Membrane Technology

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Lecture No 1

Separation Processes, Historical Development, Definition and Types of Membranes

Good morning, students. This is the first class of this course membrane and technology module 1

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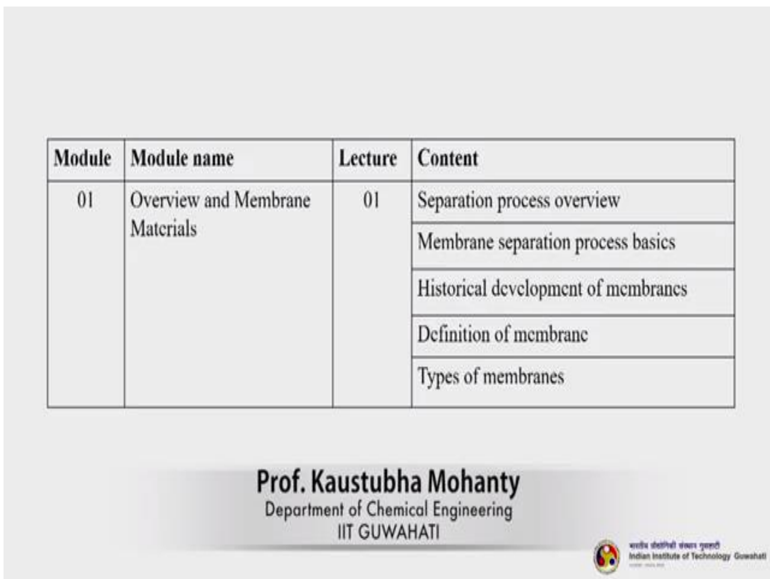

Module	Module name	Lecture	Content
01	Overview and Membrane Materials	01	Separation process overview
			Membrane separation process basics
			Historical development of membranes
			Definition of membrane
			Types of membranes

And lecture 01. As you know that we have divided the course into 12 modules, and each module have 3 lectures so totally there will be 36 lectures. So today, the first module first lecture. Under this lecture will cover and learn the Overview of separation processes, Membrane separation basics and Historical developments of membranes. What is a membrane? Basically the definition of membrane and the different types of membrane.

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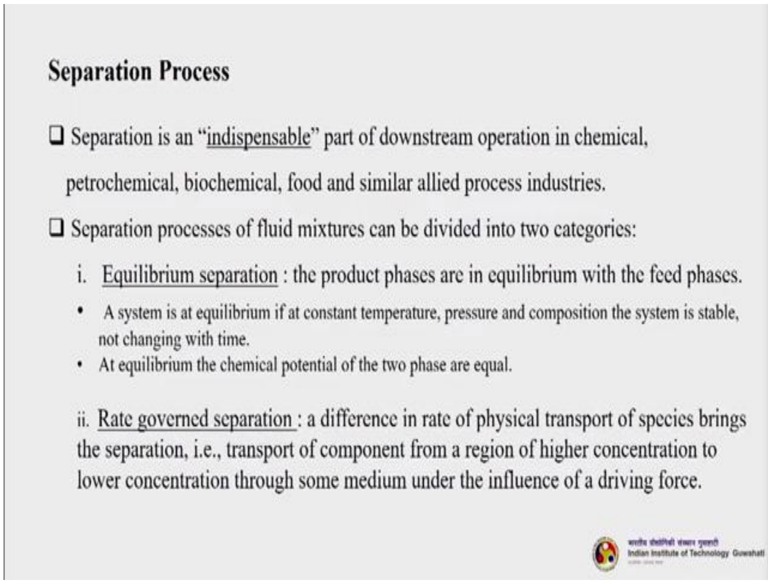

So, as you know, separation is an indispensable part of any downstream operation, in most of the industries. Whether it is chemical, petrochemical, biochemical, food, pharmaceutical or any other allied process industries. So, we can divide the separation processes of fluid mixtures into two categories. The first one, each equilibrium separation and the second one is Rate governed separation. So let us just try to understand what is equilibrium and what is Rate governed?

Now, as the name indicates, equilibrium separation is a process in which the product phases are in equilibrium with the feed phases. Now what is the inherent meaning of equilibrium. Now a system is its equilibrium, keep it constant pressure, temperature and composition. The system is stable, not changing with respect to time. So, at equilibrium the chemical potential of the two phases are equal. So, in the Rate governed separation.

So the separation, actually happens due to the difference in the rate of physical transport of species. And that is the transport of component from a region of higher concentration to lower concentration, using some medium and under the influence of a driving force.So most of the memory and processes are actually comes under Rate governed separation process.

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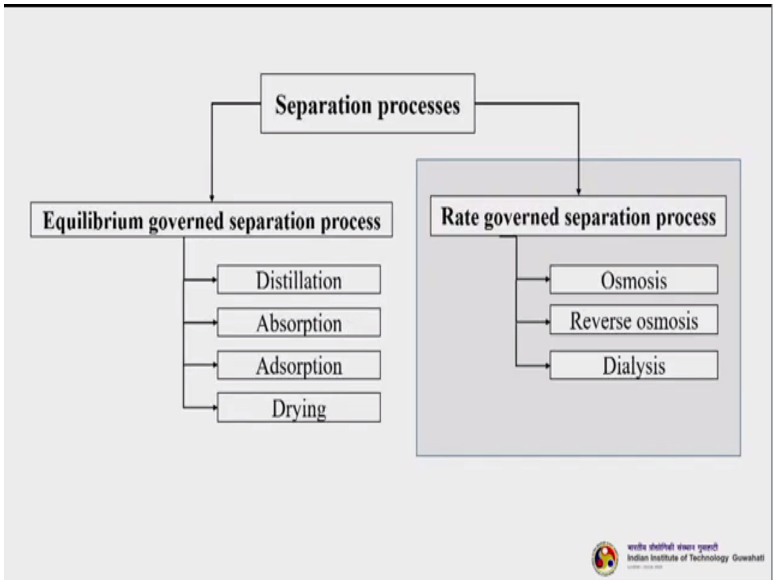

These are some of the examples of the equilibrium governed separation, like distillation Absorption, Adsorption and drying and under the Rate governed separation process most membrane processes comes under that, whether it is Osmosis, Reverse osmosis, dialysis filtration or microfiltration, etc.

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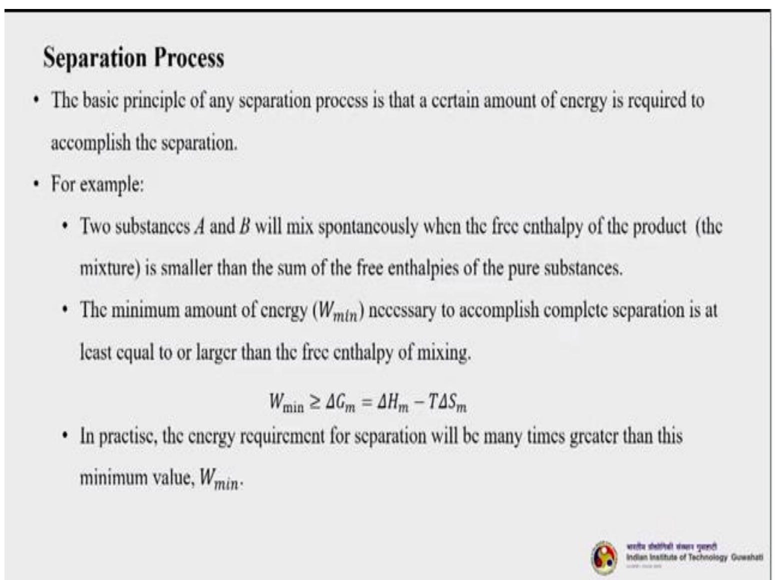

So, the basic principle of any separation process is that a certain amount of energy is required to accomplish that separation. Now let us take an example, let's see there are two substances out there. A and B, which will mix spontaneously. When they will mix, basically the criteria. So when the pre enthalpy of the product that is a mixture. It is smaller than the sum of the pre enthalpy of the pure substances.

So the minimum amount of energy necessary to accomplish complete separation is at least equal to or larger than the pre enthalpy of the mixing. So in practice the energy requirement for separation will be many times greater than this minimum value, which is denoted by the Wmin. So, different types of separation processes exist and each require a different amount of energy.

For example, let us take a simple example which is production of fresh water from seawater. The desalination and actually. So, the desalination of seawater can be achieved in many ways. So, are many processes. So the first one is distillation. So, in distillation, heat is applied to the solution in such a way that the water distill off. And second is freezing. The solution is coold and pure ice is obtained. Third is Reverse osmosis, which is a membrane process.

So here the solution is pressurized allowing water molecules to pass through membrane. While all the salt molecules are retaind. Then electrolysis another membrane process here in electric field is applied to a salt solution between number of charged membranes and ions are forced into certain compartments leaving water molecules in other compartments. So, and the last one is membrane distilation.

And so there are other methods also. In membrane distillation heat is applied to salt solution causing transport of the water vapor through a non-wetted membrane. So, what do we understand from this particular slide is that. So desalination of seawater is a very important process. And it can be achieved in many ways.

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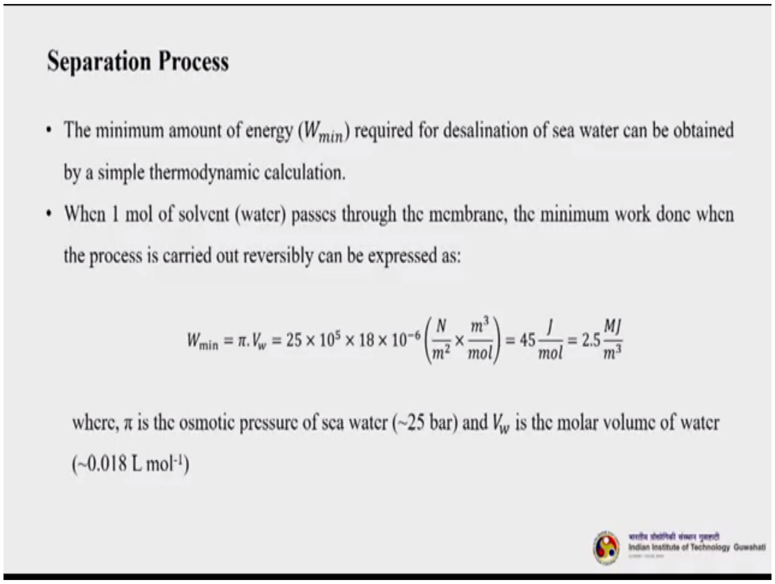

The minimum amount of energy required for desalination of seawater can be obtained by simple thermodynamic calculation. we just see this equation. So, when we take one mole of solvent. Let us say water in this case passes through the membrane, the minimum work done. When the process is carried out reversibly can be expressed as this equation. So Wmin minimum equals two pi into Vw so where pie is the the osmotic pressure of the seawater.

It is approximately 25 bar and Vw is the molar volume of water, which is 0.018 liters per mol, so you get 2.5 mega joules per metric cube.

