across the membrane surface permeates coming here you are pressurizing here and you are getting the concentrated the retentated here the flux profile is little better or why little is far better than the dead end filtration. So, you can see there is no instantaneously decrease. In the this one flat, it is more or less better profile and the thickness are also complimentary to each other. So, you can say that cross flow filtration and is always better. However, those infiltrations are also used in lab scale to characterize membrane and to generate debtors.

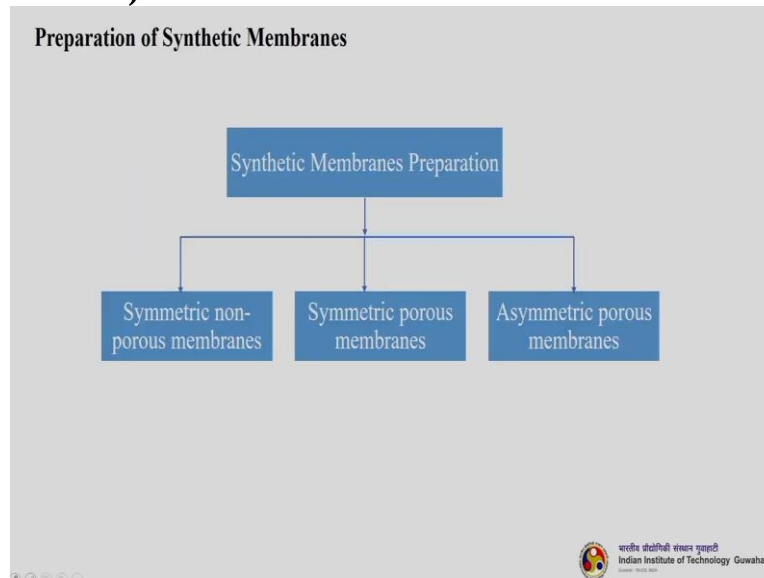
(Refer Slide Time: 20:00)



So, various types of flow can be distinguished inside the modules. So, co current counter current cross flow and perfect mixing or completely mixed flow. So, in co current and counter current operations the feed and permeate steam flow co currently parallel plug flow or counter currently along the membrane. So, this is the first one is the co current so, feed and permeate feed and sweep is getting actually flowing in the same direction.

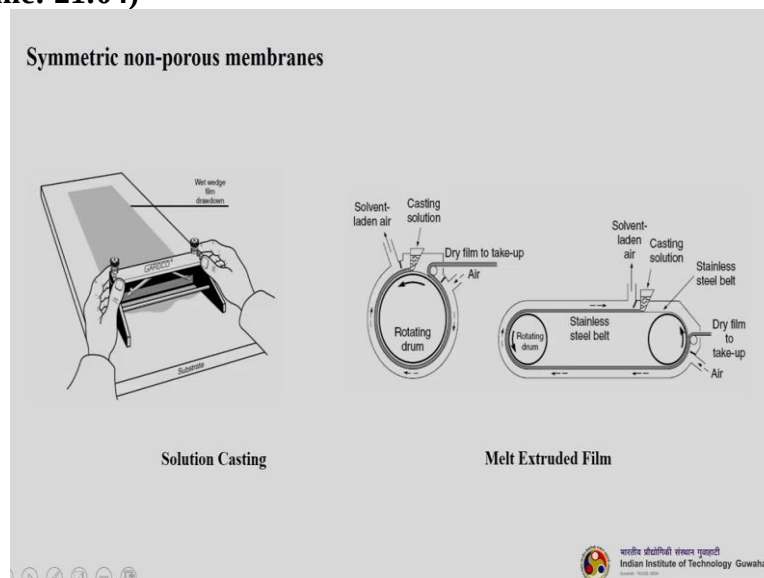
So, in the second is counter current in his feed and sweep is flowing in opposite direction the third is called cross flow the usual cross flow which we just discussed and 4th is the perfect mixing here both the permeate side and the pet side are getting will mixed. So, the mixing enhances the rate of masters for basically that is the idea to mix it, but it is not done always in all the systems.

(Refer Slide Time: 20:49)



So, now, let us just quickly discuss the different preparation methods. So, first the preparation of synthetic membranes so we can have symmetric non porous membranes, we can have symmetric porous membrane, we can have a symmetric porous membrane, so we will just see one by one in a single slide.

(Refer Slide Time: 21:04)

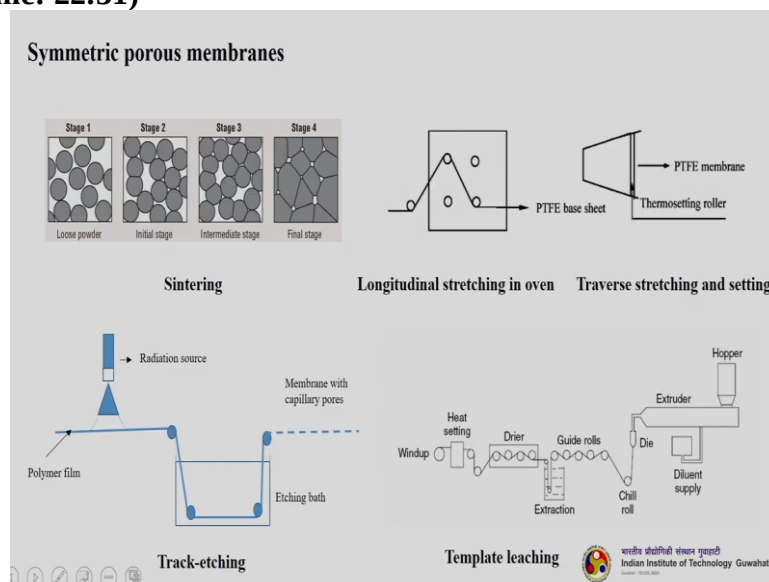


So, symmetric non porous membrane we have solution casting. So, if you recall, we have discussed how to do that. So, you take a polymer sample basically it is a solid dissolve it in a solvent in which it is completely dissolvable. So, you have got a solution which is called polymer solution then you cast it on a plate something which is being shown here, it can be a stainless steel it can be a glass plate, you once you cast it, then there is some roller type of arrangement with a knife then evaporation will take place.

The material will settle down and then finally, this can move here in this direction in this direction, it will decide the thickness of the membrane. So it is a very crude way you prepare symmetric non porous membrane is called solution casting. Then we have melt extruded film here, the same once you cast the solution that means the polymer solution you are pulling here? Conveyor belt system arrangement.

So it is rotating in this direction the stainless steel balls and there is a conveyor belt here basically stainless steel and then you have a pushing air here. So basically it is dryer it is a dry air is helping in the evaporation of the this one solvent from the solution then you take a dry film and this is any way a good way to prepare actually symmetric nonporous membranes and mostly commercial applications this type of technology is being adopted.

(Refer Slide Time: 22:31)



Then symmetric porous membrane so, we have other so many different types of processes. I am just tried to give you the symmetric to understand something. So, the first one is let us understand sintering. Sintering is a process in which we are taking powder materials, it can be

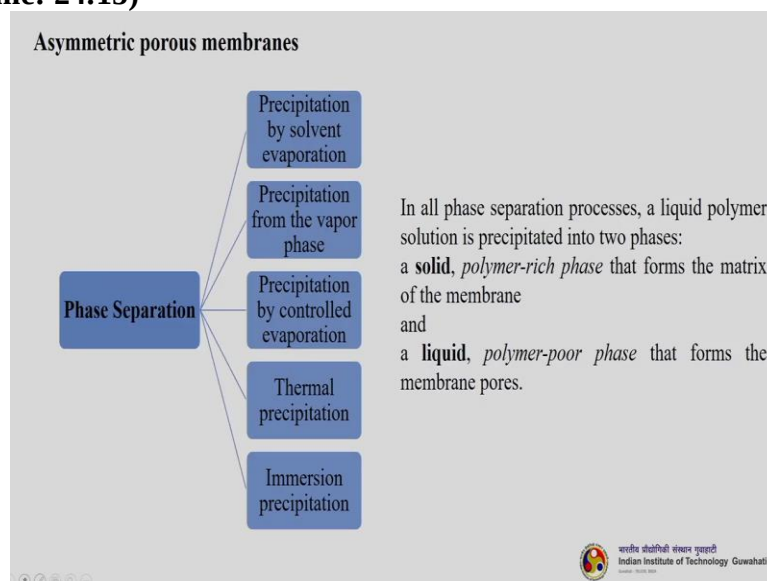
any other materials also and doing some thermal treatment at very high temperatures. So, let us discuss about the powder material as you see the first one is the loose powders.

So, initially you just pack it so it becomes a little better packing. Initial stage then the temperature is being applied here. Then it is the intermediate stage and slowly the interest process will disappear this will disappear and it will result in pores. So, these are basically the pores. So, it is the easy process easy way to do the second one is stretching. So, basically once you have a once your something is coming from the extruder.

So, after extrusion basically, so, that goes to stretching you are just stretching manual stretching also can be done as well it was done when membrane are being prepared in labs. So, you can do the longitudinal stretching inside and oven also so, that evaporation also happens, all you can do the crossover stretching, then go for setting. So, then we can have track etching.

So, you are track etching the polymer which is already been casted into a film will be subjected to various different intensity of radiation sources, so the radiation will fall on the (())(23:39) And it will develop cracks the cracks will have the loose materials those can be cleaned when it goes through a etching bath in template leaching more or less the same process. So, you can just go back and again see what we have discussed

(Refer Slide Time: 24:15)

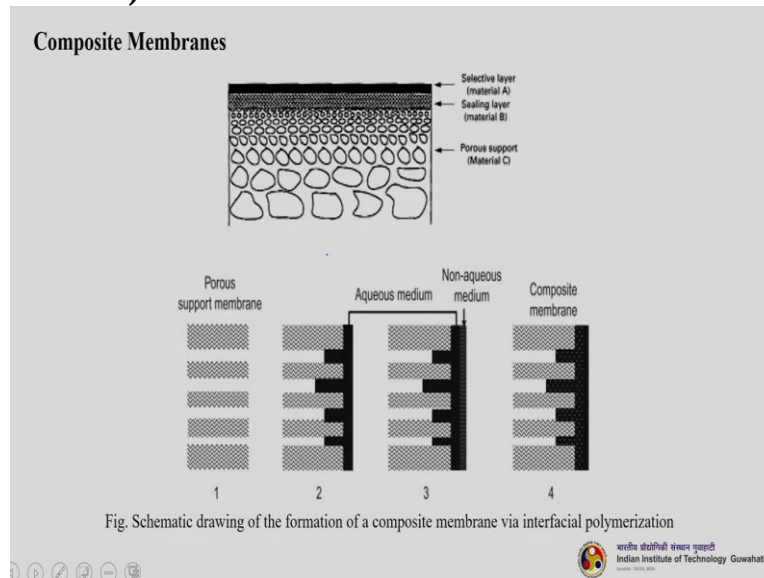


During our template leaching discuss it. So, then is there a symmetric porous membrane. So, you can have precipitation by solvent evaporation, we can have precipitation from the vapor

phase, we can have precipitation by controlled evaporation we can have thermal precipitation we can have immersion precipitation. So, in all the cases all phase up these are all phase separation processes.

A liquid polymers solution is precipitated into 2 phases the first is solid, which is a polymer rich phase secondary liquid which is a polymer poor phase that forms the membrane pores.