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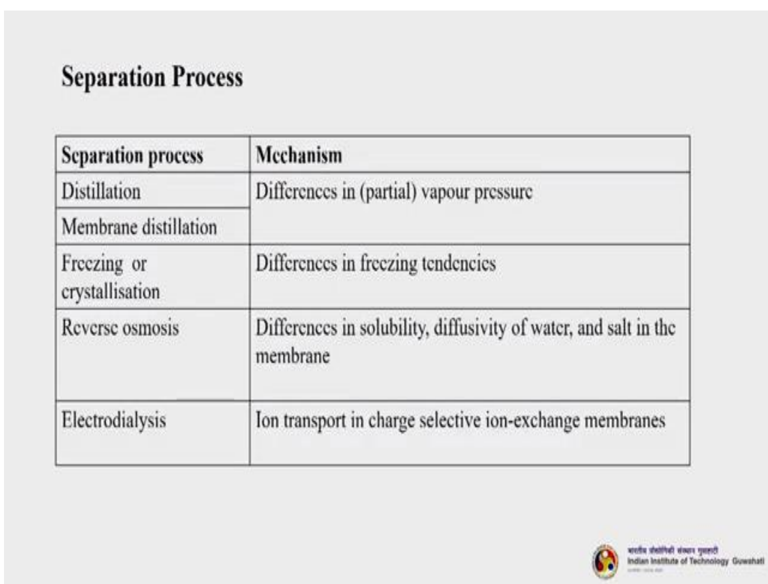

Separation process	Mechanism
Distillation	Differences in (partial) vapour pressure
Membrane distillation	
Freezing or crystallisation	Differences in freezing tendencies
Reverse osmosis	Differences in solubility, diffusivity of water, and salt in the membrane
Electrodialysis	Ion transport in charge selective ion-exchange membranes

There are different separation processes, which works under different mechanism distillation and membrane distillation. These two works in the differences in partial vapor pressure. Similarly freezing or crystalisation works under the mechanism of differences in freezing tendencies and reverse osmosis works on the mechanism of differences in solubility, the diffusivity of water and salt in the membrane.

Electrodialysis works under the mechanism of iron transport in charge selective, ion-exchange membarane.

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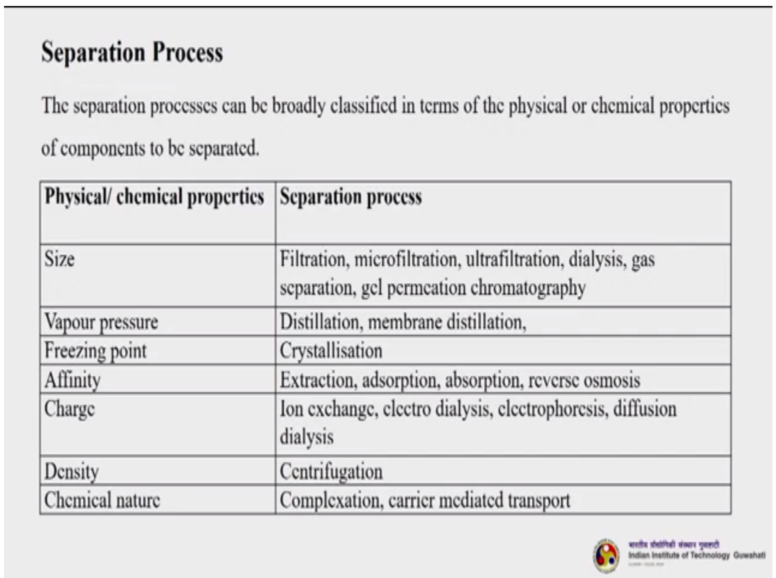

Separation Process

The separation processes can be broadly classified in terms of the physical or chemical properties of components to be separated.

Physical/ chemical properties	Separation process
Size	Filtration, microfiltration, ultrafiltration, dialysis, gas separation, gel permeation chromatography
Vapour pressure	Distillation, membrane distillation,
Freezing point	Crystallisation
Affinity	Extraction, adsorption, absorption, reverse osmosis
Charge	Ion exchange, electro dialysis, electrophoresis, diffusion dialysis
Density	Centrifugation
Chemical nature	Complexation, carrier mediated transport

The separation processes can be broadly classified in terms of the physical, chemical properties of the components to be separated so that table will list out actually different physical and chemical properties and based on which the separation processes are actually designed. So, if you look at the first one which is size. So filtration, micro filtration ultrafiltration, dialysis, gel permeation chromatography, gas separation, all these processes are based on size.

And similarly vapor pressure. So distillation and membrane distillation, comes under that. crystallisation comes from the freezing point, and based upon Affinity extraction, adsorption, absorption and reverse osmosis are designed to based on the charge of the solute. So ion exchange, electro dialysis. This is this processes works. Based on density, our centrifugation technology works.

And based on chemical nature, either complex system or carrier mediated transport works. So, this table tells us that the size, the different chemical and physical properties of the solute plays an important role. And that is one of the deciding factor based on which you will decide which separation process to be adopted.

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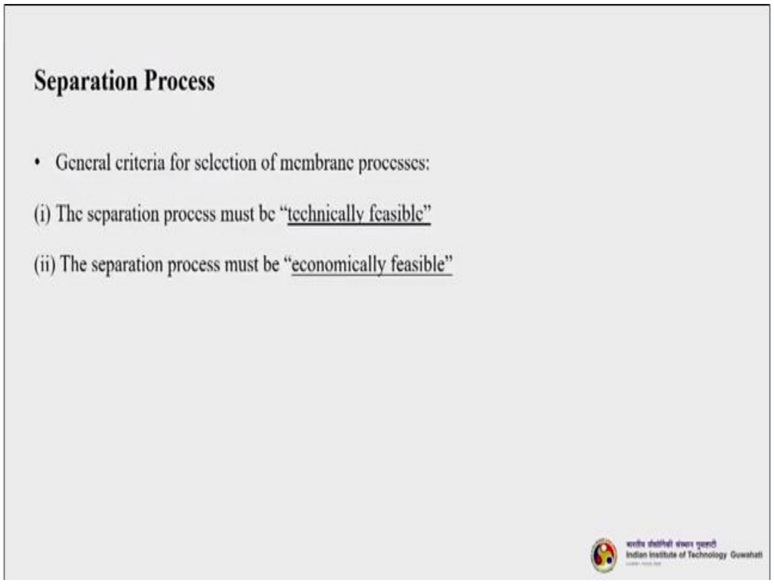

So as you know, a separation process. how do you, it basically, select a membrane process. So, the separation must be technically feasible and the separation must be economically feasible, these two are very important things. So let us say what is the meaning of technically feasible. So, a process must be technically feasible, that means that separation process must be capable of accomplishing a desired separation.

So whatever we want to separate suppose let us say there is a component present in a solvent mixture, and I want it to be purifed to be 95%. So, I should design and develop or adopt such a technology which will give me 95% pure solute, which is my disired product. So accomplishing the desired separation achieve a quality product and combination of two or more separation processes are sometimes required to meet such requirements.

This combination of two or more separation processes are called hybrid technology, in which more than one unit operations are clubed together so that they will give us a disired quality product, as well as disired efficiency.

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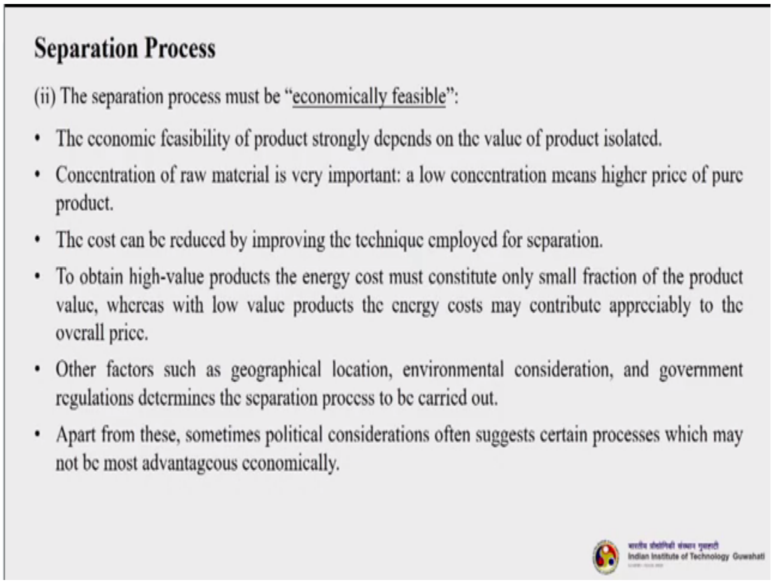

So, economically feasible means product strongly depends on the value of the product isolated. So if the product isolated is of low value, then it will not be economic equal that process may not be economically viable, or the concentration of raw material is very important. So, which means a low concentration means a higher price of pure product. The reason is that if the product which is very important for us, and present in very low concentration.

Then we have to go for extensive downstream purification and separation part, which are very costly so the end product cost will increase basically. So, we can, nevertheless, we can reduce the cost of the product by improving the technic employed for separation so you can choose a particular separation process, which will give a proper efficiency, as well as a pure quality of the product.

So, energy cost is one of the most important costs that is associated in downstream separation, and to obtain high value products the energy cost must constitute only a very small fraction of the product, whereas low value products energy cost may be appreciably little high. It is acceptable and other factors such as geographical location and environmental consideration government regulation.

These are also plays an important role, while deciding which separation processes to be adapted. So apart from this what happens sometimes political considerations also do play a role, which may not be advantageous economically but we need to adapt it due to political consequences.

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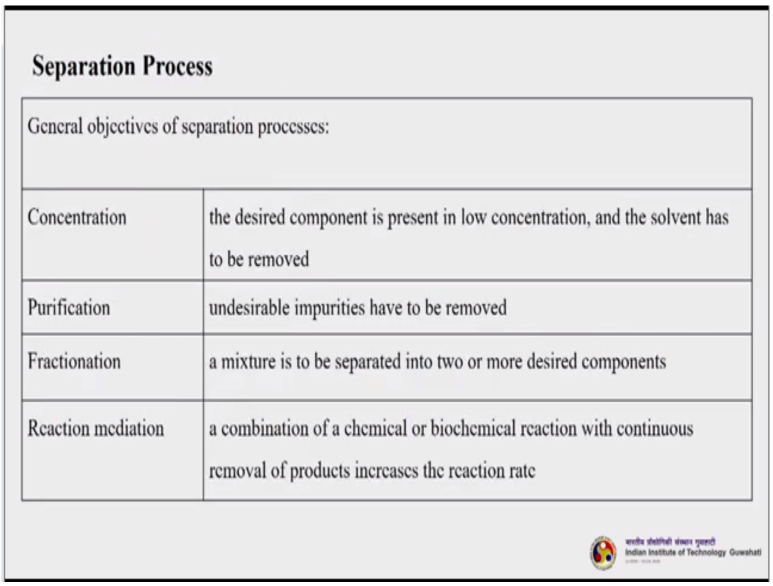

So, the general objectives of separation processes ae concentration, purification, fractionation and reaction mediation. Now, these are the four things based on which a separation processes are designed so concentration means the desired component is present in low concentration in the feed solution basically, and the solvent has to be removed. And purification means there are many undesirable impurities, which are present with the product, and that needs to be removed.

So we are purifying the product from other impurities basically and fractionation means, either it can be binary tertiary or can be multiple fractionation. So means there is a mixture to be separated into 2 or more desired components, let us say, one mixture is containing two solutes, and both the solutes are important for me so I can choose a binary factionism process in which the feed seems will be divided into two streams.

Basically with the help of membrane and it is very easy to do that with the help of a membrane. So, one part will be retained. And another part will go to the permeate. So we get two pure product, using a single membrane process. Under the Reaction mediation, a combination of a chemical or biochemical reaction with continuous removal of product increases the reaction rate. So in the reaction is processed.

Basically, it can be a chemical reaction or it can be a biochemical reaction, and we are withdrawing that product intermittently or continuously, then that will increase the rate of the reaction.

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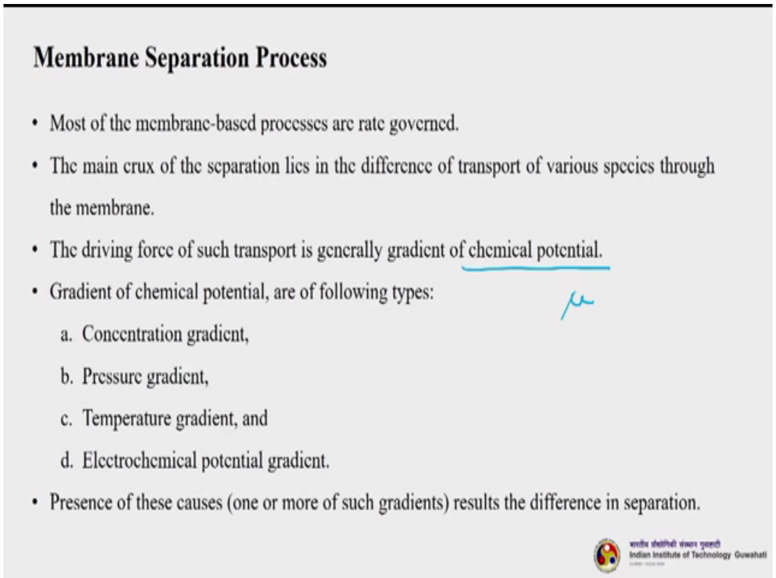

Now let us focus on the membrane separation process. So as you know most of the membrane separation process are rate governed. So the main crux of the separation lies in the dependence of the transport of various spieces to the membrane how a particular solute is getting transported so the membrane. And what is the role of the membrane in transporting that particular solute is the most important thing.

So the driving force for each such transport is generally gradient of chemical potential. And students, let us understand what is actually the meaning of chemical potentialsoyou usually, write it as a new. And you know, chemical potential actually is the energy that is either it will be absorbed, or it will be released by species. When number of that particular species in a particular reaction, either increases or decreases.

So, in other way, we can say, the chemical potential is the free energy that is available during the, the reaction, that is proceeding. And since we cannot measure chemical potential directly. So we always try to express chemical potential in other readily measurable parameters which are concentration gradient, pressure gradient, temperature gradient and electrochemical potential gradient.

So we express chemical potential basically under this four groups so presence of these one or more sets, gradients will result the difference in separation.

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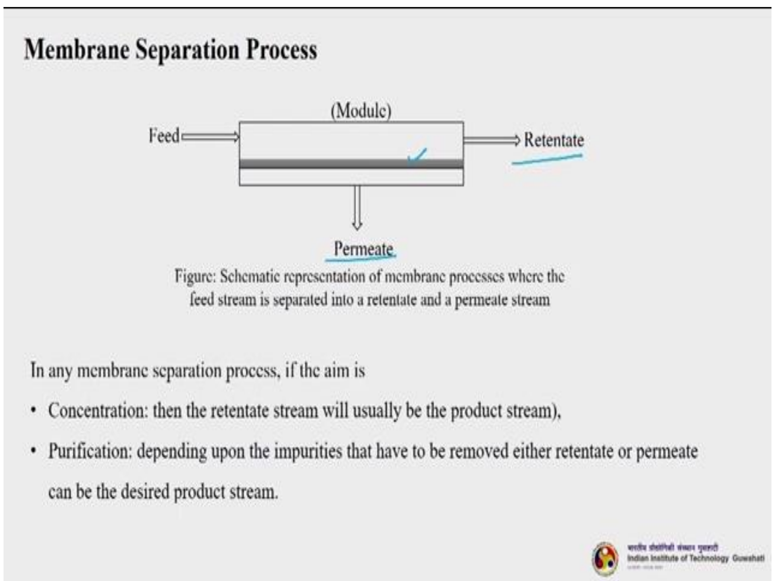

Please look into this particular slide in which I'm showing a schematic representation of a membrane process, but the feed stream is separated into a retentate and the permeate stream. Now students this is the simplest form of a membrane separation device, in which this is a membrane and feed is entering from one position and retentate, or the consentrate, both are the leaving from this, and the permeate is coming from this side.

So, the membrane is being cold. You can see this one. There is a module, we call it is a module so the module is housing the membrane. So you need a technique to house the membrane basically. So, this is how the membrane is being housed inside a module. So, if any membrane separation process. The aim is concentration, if I'm trying to concentrate something, then the redundancy means usually with a product stream.

But there is no hard and fast rule like that we can design according to our own convenience and if we are aiming for a purification, then depending upon the impurities, what are the molecular weight of these impurities present. So either we can remove the impurities, or retain them on the surface of the membrane, otherwise you can pass them through the permeate. Now, which component has to be retained on the surface of the membrane.

And which components of solutes will pass through the membrane, to the permeate steam. So the it is, there is no hard and fast rule it has to be decided based upon certain criterias. So criteria is first and foremost thing is that what are the solute and the inpurities whatever it is present their physical and chemical properties, that's what we just discussed their size, hydrodynamic conditions and molecular weight or shape, all these things, charge us also.

And then accordingly we can decide a membrane cut off. So I can give you a very simple example, let us say there is a mixture in which there are two components and I want to remove both the components and they are both of them are important for me. So one solute is molecular weight is 10 kilo Delta, and another solute to molecular weight is let us say, 50 klilo delta, so I can either.

I have to choose a membrane in such a way that the molecular weight cut off of the membrane lies in between this 10 and 50. So, eventually, I can go for a membrane cut off which is either 20,25 or 30 or 40, depending upon the availability also so that the solute which is 50 kilo delta will return on the surface of the membrane and the solute which is 10 kilo Delta, and each side is much lower than the pore size of the membrane.

If I choose a molecular weight cut off 20,25 in such a way that, so it will pass through the permeate.

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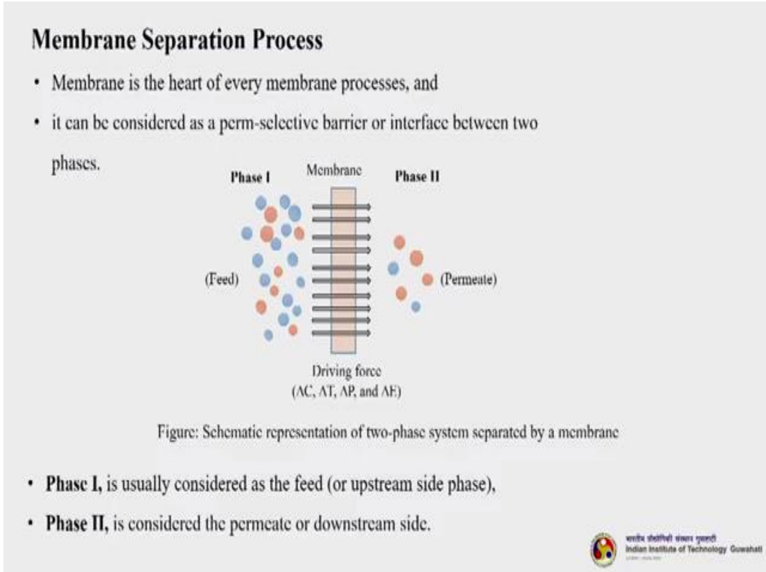

So, in membrane separation process membrane is the heart of the membrane process, and it can be considered as a perm-selective barrier or interface between two phases. Now, the perm-selective is also called, select, semipermeable. Now, what is the meaning of we need to understand the actually what is perm-selective or semipermeable. Now the semi permeability of the membrane means that the membrane will allow certain solutes to be retained.

On the surface of the membrane and will allow certain other things to pass to the permeate. So, usually the solutes or ions will be returned on the surface of the membrane, and it will allow the solvent to pass through. So the driving force. As you can see, it can be either concentration, it can be either temperature it can be pressure or electromotive forces. So, any one of these, or a combination of multiple of these also will result in this separation, the components.

So phase one is usually considered the feed. That is, we also call it upstream side phase and Phase Two is considered the permeate or downstream side.

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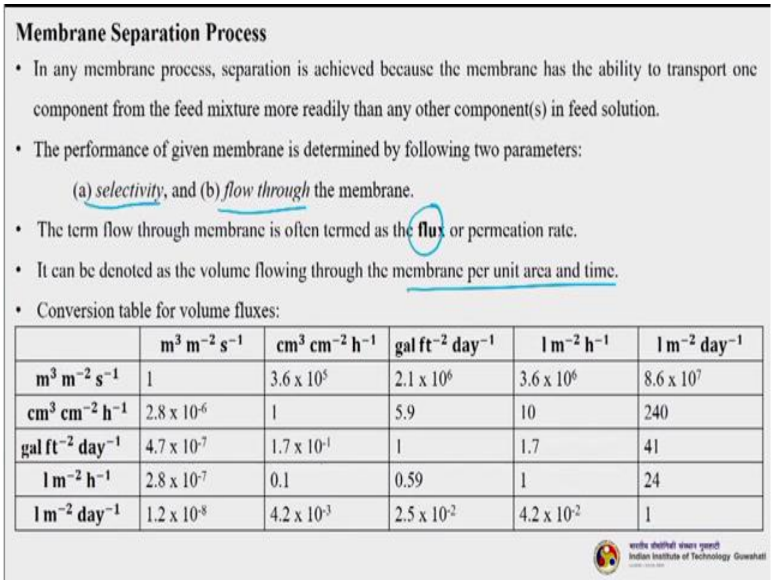

	$m^3\ m^{-2}\ s^{-1}$	$cm^3\ cm^{-2}\ h^{-1}$	$gal\ ft^{-2}\ day^{-1}$	$l\ m^{-2}\ h^{-1}$	$l\ m^{-2}\ day^{-1}$
$m^3\ m^{-2}\ s^{-1}$	1	3.6×10^5	2.1×10^6	3.6×10^6	8.6×10^7
$cm^3\ cm^{-2}\ h^{-1}$	2.8×10^{-6}	1	5.9	10	240
$gal\ ft^{-2}\ day^{-1}$	4.7×10^{-7}	1.7×10^{-1}	1	1.7	41
$l\ m^{-2}\ h^{-1}$	2.8×10^{-7}	0.1	0.59	1	24
$l\ m^{-2}\ day^{-1}$	1.2×10^{-8}	4.2×10^{-3}	2.5×10^{-2}	4.2×10^{-2}	1

In any membrane separation process separation is achieved, because the membrane has the ability to transport one component from the feed mixture more readily than any other component in the feed solution. So perfomance of the membrane is given by the two parameters. First one is selectivity. Okay. And the second one is flow through the membrane. The term flow through is actually called is flux.

Or the permission read so flux is most important in membrane studies so we'll discuss the next slide, what is flux actually, so it can be denoted as the volume flowing to the membrane per unit 10 and per unit area. So, what is the amount of volume that is passing through the membrane per unit area and per unit time is called as flux, so please see the conversion table for Volume fluxes. So you can use this table to convert Fluxes into volume fluxes. And in to different other fluxes,

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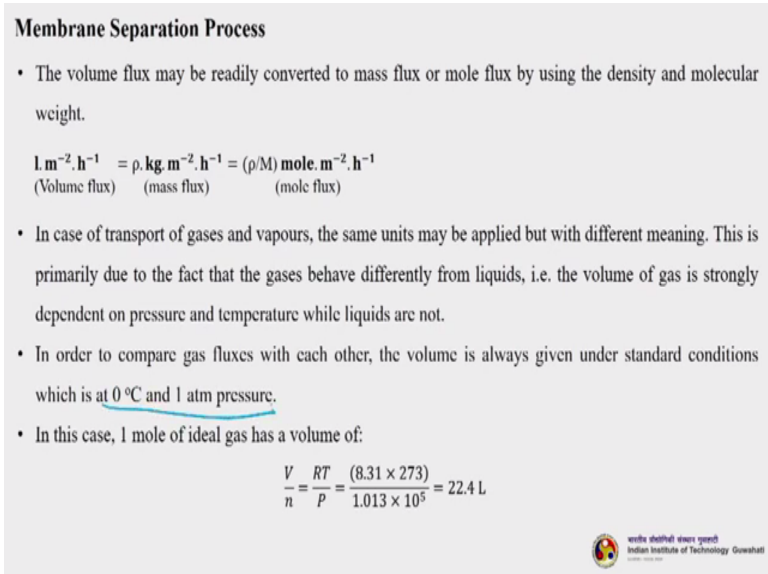

And the volume flux may easily be converted into mass flux or mole flux, by using the density and molecular weight, you can see the equation. So the volume flux is converted to mass flux by multiplying with density and converted to mole flux by multiplying with density and dividing by the molecular weight. So, m capital M is the molecular weight.