(Refer Slide Time: 24:48)



Then let us understand composite membrane so, composite membranes are an isotropic membrane basically. So, we can have a 2 layer composite membranes and we gave a 3 layer composite membranes and we can 4 layer composite membranes. So first one as we have already discussed the selectively the material which is doing the separation the thickness would be as low as possible.

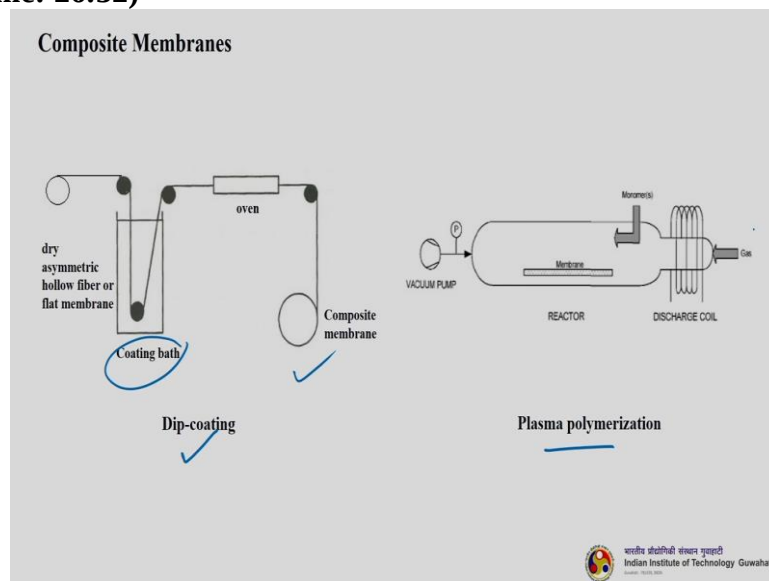
So, that resistance to flow will be less then we have another layer basically maybe ultrafiltration then we have a microfiltration sealing layer and we can of course porous layer here. So, this is how actually this one composite membrane is prepared by interfacial polymerization and this is one of the most important developments in the membrane science, the technology development of interfacial polymerization.

So, one porous support membrane is there. So, I am impregnated this with some amines. So, this block whatever you have seen, so, this is a means, so, now the membrane is amines loaded now, this once it is done, so, another non aqueous medium, I am bringing in contact

with them which is basically diacid. So, diacid it chlorides whatever it is, so, it can be different. So, this mean diacid will react with each other and it will do cross linking.

So, this cross linking will result in the polymers. So, now you are seeing the some cross linking the extent happening here, then it will become a polymer structure and it will be so nicely attached to the pores of the membrane the membrane support that it will not come out easily because it is a reaction by reaction it has been developed. So, this is how by professional elimination, you develop different types of composite membrane.

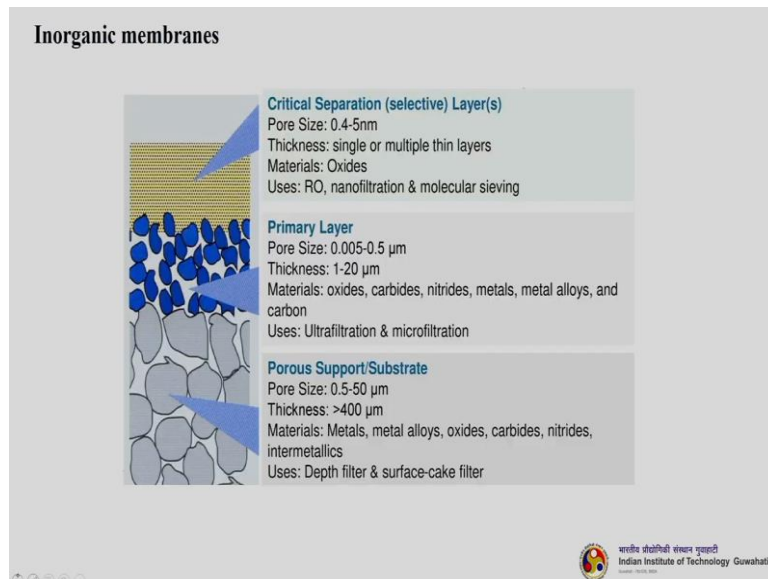
(Refer Slide Time: 26:32)



So, you can have composite membrane by the usual dip coating method which is extensively used in the lab scales. So, let us say you have a small circular ceramic membrane and I want to develop a composite membrane, I want to put a very thin layer of polymeric support about it. So what I do I debit inside the polymeric solution or the coating bath. Slowly and tech out slowly how are you at dipping it? At how what rate you are taking it all these are parameters to be that affects the final pitches.

Then you write and you get here composite membrane and easy way to do it. So, otherwise you can have plasma polymerase and its excellent method you are generating plasma to do polymerase and basically. So, the gas is coming it is getting ionized plasma is getting this one generated, then those are getting deposited on the surface of the membrane and in the victimized oven and it is happening. However, the process is very costly.

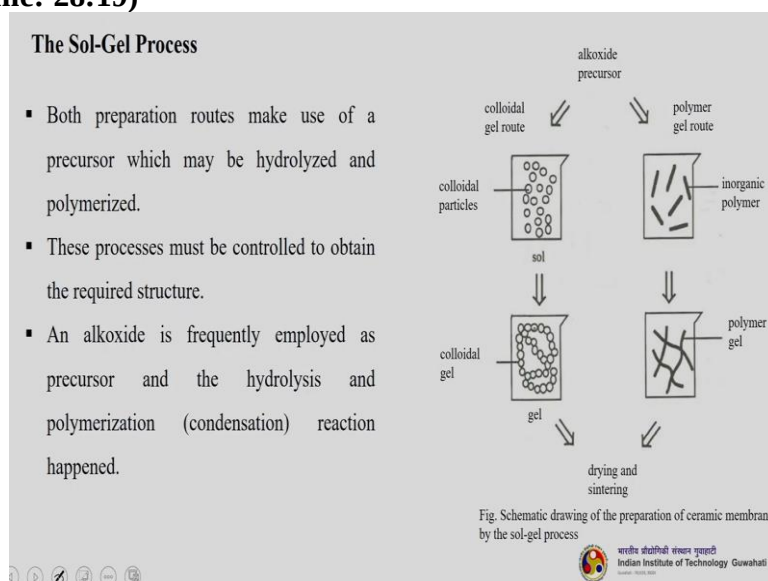
(Refer Slide Time: 27:34)



Those who have discussed this, I wanted to show you this slide to understand again or recall again, how the composite membrane looks like basically. So, the first one is the critical separation like the selectively this one. Pore size it is usually 0.4 to 5 nanometer thicknesses singular multiple thickness materials are basically oxides the users in reverse osmosis and Nano filtration and molecular sieving than the primary layer.

The pore size is almost 0.005 2.5 micron 1 to 20 micron thickness the prints see you this is ultrafiltration and microfiltration then we have pore supporter subset 0.5 to 50 micron thickness is greater than 400 micron depth filter and surface cake filter even coarse filter also.

(Refer Slide Time: 28:19)

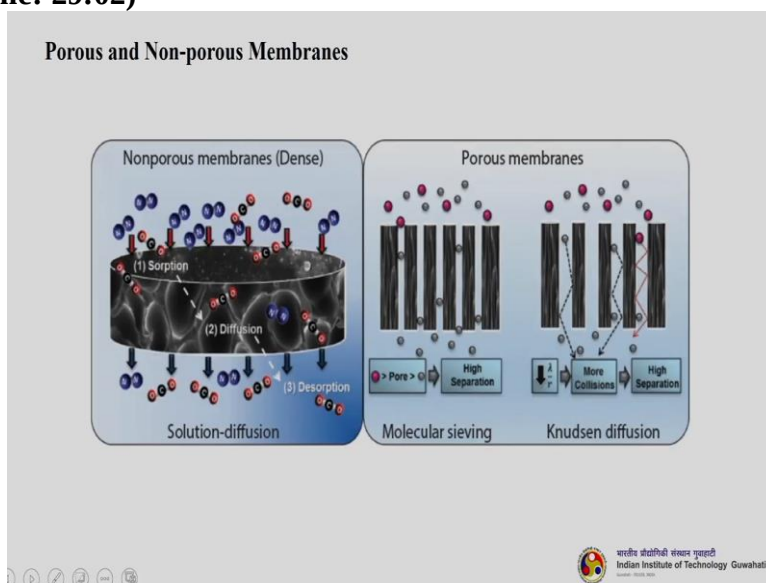


So, now, let us understand quickly the sol gel process one of the most important breakthrough again just like interpersonal polymerization in ceramic membrane development so, we can

have 2 different routes. So, we have alkoxide precursor we can have a colloidal gel route, we can have a polymer gel route. So, both represent routes make us precursor which may be hydrolyzed and polymerized to reaction are happening.

I am not saying again the reaction here you can just revisit and see the reactions. So, one is hydrolysis reaction. The next is polymerizing reactions. Now these processes must be controlled to obtain the required structure and alkoxide is frequently employed as a precursor and the hydrolysis and polymerization condensation and reaction happened.

(Refer Slide Time: 29:02)



Let us understand how actually transport happening in porous non porous membrane in non porous membrane which is dense membrane the separation is happening through solution diffusion. So the solutes are coming and they are getting deposited on the surface of the membrane slowly they will get themselves dissolved or solubilize inside memory and material then they will diffuse again molecular diffusion of course, then they will permeate.

So, this is what is called solution diffusion solubility diffusivity both are important porous membrane so many different types of things. So, if the pores are the solute is bigger than the pore size then the separation will be high because most of them will be retained on the surface that is called molecular saving mechanism. And if here λ by R is lesser than lesser or let us say the mean free path is higher than the pore diameter pore mouth then we will have Knudsen diffusion this is more prevalent for gas separation.

(Refer Slide Time: 30:08)

The characterization of porous membranes

- One important, but often not clearly defined variable in the characterization of porous membranes is the *shape* of the pore or its *geometry*.
- In order to relate pore radii to physical equations, several assumptions have to be made about the geometry of the pore.
- For example, in the Poiseuille equation the pores are considered to be *parallel cylinders*, whereas in the Kozeny-Carman equation the pores are the *voids between the close-packed spheres* of equal diameter.

$$J = \frac{\Delta p d_p^2 \varepsilon}{32 x \mu_p}$$

Poiseuille equation

J = permeate flux,
 Δp = transmembrane pressure,
 d_p = diameter of the pores,
 ε = surface porosity of the membrane,
 x = pore length, and
 μ_p = viscosity of the permeating fluid.

$$J = \frac{\varepsilon^3}{K \eta S^2 (1 - \varepsilon)^2} \frac{\Delta P}{\Delta x}$$

Kozeny-Carman equation

K = Kozeny-Carman constant
 S = Specific surface area



Now, then the next thing that we have discussed in subsequent few lectures 1 or 2 or 3 I think so, is the characterization different types of membrane porous membrane and non porous membrane then we have discussed also the characterization of your iconic membrane. So, one important but often not clearly defined variable in the characterization of porous membrane is the shape of the pore or its geometry.

It also plays a very big role in order to let for the ideas to the physical equations; several assumptions have to be met 2 questions which we have already discussed many times. First one easier Hagen poiseuille equation or poiseuille equation. The second is the kozeny carman equation. Now, what is the difference between these 2 equations is just the assumptions. So, in poiseuille question the pores are considered or assumed to be parallel cylinders which is not true in of course, real life and in kozeny carman equation.