So, in case of transport of gases and vapors same units may be applied, but with different meaning. The reason is that the gases behave differently from liquids. The volume of gas is strongly dependent on pressure and temperature, while liquids are not. So in order to compare gas fluxes with each other. The volume is always given under standard conditions, which is at zero degrees centigrade and one atmospheric pressure. So, in case of one mole of ideal guess the volume is V/n = RT/p is 22.4. liters.

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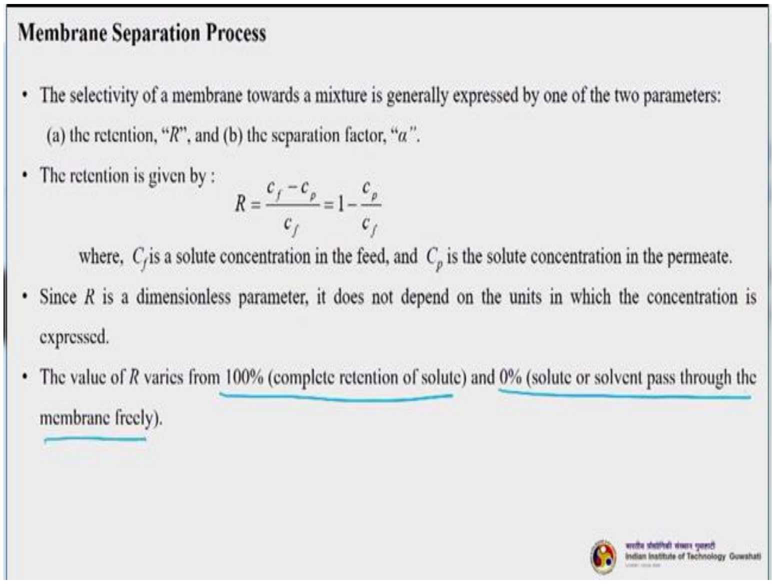

So now let us discuss what is selectivity of the process. So selectivity of a membrane towards a mixture is generally expressed by two parameters. One is called retention. Another is a separation factor, you will be hearing this term written so many times in our discussion so in our subsequent lectures. So the retention is given by this equation, R equals to Cf- CP by Cf, which is 1-cp/cf.

So here cf is the solute concentration in the field side and CP is the concentration of the solute in the permeate side. Since R is a diamensionless parameter, it does not depend on the units in which the concentration is expressed. The value of R actually varies from 100% - 0%. So if it is hundred percent that means it is complete retention of the solute everything is getting retented on the surface of the membrane.

And if it 0%. That means, the solute or solvent pass through the membrane and freely and nothing is getting returned.

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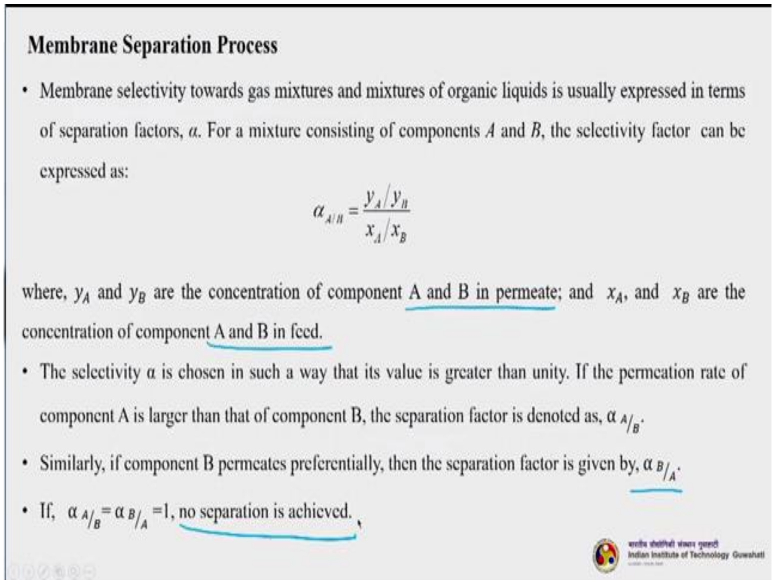

So membrane selectivity towards gas mixtures and mixtures of organic liquids is usually expressed in terms of separation factor alpha. So many of you who have studied this lesson, they may be knowing alpha which is elective volatility in distress and so here we define alpha for a mixture of components, A and B is alpha A by B equals two yA by yB divided by xA by xB yA and yB are the component of the concentration of component A and B in permeate.

While xA and xB are the concentration of component A and B in feed. So basically it is the mole fraction of the component A and B in permeate to that of the mole function of the the component A and B in feed. So selectivity alpha is to journey in such a way that the value is really greater than unity. So, if the permeation rate of component A is larger than that of component B, the separation factor is denoted as alpha A/ by B.

So similarly, if the component B's permeates preferentially then component A, then we can write as alpha B by A. So, if alpha. A by B equals to alpha B by A equals to 1. That means no separation is achieved. So separate, if the separation has to be achieved the separation factor, alpha will be always more than 1.

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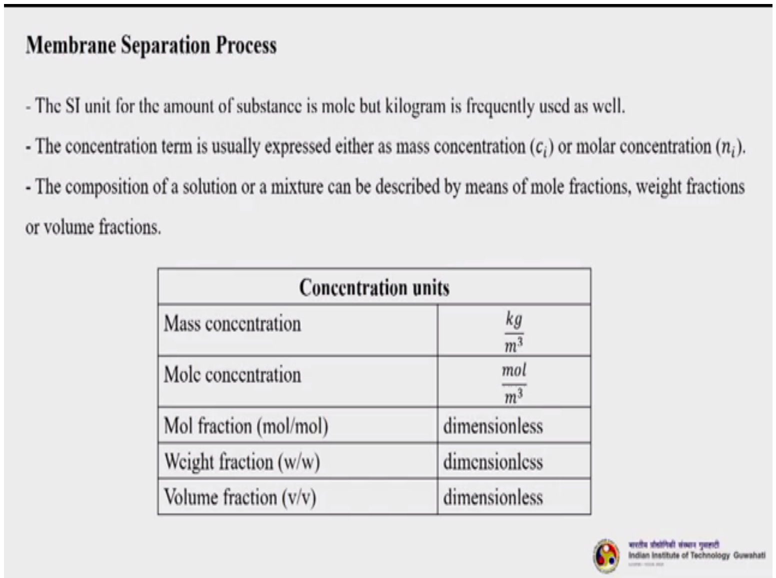

So, the SI unit for amount of substance is usually more but kilogram is also used frequently, as you know, the concentration term is usually expressed either is mass concentration. That is denoted by ci, or molar concentration denoted by ni so many books use different notations. But you should not confuse with this, you must understand the inherent meaning of the term actually, and the composition of a solution mixture can be described by mean small fractions.

Weight fractions or volume fractions. So, these are the concentration units for mass concentration, it is kilograms per meter cube. For mole concentration, it is moles per meter cube for mole fraction that is mol by mol, it is dimensionless. Weight fraction w by w it is dimensionless and volume presently v by v it is again dimensionless.

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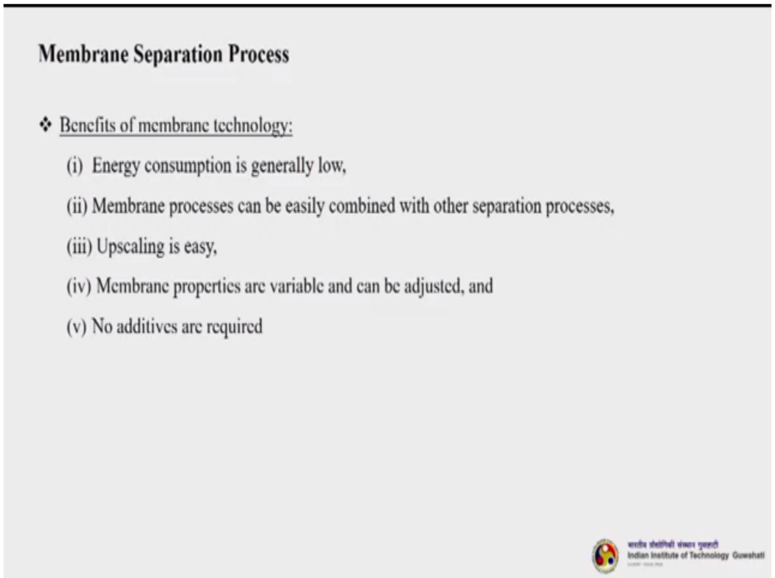

So, let us understand what are the benefits of membrane technology. So, one of the most important benefit of the membrane technology is the energy consumption is really low. So since membrane is the heart of the process, and it doesn't require any energy to run the membrane process, apart from the energy that is only required to supply the feed or pump the feed from the feed tank to the membrane. And sometimes you need to supply some.

This one, proper solution for that also needs to be pops at the pumping cost actually comes into picture. And number and processes can be easily combined with other separation process that is another beauty of this membrane process that it can be hybridized very nicely with another process one of the classic example of membrane hybridization is with distillation, so this will discuss in one of our classes we will discuss actually permeate operation.

Later on, and upscaling is easy for membrane process. So since membrane in this one scale up is mostly it is linear, which is also not a very good thing actually, when you go for upscaling why it is because the scale of character is linear, so it directly depends on the membrane areas, let us say, if I'm processing one liter of a mixture, using a 10 centimeter square membrane, then I can scale it up easily 200 meters by multiplying a factor of hundred into 10 centimeter square.

So into 10 centimeter square in 200. OK, so it will be 1000 centimeter square of the membrane. Now since the scale up is so linear the problem is that I cannot easily make a membrane module in such a way that I can have 100 meters square or thousand meters square of the membrane set and house in a module, so that is not possible, technically, so that is a little problematic, though, for design purposes upscaling is easy.

However, since the factor is linear. So, that is not so advantages. So, membrane properties are variable and can be adjusted so I can always prepare a membrane, which will suit to my requirement. So for example, let us say, I am trying to separate certain ions, certain solutes which are charges, so I can design a either a cut and extend membrane, or an extent membrane in such a way, by importing certain functional groups.

Which are having fixed either catalytic challenges or Anatic charges. Okay. During the preparation of the membrane, so that this particular separation can be achievable. So, the meaning inherent meaning of this is that I can always play with the membrane material property, and always can make a membrane tellerment. So, and another beauty of the membrane processes is that no additives are required.