The pores are considered to be the words between them closely packed spheres. So, you can see something like this. So, this is what is the pores and here in the case of parallel cylinders it is just like this. So, only geo lights have such distinct features parallel otherwise you do not get in any other commercial membrane.

(Refer Slide Time: 31:23)

The characterization of porous membranes: Nominal and absolute rating

- The membrane can be characterized by a *nominal* or an *absolute* pore size .
- With an absolute rating, every particle or molecule of that size or larger is retained.
- The absolute rating should not be confused with the largest particle passed by a filter under operating conditions.
- It simply determine the size of the largest particle which will pass through the filter under very low pressure differentials and non-pulsating conditions.
- On the other hand, a nominal rating indicates that a percentage (95% or 98%) of the particles or molecules of that size or larger is retained.

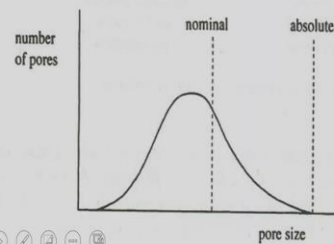


Fig. Schematic drawing of the pore size distribution in a certain membrane

So, we need to understand the nominal absolute rating which we have discussed during the characterization. So, the membrane can be characterized by a nominal or absolute pore size. So, with an absolute rating which is this? So, every particular molecule of that size or larger is getting written on the surface of the membrane compared to what compared to the process so, the absolute rating should not be confused with the largest particle passed by a filter under operating conditions.

So it simply determines the size of the largest particle which will pass through the filter under very low pressure differentials and non pulsating conditions. On the other hand, a nominal rating indicates the percentage of 95% to 98% of the particles that is getting a retained on the surface of the membrane.

(Refer Slide Time: 32:11)

The characterization of porous membranes

Two different types of characterization methods for porous membrane can be distinguished from the discussed considerations:

Structure related parameters:

- Determination of pore size, pore size distribution, top layer thickness and surface porosity.

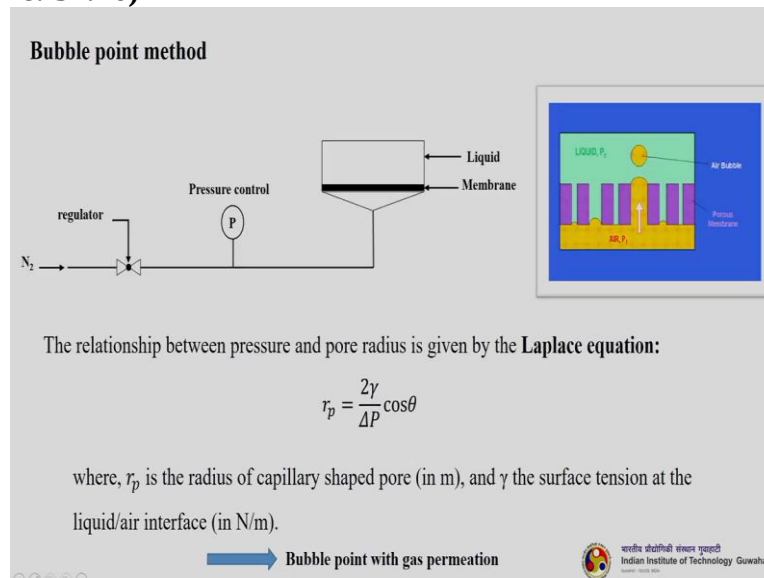
Permeation related parameters:

- Determination of the actual separation parameters using solutes that are more or less retained by the membrane ('cut-off' measurement)
- It is often very difficult to relate the structure-related parameters directly to the permeation related parameters because the pore size and shape is not very well defined.

So, when you talk about the characterization porous membrane, so, we characterize 2 different things firstly structural related parameters, which are pore size distribution top layer thickness and surface porosity and then permeation and related parameters. So, determination of the actual separation parameters using solutes that are more or less retained by the membrane.

Which is called cut off membrane or cut off measurement or we can call it molecular weight cut off experiments also, it is often very difficult to relate the structure related parameters directly to the permeation related parameters because of the pore sizes and shape is not very well defined.

(Refer Slide Time: 32:46)



So, the first one is the porous membrane character is a microfiltration and basically the bubble point method here, what has been done is this. So, you take the membrane and put it in some module or some arrangements something like this then a wide the membrane. So, the top portion of the membrane is getting waited the pores are also getting feed. So, with the liquid you can see the pores are getting filled here then you pass nitrogen or some inert gas from the bottom.

So, the air or nitrogen will push them itself through the bottom of the membrane and the better a very nice thing about is this particular simple method is that only the pores which are active will be characterized because the dedence pores which are blocked that the pore is blocked like this and the flow pore is open. So, these are this is a pore this is a pore. So, only

the active pore will be corrected this dedence pores will not be characterized you use the Laplace equation $r_p = \frac{2\gamma \cos \theta}{\Delta p}$ to find out the pore radius.

So, this is the surface tension. r_p is the radius, and θ is the angle so a little modification of this method is bubble point with gas information in which actually first initially you measured the flux using the drive membrane, then wide membrane and again see how the this one gas is basically getting diffused inside the pores of the membrane and displacing the liquid.

(Refer Slide Time: 34:16)

Mercury intrusion method

- In this method, mercury is forced into a dry membrane with the volume of mercury being determined at each pressure.
- Since, mercury doesn't wet the membrane (i.e. the contact angle is greater than 90°), the above equation can be re-written as: $r_p = -\frac{2\gamma \cos \theta}{\Delta P} = \frac{7492}{\Delta P}$
- Since, the volume of mercury can be determined *very accurately*, pore size distribution can be determined quite precisely.
- At the *lowest pressure*, the *largest pores* will be filled with mercury.
- On increasing the pressure, the progressively smaller pores will be filled. This will continue until all the pores have been filled, and a maximum intrusion value is reached.