So I can give you an example of such a process, let us say there are two, there is a mixture of closed boiling point mixtures, which is usually a separator using a topic discussion, in which we added a car component to separated in case of membrane and if we can separate it using a memory process where no additives will be required. So this steps the extra cost. Actually,

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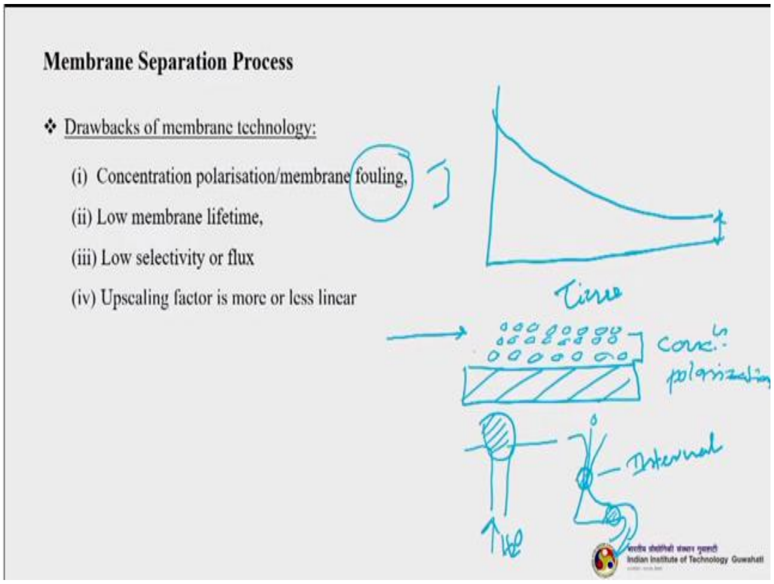

But all is not so well for the memory processes, there are certain drawbacks and disadvantages. Also, the major problem is concentration and fouling. So let us try to understand what is concentration. Let us see. This is the membrane membrane, in which our separation is happening, the feed is coming in such a way. So, the solutes are getting deposited on the surface of the membrane. So initially there will be the molecular deposition.

So when the process proceeds. So we'll have another by layer, deposition. So this is, this buildup of actually deposition is actually called is concentration polarization. So, which is deposition of the solutes on the surface of the membrane. Now, as the membrane processes, continuous this will increase more and more solutes will get deposited on the surface. Now let us understand what is the meaning of fouling.

So, in membrane fouling can be of two types one is external fouling, and another is internal fouling. So since a membranes are porous in nature, let us say, this is one of the poor and external fouling can happen if the solute is getting deposited on the surface of the membrane, like this. So it is blocking the basically the pore of the membrane. So this is what is called external fouling.

And let us say, another pore, in which pores can be of different types and sizes okay. So yeah another pore let us say very small solute okay, it passes through the membrane and it gets deposited on this particular area which is a constricted passes inside the pores so this can be internal fouling or it can come here and get deposited here. And but not moving out here so this means the membrane.

The particular pore of this particular membrane is getting fouled and this is called internal fouling. So either external or internal fouling and what are not good for the membrane processes. But however we can always clean the membrane from the backside by using bed flossing so I can always use and water or other chemicals to flush it from the backside. So that all these depositions will go away.

So this is possible but in a long-term process perspective when I am using the membrane continuously for a infinite period of time then these are the things which we need to take care of so another input input. And thing or is the membrane lifetime, so usually the lifetime of membrane is less than two other separation processes and the low selectivity of the flux. So flux will be usually if you look at.

So initially when the process, let us say this is time and this is flux so in when the process membrane process will start so your flux will be higher then slowly, slowly, slowly ,slowly it will gradually decrease and it will become constant okay so this process is called flux decline profile. We will discuss in detail in one of our classes about this Buster's trying to understand that the membrane separation process that initially the flux will be higher.

Then it gradually decreases and it decreases due to this concentration polarization and fouling so and up scaling factor is more or less linear this is what I just described you why the up scaling is easy and why the upskilling is not so good because of linearity.

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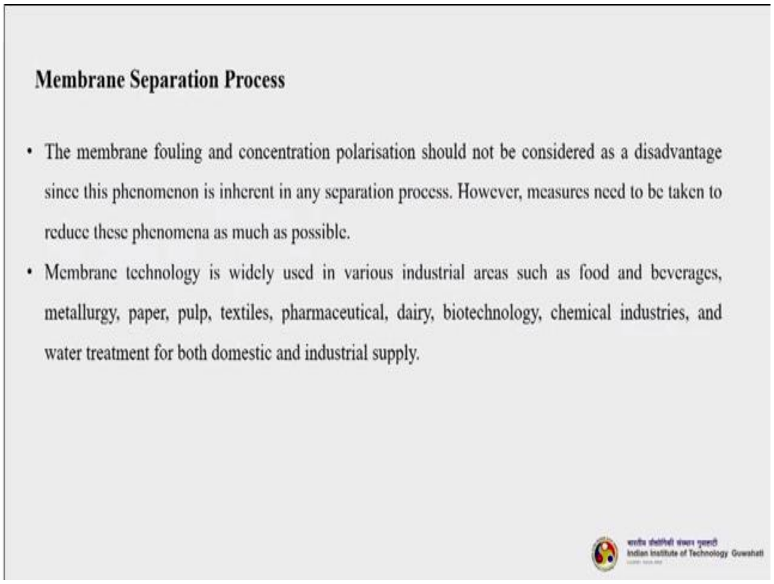

So let us move ahead, although I told you that membrane fouling and concentration polarization should not be considered as a disadvantages okay. Because this phenomena is anyway inherent in any separation process however what is require is that we needs to take certain measures such that this phenomena has to be reduced we cannot do ever with it exclusively. So what will be the target is our target is that how to reduce concentration polarization and fouling.

Because you do anything you take any measure there will be certain concentration polarization or deposition of the solutes on the surface of the membrane as well as certain solutes will block the pore of the membrane as well as they will get inside the membrane pores and thereby blocking the pore for further use. So a membrane technology is widely used in various industrial areas such as food and beverages.

But paper, pulp, textiles, pharmaceuticals, diary, biotechnology industries, chemical industries and water treatment for both domestic and industrial supply. Whenever we say water this water usually takes into account both the portable water treatment as well as the waste water treatment

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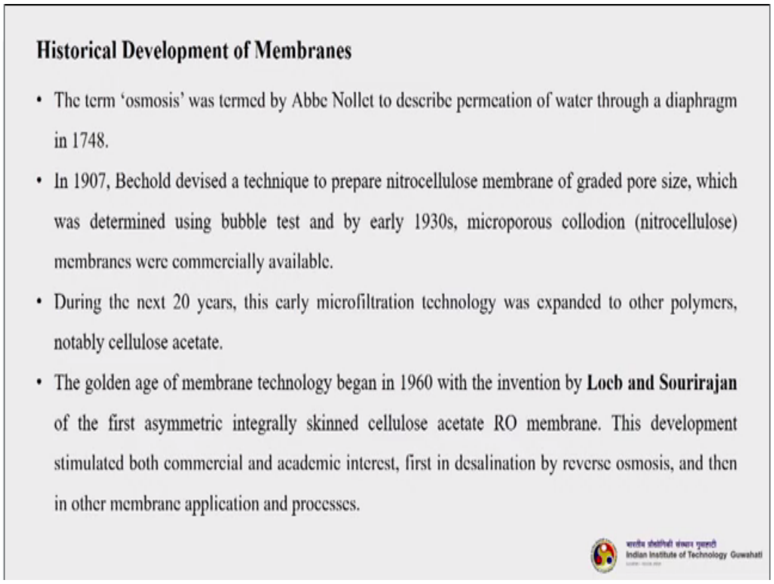

So let us now discuss the historical development of membranes actually membrane is nothing new if you look at this particular size you can understand that in 1748 Nollet is the first person who has discovered the phenomenon of osmosis okay. So by permeation of water through a diaphargram it long back So in 1907 Bachold devised a technique to prepare a nitrocellulose membrane of graded pore size which was determined using a bubble test.

And by the early 1930s microporous collodion which is nitrocellulose membranes were commercially available. So during the next 20 years by 1950 the early the micro filtration technology was expanded to other polymers notably cellulose acetate the golden age of membrane technology actually began in 1960 with the invention of Loab and Sourirajan, the first asymmetric integrally skinned cellulose acetate RO membrane reverse osmosis membrane.

So this is one of the most important breakthrough in membrane science and technology so this particular development by Loab and Sourirajan these are the two scientists to is manufactured or designed this first symmetric skin membrane so this actually stimulated both commercial and academic interest and the first in desalination by reverse osmosis and then in other membrane applications and processes.

So after that actually so many researchers are scientist have taken keen interest in the development of membranes.

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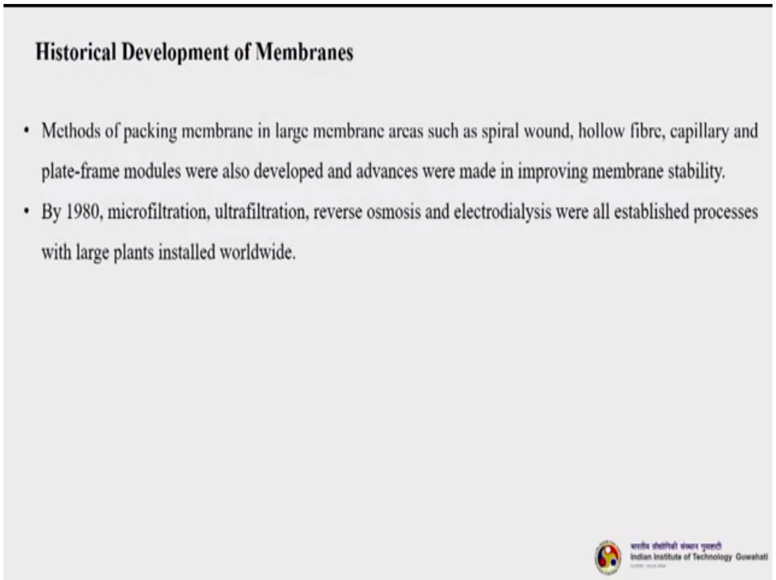

And so many notable things actually developed, so methods of packing of membrane elast membrane area such as spiral wound, hollow fiber, capillary and plate-frame modules were also developed and advances were made in improving the membrane stability. Stability is also very important issue and by the year 1980 microfiltration, ultrafiltration, reverse osmosis and electrodialysis.

Were all established processes with large plants installed worldwide, everywhere you will see now these are all commercial technologies.

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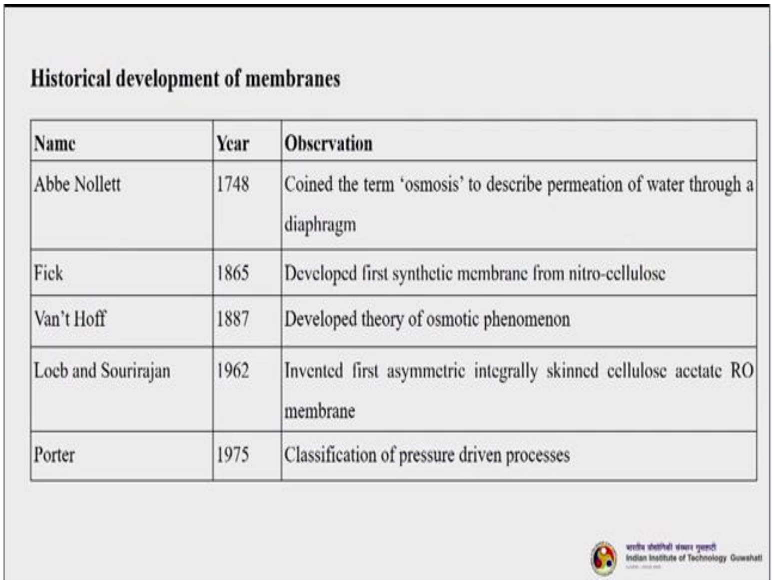

Historical development of membranes

Name	Year	Observation
Abbe Nollett	1748	Coined the term 'osmosis' to describe permeation of water through a diaphragm
Fick	1865	Developed first synthetic membrane from nitro-cellulose
Van't Hoff	1887	Developed theory of osmotic phenomenon
Loeb and Sourirajan	1962	Invented first asymmetric integrally skinned cellulose acetate RO membrane
Porter	1975	Classification of pressure driven processes

So this slide will just let you know in a tabular format how the development of membrane has taken place Nollet in 1748 has coined the term osmosis. Then Fick in 1865 proposed the first synthetic membrane from nitro-cellulose then in 1887 Van't Hoff developed the theory of osmotic phenomena that's the theoretical development bassicaly, and in 1962 Loab and Sourirajan has discovered the first asymmetric skin membrane in 1975 Porter has given the classification of the membrane pressure based membrane processes.

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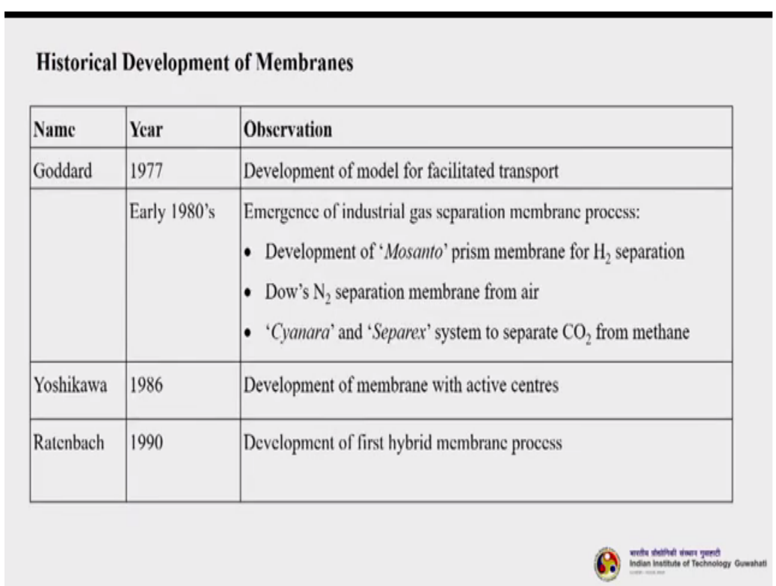

Historical Development of Membranes

Name	Year	Observation
Goddard	1977	Development of model for facilitated transport
	Early 1980's	Emergence of industrial gas separation membrane process: • Development of '*Mosanto*' prism membrane for H_2 separation • Dow's N_2 separation membrane from air • '*Cyanara*' and '*Separex*' system to separate CO_2 from methane
Yoshikawa	1986	Development of membrane with active centres
Ratenbach	1990	Development of first hybrid membrane process

And in 1977 Goddard has developed the model for facilitated transport. This is another milestone in membrane technology with the invent of facilitated transport and in 1980s the emergence of industrial gas separation membranes processes has come into picture. So in the development of mosanto a membrane for hydrogen separation, Dow's a nitrogen separation membrane from here from air cyanara.

And separex membranes for separating carbon dioxide from methane usually from the biogas. Then in 1986 yoshikawa has developed the membrane with active centers. And in 1990 return back has developed the first hybrid membrane processes, now these are the hybrid processes are also commercialized and are you know present in many industries

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Historical Development of Membranes

Membrane process	Country	Year	Application
Microfiltration	Germany	1920	Laboratory use (bacteria filter) (small scale)
Ultrafiltration	Germany	1930	Laboratory use (small scale)
Haemodialysis	Netherlands	1950	Artificial kidney (small scale)
Electrodialysis	USA	1955	Desalination (industrial scale)
Reverse osmosis	USA	1960	Desalination (industrial scale)
Ultrafiltration	USA	1960	Concentration of macromolecules(industrial scale)
Gas separation	USA	1979	Hydrogen recovery (industrial scale)
Membrane distillation	Germany	1981	Concentration of aqueous solutions(small scale)
Pervaporation	Germany/ Netherlands	1982	Dehydration of organic solvents (industrial scale)

Including the refineries so if you look at country-wise so microfiltration, ultrafiltration these are developed in 1920s and 30s in Germany. However there are they're all small-scale and later on in 1950,1955 hemodialysis and electro dialysis membranes were developed in Netherland in United States. The artificial kidney which was actually developed in Netherlands in 1950 was a small-scale one now we have industrial scale production of these things.

And the first desalination plant that was designed in the United States in 1955 is a industrial-scale electrodialysis plant then later on in United States ultra filtration and gas separation was developed in 1960, 79, 80s. So for hydrogen recovery and as well as concentration of macromolecules. Then membrane distillation was invented in 1981 and commercialized in Germany for the concentration of eco solutions but that was in small scale.

Now it is available in large scale, and in pervaporation another beautiful membrane technology that was developed in Germany and Netherlands in 1982 for the dehydration of organic solvents in industrial scale.

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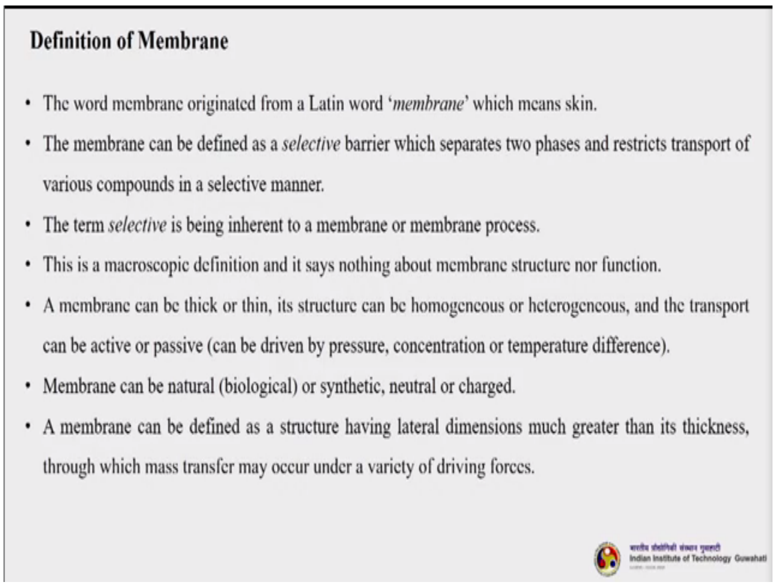

Now, understand what is the definition of a membrane? So a long back editor-in-chief of the Journal of membrane size has actually thrown into public that please suggest what can be the definition of a membrane so leading membrane scientist across the world has proposed so many different types of definition of the membrane, according to their wisdom and few of them are listed whether editor in chief and published in the Journal of membrane size.

So you can refer to it later on mmm so the word membrane actually originated from a Latin word which is called membrane which means essentially skin. So the membrane can be defined as a selective barrier which separates two phases and restrict the transport of various compounds in a selective manner. So the term selective is being inherent to a membrane or membrane process so this is a macroscopic definition.

Please note that it says nothing about the membrane or membrane process. So a membrane can be thick or thin its structure can be homogeneous or heterogeneous and transport can be active or passive. So passive transport can be driven by pressure concentration or temperature dispersed basically by the virtue of a gradient and membrane can be natural basically biological or it can be synthetic it can be neutral or it can be charged also.

So a membrane can be defined as a structure having lateral dimensions much greater than its thickness through which mass transfer may occur why under a variety of driving forces.

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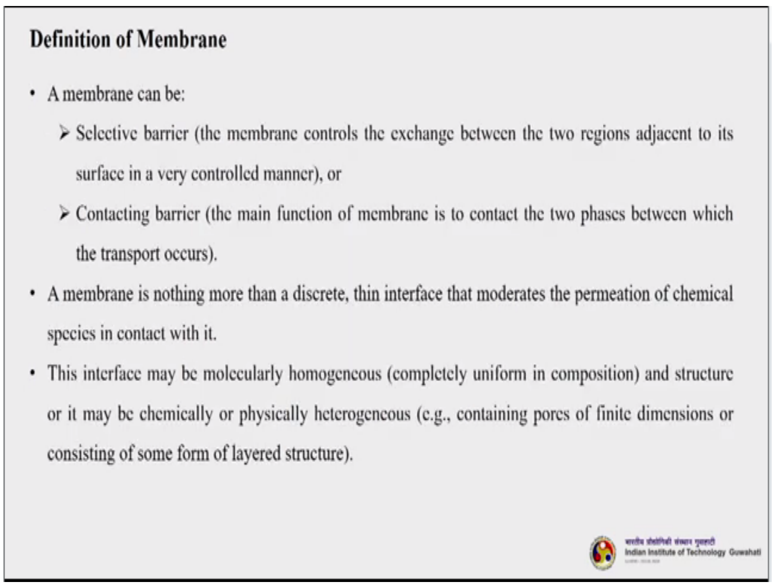

So a membrane can be a selective barrier or it can be a contacting barrier. If it is a selective barrier then the membrane controls the exchange between two region adjacent to its surface in a very controlled manner, and if it is only a contacting barrier then the main function of the membrane is to contact the two phases between who is the transport will occur and a membrane is nothing more than a discrete thin interface.

That moderates the permeation of chemical species in contact with it. Now this interface phase may be molecularly homogeneous. So that means it is completely uniform in composition and structure or it may be chemically or physically heterogeneous we say which essentially means that containing . So many parts of finite dimensions and consisting some form of layer structures.

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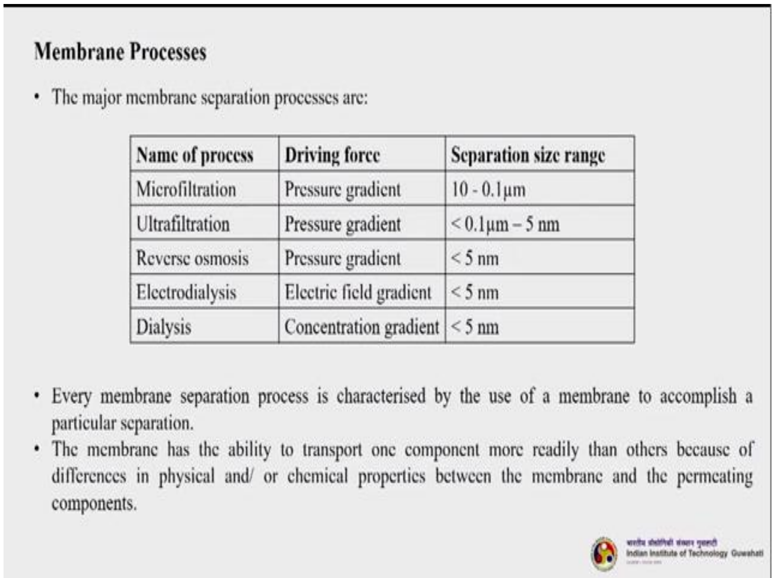

Membrane Processes

- The major membrane separation processes are:

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

- Every membrane separation process is characterised by the use of a membrane to accomplish a particular separation.
- 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 let us see what are the different types of membrane processes what are their driving forces and separation sizes the basic membrane processes are starts with microfiltration, ultrafiltration then reverse osmosis, electro dialysis dialysis and nano filtration. So nano filtration and reverse osmosis is actually overlap each other in terms of driving force as well as separation sized ends. So microfiltration, ultrafiltration, reverse osmosis and nano filtration.