Indian Institute of Technology Guwahati

So, another one is the mercury intrusion method this gives excellent accurate measurement because mercury does not wet the membrane. So, you can use this again the same Laplace equation by substituting the θ and this interperosnal surface tension values we can reduce this equation getting reduced to 7492 divided by Δp he says what r_p is a direct consequence of Δp .

So, the volume of mercury can be determined very accurately. So, the pore volume determinism can be done very accurately pore size distribution can be also done accurately. So, at lowest percent the largest pore will be initially filled the new increase the pressure the smallest but also will be filled.

(Refer Slide Time: 35:01)

Permeability method

- If capillary pores are assumed to be present, the pore size can be obtained by measuring the flux through the membrane at a constant pressure using *Hagen-Poiseuille equation*:

$$J = \frac{\epsilon r^2 \Delta P}{8 \eta \tau \Delta x}$$

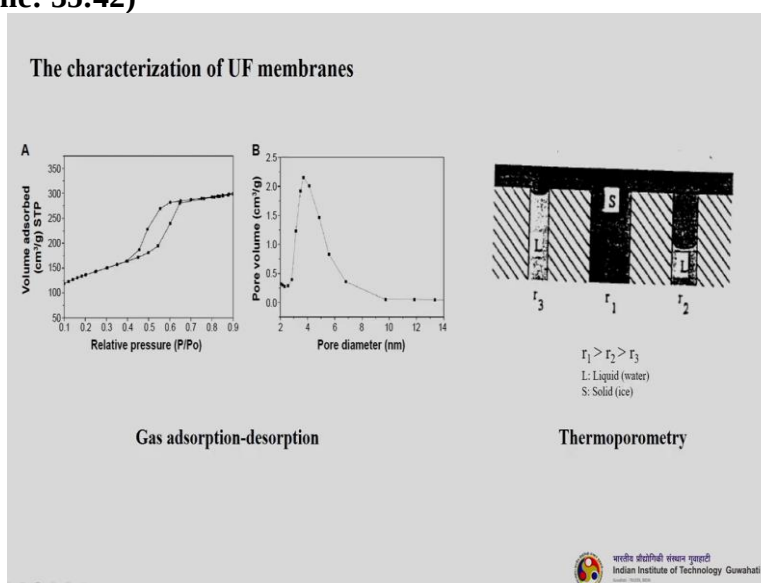
- Here, J is the water flux through the membrane at a driving force of $\Delta P / \Delta x$, ΔP being pressure difference (N/m^2) and Δx the membrane thickness (m).
- The proportionality factors contains the pore radius ' r ' (m), the liquid viscosity ' η ' ($Pa.s$), surface porosity ' ϵ ' and tortuosity factor ' τ '.
- The pore size distribution can be obtained by varying the pressure. It is not essential that the liquid should wet the membrane.



The cost is very high of this particular apparatus. So, the next is permeability methods, which are actual real experimental if you assume capillary pores to present the pore size can be obtained by measuring the flux through the membrane at a constant pressure using the Hagen-Poiseuille equation. So, here J is the water flux through the membrane at a driving force of $\Delta P / \Delta x$, ΔP being the difference in pressure in N/m^2 and Δx is a membrane of thickness.

So, now is the tortuosity factor ϵ is the surface porosity then we have this r in pore radius and this is it is viscosity pore size distribution can be obtained by varying the pressure it is not essential that the liquid should wet the membrane.

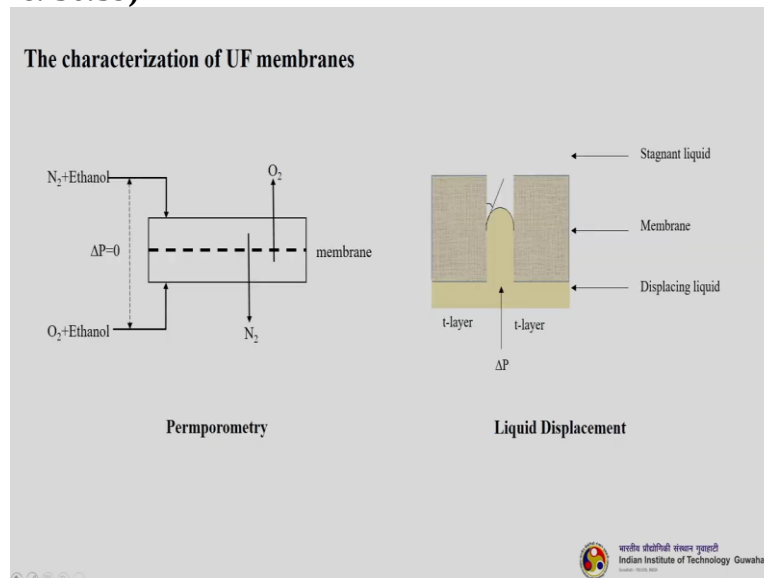
(Refer Slide Time: 35:42)



And then if you talk about the characterization of ultrafiltration membrane the most important experimental method or article method is the gas absorption and desorption. You are observing a particular gas on the surface of the membrane and then again desorbing it. So, you will see this is the this is a hysteresis loop. We have discussed in detail what is hysteresis? What are the different types of hysteresis, why hysteresis happens, but please go back and just revise and recall what we have discussed?

And we can have a thermo porometry. So, what you need is a DSC instrument differential scanning calorimetric system, which is again a costly instrument and the calorific measurement of this solvent or liquid is being carried out in this particular distance. So, the extent of cooling or under cooling is being measured. In thermo porometry method, this is also very good method, but you need a DSC for that.

(Refer Slide Time: 36:39)

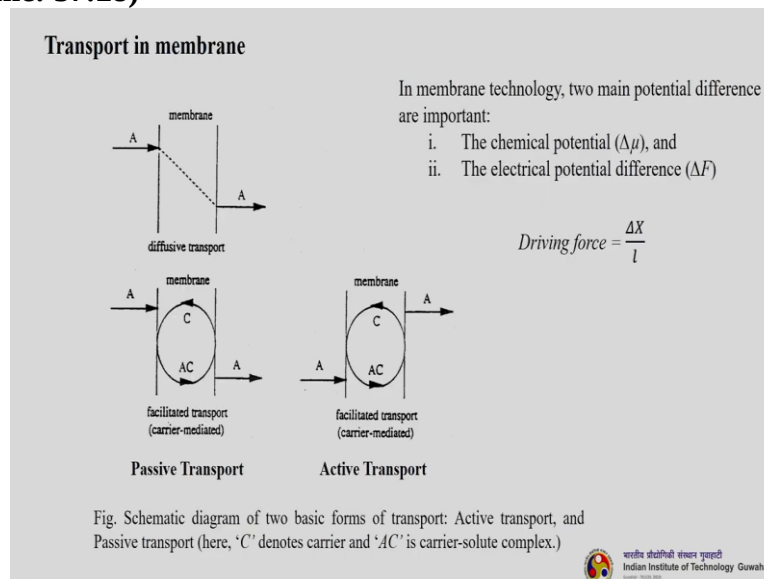


So, we can have permporometry saying permporometry will have a condensable gas and non condensable gas. So, nitrogen oxygen or non condensable ethanol is condensable. So, the diffusivity of oxygen this side and the diffusivity of nitrogen decide in the presence of ethanol is being measured. So, that will give us the pore size pore diameter. Everything so, liquid displacement is another method in this like bubble point method here gas is not being used to displace the liquid here another liquid.

Which is impossible with the already present liquid is being used to displace the liquid. So, you see this is a distressing liquid which is of course immiscible with a stagnant liquid this is

also a very good method you should ensure that both the liquids this would not be miscible at all.

(Refer Slide Time: 37:28)



Then let us quickly discuss about the transport in membrane so, 2 types of transport happens passive and active transport. Passive transport is a direct consequence of the differences in concentration or the process. So, that means it is happening from higher concentration to low concentration where its active transport happens from a lower concentration to higher concentration against that gradient of its concentration.

Are there any other things so, to do that you can understand that you need some sort of energy so, we need some extra energy to carry out this. So, you can have facilitator transport where there is a carrier present. So, the carrier will bind to the solute and help to defuse the solute that is being transported to the membrane. And it will take it to the permeate side then it will again dissociate itself.

So, the driving force is $\Delta x / l$ Δx is the gradient and L is of course, the thickness of the membrane. So, you can have either potential chemical potential as a grid or we can have an electrical potential is a gradient. So, these active transports are mostly their biological systems we will see in biological systems. So, glucose transports, so, transport of glucose, glucose from blood to liver cells, because in liver cells that glucose is present in very high concentration.

So we are trying to act against the concentration gradient from low to high we are going not from high to low. So, we need some energy. So, energies are being provided in biological system by ATPs, adenosine triphosphate or ATP or an independent there are so, many other varieties also.

(Refer Slide Time: 39:16)

Membranes Transport Theory

- The most important property of membranes is their ability to control the rate of permeation of different species.
- Permeation mechanism can be explained by
 - ❖ Transport through porous membrane (MF and UF)

Separation occurs through pores
 - ❖ Transport through non-porous membrane (Dense membranes)

Permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient.

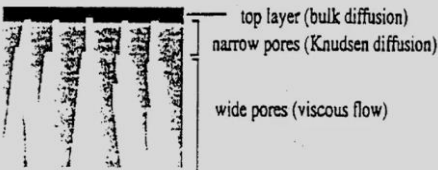

 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
 Indian Institute of Technology Guwahati
 Guwahati - 781 005

The most important property of the membranes is their ability to control the rate of permeation of different species. Permeation mechanism can be explained by 2 things firstly the transport through porous membrane separation occurs through pores then transport through non porous membrane dense membrane. So, here permeate dissolve in the membrane material, then diffuse through the membrane down a concentration gradient. Solution diffusion model is being used here.

(Refer Slide Time: 39:44)

Transport of gases through porous membranes

- When an asymmetric membrane or composite membrane is used in gas separation, the gas molecules will tend to diffuse from the high-pressure to the low-pressure side.
- Various transport mechanisms can be distinguished depending on the structure of the asymmetric membrane or composite membrane,
 - a) Transport through a dense (nonporous) layer
 - b) Knudsen flow in narrow pores
 - c) Viscous flow in wide pores
 - d) Surface diffusion along the pore wall



top layer (bulk diffusion)
 narrow pores (Knudsen diffusion)
 wide pores (viscous flow)

Fig: Transport in an asymmetric membrane as a result of various mechanisms


 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
 Indian Institute of Technology Guwahati
 Guwahati - 781 005

So, transport of gases through porous membrane when asymmetric membrane or composite membrane is used in gas separation, the gas molecules will tend to diffuse from the high pressure to the low pressure side. The various transport mechanisms can be distinguished so you can have a Knudsen flow in narrow pores we can have viscous flow in wide pores we can have surface diffusion along the pore walls.

So, you can see this is a composite membrane 3 layer composite membrane, the top layer bulk diffusion is happening the narrow pores we have not seen diffusion then we mean free path but more than the pore or diameter and then we have wide pore where viscous flow is happening.