All are operated under the gradient of pressure. So these are all pressure driven membrane processes. And the separation size energy as you can see that when we proceed from microfiltration, ultrafiltration, RO and electro dialysis dialysis the size of the solutes that will be separated is usually decreasing. So which essentially means then when I am trying to separate a smaller sized solute or particles.

Then I need to have more pressure. So the pressure increases when we go from micro filtration to nano filtration. So every separate separation process is characterized by the use of a membrane to accomplish a particular separation and the membrane has the ability to transport one component more readily than others because of differences in either physical or chemical properties or the combination of put two between the membrane.

And the permeating components which essentially means that when the membrane separation is happening. So the physical chemical properties of the solutes that we want to separate as well as the physical and chemical properties of the membranes that is separating are both are essential to achieve a particular separation.

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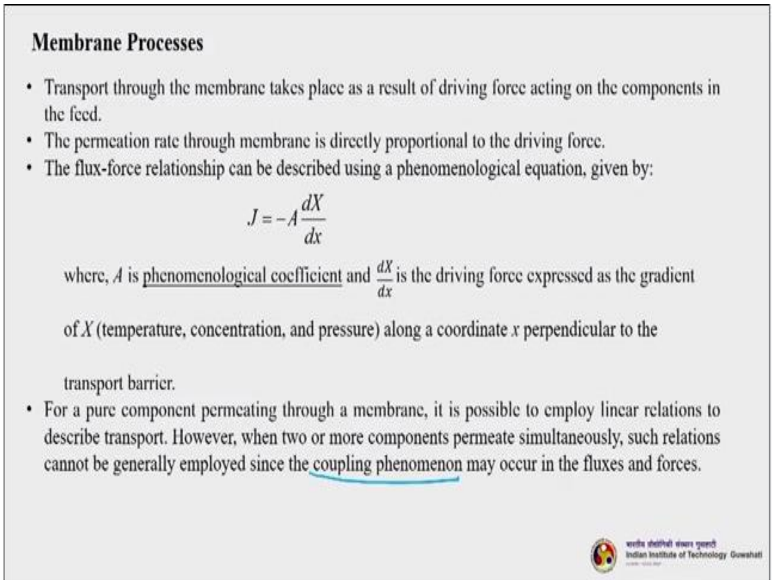

So transport through the membrane takes place as a result of driving force acting on the components in the feed. but permeation rate through the membrane is directly proportional to the driving force. So the flux force relationship can be described using a phenomenological equation which is given by this equation J, J is the flux equals to -A DX by DX. So here a is phenomenological coefficient and DX by DX is the driving force expressed as the gradient of X.

Now X can be either temperature, it can be concentration, it can be pressure or it can be electro-motive force also. So along a coordinate X perpendicular to the transport barrier. So for a pure component permeating through the membrane it is possible to employed linear relationships to describe transport, however when two or more components permeate simultaneously such relations cannot be generally employed.

Since coupling phenomena may occur in the flux Aysen process. We will discuss what is this coupling phenomena later on in one of our classes when we discuss nonlinear thermodynamics.

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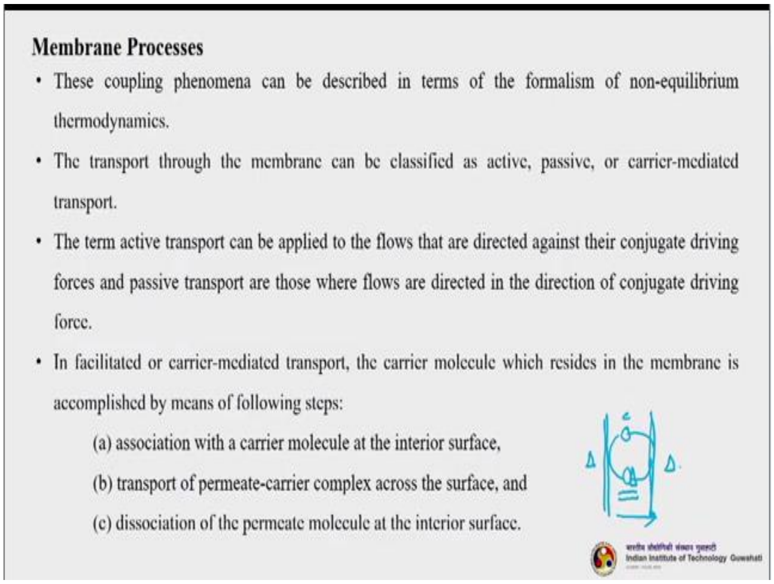

So this coupling phenomena can be described in terms of the formalism of non-equilibrium thermodynamics. The transport through the membrane can be classified as active passive or carrier mediated transport, the term active transport can be applied to flows that are directed against the conjugate driving forces and passive transport are those where flows are directed in the direction of the conjugate driving forces.

And in facilitated carrier mediated transport there is a carrier molecule which is a extra thing which research in the membrane okay and it is accomplished by means of the following steps. So association with a carrier molecule at the internet surface. So that means the solute which we want to separate is first getting associate itself with the carrier molecule in the interior surface of the membrane then transport of this permeate.

And carrier complex across the surface of the membrane and then dissociation of the polymer molecule at the interface surface. Let us see how this will happen let us say this is a membrane okay and this is a carrier molecule which is present inside the membrane and this is a solute now this solute when it comes into contact with the membrane okay come to this interface okay then it will try to associate with this carrier now then they will form and they will try to associate.

And they will form a intermediate complex. So this is a intermediate complex permit carrier complex, now this should transport across the membrane then what it comes to the permeate side of the membrane here in this interface then it will dissociate itself . So the solute will come here and the carrier will again we will go back to the membrane and it will remain inside the membrane.

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Membrane Processes

Table: Phenomenological equations

Mass flux	$J_m = -D\frac{dc}{dx}$	Fick's Law
Volume flux	$J_v = -L_p\frac{dP}{dx}$	Darcy's Law
Heat flux	$J_h = -\lambda\frac{dT}{dx}$	Fourier Law
Momentum flux	$J_n = -\nu\frac{dv}{dx}$	Newton's Law
Electrical flux	$J_i = -\frac{1}{R}\frac{dE}{dx}$	Ohm's Law

So these are some of the phenomenological equations of different fluxes. So mass flux, volume flux, heat flux, momentum flux and electrical flux. So in mass flux which is fixed like actually the D is the diffusivity which is the phenomenological equation in Darcy's law it is LP permeability in Fouriers law it is lambda, and in Newton's law it is the kinematic viscosity and in Ohm's law it is the resistance. So these equations are very important this will be using for various processes later in in our classes.

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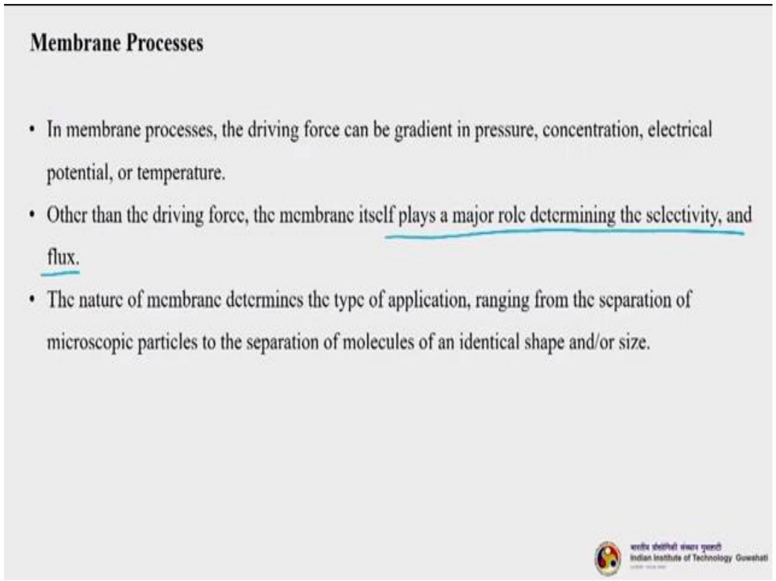

And in membrane processes that driving force can be gradient in pressure, concentration electric potential or temperature this we have discussed earlier also. So other than the driving force the membrane itself plays a major role, determining the selectivity and flux this is very important. And this is the inherent meaning of this the physical and chemical properties of the membrane also determines the separation.

So the 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.

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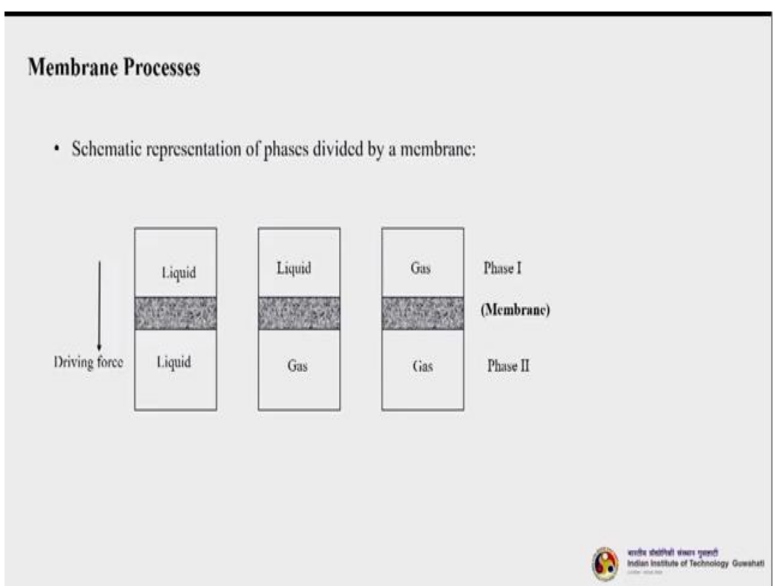

Let us look at this particular diagram. So this tells us that what are the possible applications of the membrane. So he can have a liquid liquid separation, we came here we can have a liquid and gas separation, we can have a gas and gas separation. The first one is usual microfiltration ultrafiltration reverse osmosis and these things and liquid gas separation is usually pervaporation and gas separation is a polar it can any guesses.The pressure like this separation of nitrogen from air, separation of carbon dioxide from biogas etc.

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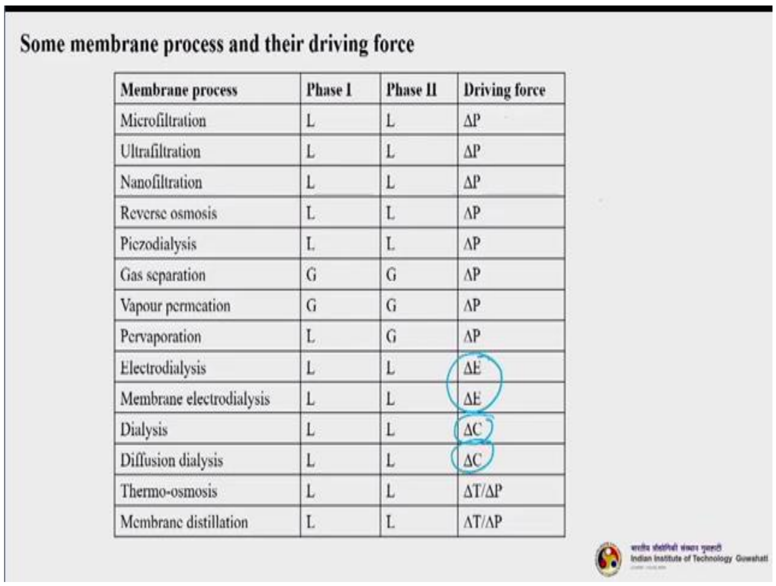

Some membrane process and their driving force

Membrane process	Phase I	Phase II	Driving force
Microfiltration	L	L	ΔP
Ultrafiltration	L	L	ΔP
Nanofiltration	L	L	ΔP
Reverse osmosis	L	L	ΔP
Piezodialysis	L	L	ΔP
Gas separation	G	G	ΔP
Vapour permeation	G	G	ΔP
Pervaporation	L	G	ΔP
Electrodialysis	L	L	ΔE
Membrane electrodialysis	L	L	ΔE
Dialysis	L	L	ΔC
Diffusion dialysis	L	L	ΔC
Thermo-osmosis	L	L	ΔT/ΔP
Membrane distillation	L	L	ΔT/ΔP

So these are the some of the membrane processes and their driving forces. So phase 1 phase 2 and driving forces. So under micro filtration we can go for a liquid liquid separation the driving force is of course pressure. You can see that for microfiltration, ultrafiltration, nanofiltration reverse osmosis all these thing and vapour permeation the driving force is our Delta P and for gas separation alsothe driving force is Delta P for pervaporation it is separating a liquid.