(Refer Slide Time: 40:17)

Transport through non-porous membranes

- When the sizes of molecules are in the same order of magnitude, as with oxygen and nitrogen or hexane and heptane, porous membranes cannot effect a separation.
- In this case, nonporous membranes must be used. However, the term nonporous is rather ambiguous because pores are present on a molecular level in order to allow transport even in such membranes.
- The existence of these dynamic molecular pores can be adequately described in terms of free volume.
- Initially, transport through these dense membranes will be considered via somewhat simple approach. Thus, although there are some similarities between gaseous and liquid transport, there are also a number of differences.



www.iitg.ac.in
Indian Institute of Technology Guwahati

And transport in non porous membrane. So, when the sizes of the molecules are in the same order of magnitude as with oxygen nitrogen or hexane heptane porous membrane cannot effect a separation. So, in this case non porous membrane must be used however, the term non porous is rather ambiguous because pores are present on a molecular level in order to allow transport even in such membranes.

The existence of these dynamic molecular pores can be adequately described in terms of free volume. Initially transport through these dense membrane will be considered via somewhat simple approach thus although there are some similarity between gaseous and liquid transport there are also a number of differences.

(Refer Slide Time: 40:52)

- In general, the affinity of liquids and polymers is much greater than that between gases and polymers, i.e. the solubility of a liquid in a polymer is much higher than that of a gas.
- Sometimes, the solubility can be so high that crosslinking is necessary to prevent polymer dissolution.
- In addition, a high solubility also has a tremendous influence on the diffusivity, making the polymer chains more flexible and resulting in an increased permeability.
- Basically, the transport of a gas, vapour or liquid through a dense, nonporous membrane can be described in terms of *solution-diffusion mechanism* i.e.,

$$\text{Permeability (P)} = \text{Solubility (S)} \times \text{Diffusivity (D)}$$

So, in general the affinity of liquids and polymers is much greater than that of between gases and polymers that is the solubility of liquid in a polymer is much More higher than that of a gas. So, sometimes the solubility can be so high that crosslinking is necessary to prevent polymer dissolution. In addition, a high solubility also has a tremendous influence on the diffusivity making the polymer chains more flexible and resulting in an increased permeability.

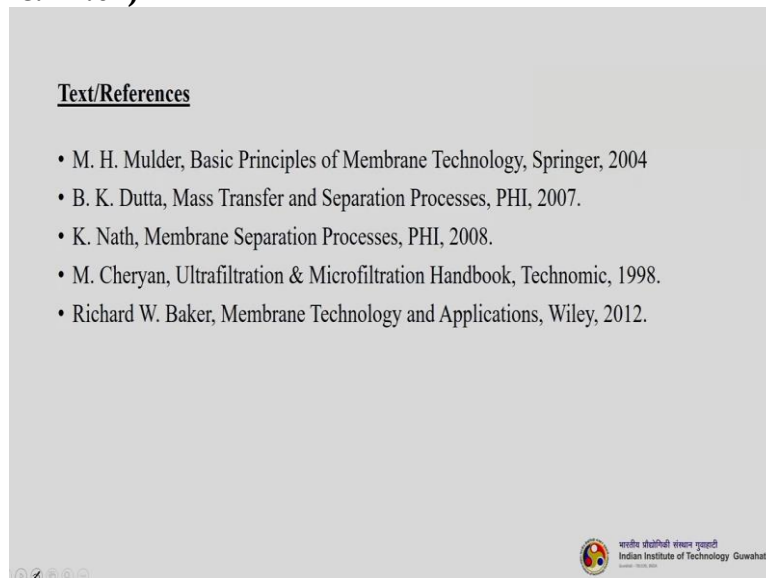
So, basically the transport of gas vapour or liquid through a dense nonporous membrane can be described in terms of solution diffusion mechanism. So, permeability equals to solubility into the diffusivity.

(Refer Slide Time: 41:28)

- Solubility is a *thermodynamic parameter* and gives a measure of the amount of penetrant sorbed by the membrane under equilibrium conditions.
- In contrast, the diffusivity is a *kinetic parameter* which indicates how fast a penetrant is transported through the membrane.
- Diffusivity is dependent on the geometry of the penetrant, for as the molecular size increases the diffusion coefficient decreases.
- However, the diffusion coefficient is *concentration-dependent* with interacting systems and even large (organic) molecules having the ability to swell the polymer can have large diffusion coefficients.

So, solubility is a thermodynamic parameter and gives a measure of the amount of the penetrant sorbed by the membrane under equilibrium conditions. Whereas, in contrast diffusivity is a kinetic parameter, which indicates how fast a penetrant is transported through the membrane. Diffusivity is dependent on the geometry of the penetrant for as the molecular size increases the diffusion coefficient decreases. However, the diffusion coefficient is concentration dependent and even large molecules organic molecules basically having the ability to swell the polymer can have last diffusion coefficients.

(Refer Slide Time: 42:02)



So, in a nutshell, we have discussed the concepts and the fundamentals of the membranes and various aspects of membrane and materials, the modules how to prepare membranes transport across membranes and how you will prepare ceramic membranes. So, I hope you have enjoyed this particular lecture. So, then next class onwards actually we have already started osmosis the concept of osmosis, which I have not covered today just last class we have discussed from the next class onwards we are starting a reverse osmosis.

So, the membrane processes that we will discuss microfiltration will discuss ultrafiltration on Nano filtration and Parma filtration various hybrid systems and so on. We will go on the other things to discuss also. So, you can refer this text books. Mostly it is taken from Mulder and of course from Professor Baker book as well as from Nath book. So thank you very much.

(Refer Slide Time: 42:56)

(Overview of next lecture)

Module	Module name	Lecture	Title of lecture
06	Reverse osmosis, Nano-filtration, and Ultrafiltration	16	Pressure requirement, high pressure and low pressure RO, membrane materials, modules, models for RO transport

And in the next class, we will discuss about the RO and the pressure requirement, high pressure, low pressure, RO membrane and materials and models, RO and the transport in the RO. So in case you have any questions query, do feel free to write to me at K. Mohanty kmohanty@iitg.ac.in. So this my web mail ID is already there in most of the lectures are you can free to ask your questions or queries in the forum also. Thank you very much.