And gas gas phase the driving force is again Delta P in case of electro dialysis the driving force is Delta E and the electrometric force and in case of dialysis greater concentration difference okay. Diffusion dialysis is also again concentration difference and in case of thermo-osmosis membrane distillation which are actually thermally driven membrane processes. So both thermal gradient, temperature gradient as well as pressure gradient is important.

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Flux range and pressure in various pressure driven membrane processes

	Pressure range (bar)	Flux range ($l\ m^{-2}\ h^{-1}\ bar^{-1}$)
Microfiltration	0.1 - 2.0	> 50
Ultrafiltration	1.0 - 5.0	10 - 50
Nanofiltration	5.0 - 20	1.4 - 12
Reverse osmosis	10 - 100	0.005 - 1.4

So let us now understand the different pressure range and the flux ranges of the important membrane processes. So I have given four processes here microfiltration ultrafiltration nanofiltration and reverse osmosis. So you can see then as we proceed from micro filtration to ultra filtration then nano filtration and reverse osmosis the pressure that is required is increasing. That is because of the fact that as we proceed from micro filtration to.

Ultra, nano and reverse osmosis in that sequence, then the flux is actually decreasing as we need more pressure and the. Solute that is getting separated or is also getting are also getting becoming smaller in size

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Types of Membranes

- In this course, our discussion will be limited to synthetic membranes, excluding all biological membranes.
- A normal filter also meets the definition of a membrane, however by convention, the term 'filter' is usually limited to structures that separate particulate suspensions larger than 1 – 10 μm.
- The principal types of membranes are listed below,
  - *Isotropic membranes* : Microporous membranes, Nonporous dense membranes, Electrically charged membranes
  - *Anisotropic membranes*
  - *Ceramic (inorganic) membranes*
  - *Liquid membranes*

So let us now discuss the types of membranes. So the membrane process classification we discuss in detail in the next class. So in this course our discussion will be mainly limited to the synthetic membranes, excluding all biological membranes. So we are not discussing any biological system here. So a normal filter also meets the definition of the usual preacher cloth filter or any such filter that is available at home or labs.

However, by convention the filter is usually limited to structures that separate particulates of suspensions, larger than 1 to 10 micron. So the definition lies actually the difference between the conventional filter and membrane is who the sizes.that is getting separated. So the principle types of membranes are listed below. So we can have isotropic membrane, anisotropic membranes we have ceramic or inorganic membranes and we can have liquid membrane.

So liquid membrane is a latest technology in one class we'll discuss in detail about liquid membrane later on. So all membranes can be classified into a symmetric and asymmetric membranes also. So isotropic membranes have symmetric membranes and anisotropic are asymmetric membranes . So under isotropic, we can have micro porous membrane non porous dense membranes and electrically charged membranes . So let us see one by one what are those things. So what are basically isotropic membranes.

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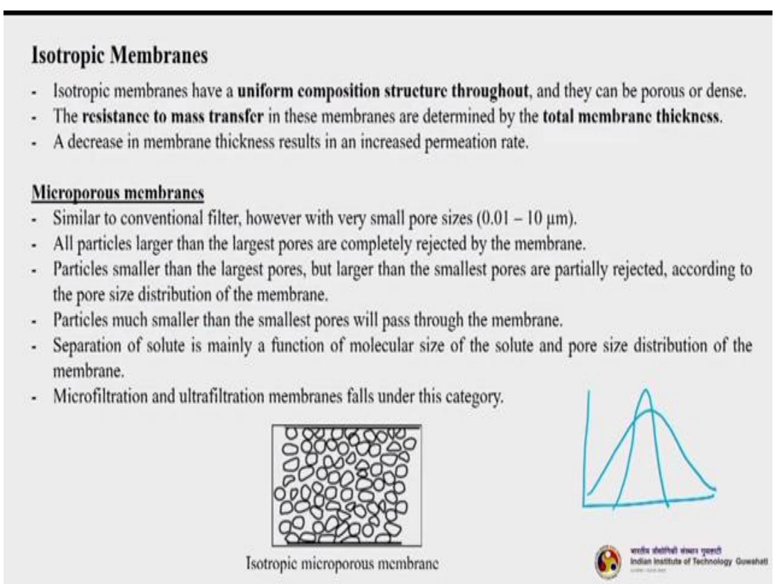

So isotropic membranes have a uniform composition structure throughout and then can be either porous or dense that means non porous their resistance to mass transfer in these membranes are determined by the total membrane thickness. So thickness of the membrane plays the most important role. So the that is the resistance the membrane thickness provides them at most resistance to the separation or the mass transfer basically.

So a decrease in membrane thickness it results in an increased permeation rate. Let us see what are the micro porous membranes. So these are similar to conventional filter however with very small pore sizes you can see in this picture how the isotropic micro porous membrane looks like all particles larger than the largest pores are completely rejected by the membrane. That means the solutes which whose sizes are more than the size of the pore will all be retained.

On the surface of the membrane and particles small less than the largest pore. But larger than the smallest pore are partially rejected according to the pore size distribution now please understand that membranes do not have uniform pores their pores they have a pore size distribution. So I can just try to draw one you can see the pore size distribution if something looks like that. So we can have a narrow pore size distribution like this also.

Or we can have a wide pore size distribution like this also. So which means which essentially means that membrane do not possess uniform pores. Except maybe Some zeolite membranes most of the membranes which are commercially available has a pore size distribution . So particles which are smaller than the smallest ports will of course pass through the membrane and separation of solute is mainly a function of molecular size of the solute and pore size distribution of the membrane microfiltration and ultrafiltration member membranes falls under this category.

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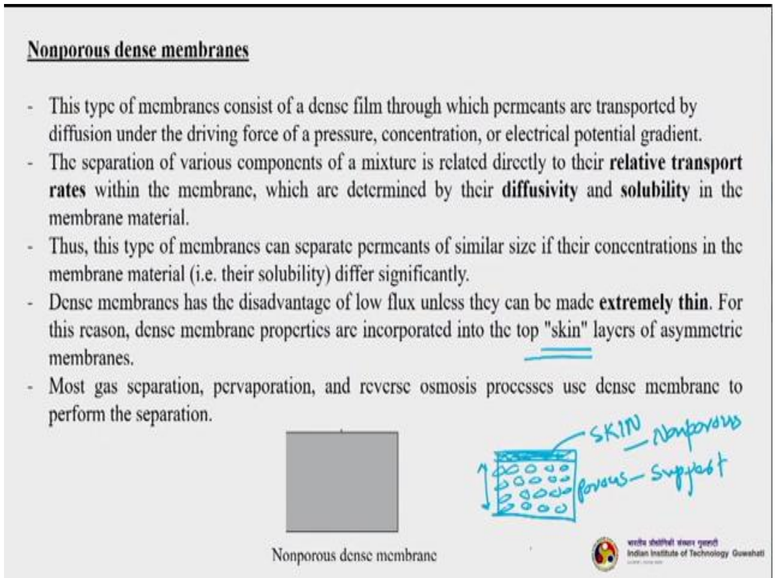

Then let us understand what is a non porous dense membrane. So this type of membrane consists of a dense fill him through which through which permeates are transported by diffusion under the driving force of a pressure concentration our electrical potential gradient. So there is no pores in this type of membranes that is why these are non porous membranes and the separation of various components of mixture is related directly to their relative transport rates within the membrane.

So how they are getting transported the diffusion rates and all these things of the solute plays a important role which are determined by that diffusivity and . Solubility in that membrane material two things are very important. First is that diffusivity and soluteability. So the . Solutes which are supposed to be transported must be . Soluble in the membrane and they should have a proper diffusive diffusion rate. So that there will be transported across the membrane.

Thus this type of membranes can separate permeates of similar size if their concentration in the membrane material differ significantly. So then dense membranes has the disadvantage of low fluxes unless they can be made extremely thin for this region dense membrane properties are incorporated into the top skin layers of the asymmetric membrane. So usually what happens we can prepare a skin membranes like this okay. So you can have a very small thin layer which is dense membrane.

And we can have a porous sub layer here usually of micro filtration days . So this is porous okay. So this provides the support and this is the skin layer okay which is non-porous please understand that this skin layer is actually we will do the separation and this particular porous layer is providing a mechanical support to hold this skin layer. So most of the gas separation,pervaporation, reverse osmosis processes uses dense membrane to perform the separation.

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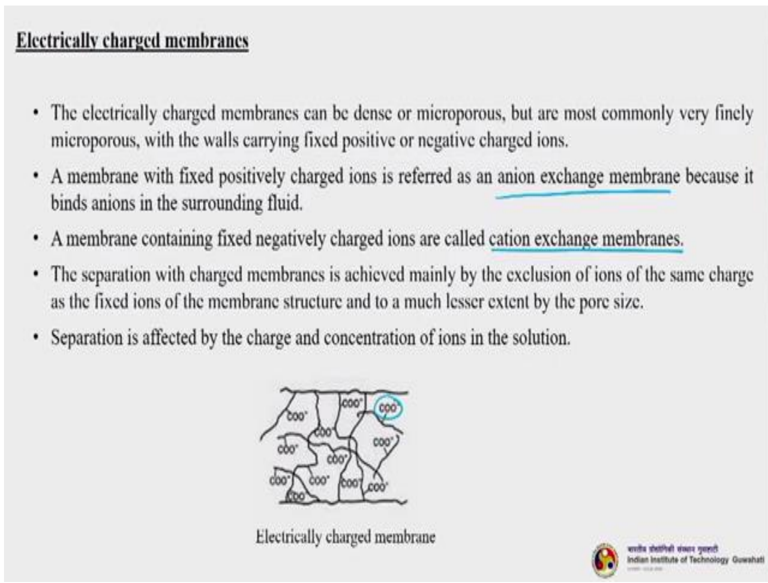

So next is the electrically charged membranes. So the electrically charged membranes can be dense or it can be micro porous both it can be both alsobut most are commonly very finely micro pores most of the electrically charged membranes are micro porous with the walls getting fixed positive or negatively charged ions. So you can see here. So these are containing . Some negatively charged ions.

So we can have positively charged ions also imparted inside the membranes. So a membrane with fixed positively charged ions are referred as anion exchange membranes because it will bind the anions in the surrounding fluid and their membrane containing fixed negatively charged ions are called cation exchange membranes. Because it will exchange cations and the separation with charge membranes is achieved mainly by the exclusion of the ions of the same charge as the fixed ions of the membrane structure.

And to a much lesser extent by the pore sizes. So pore sizes actually is not playing a major role here the major role is ion exchange and separation is affected by the charge and concentration of the ions. So concentration of the ions also very important while deciding the separation.

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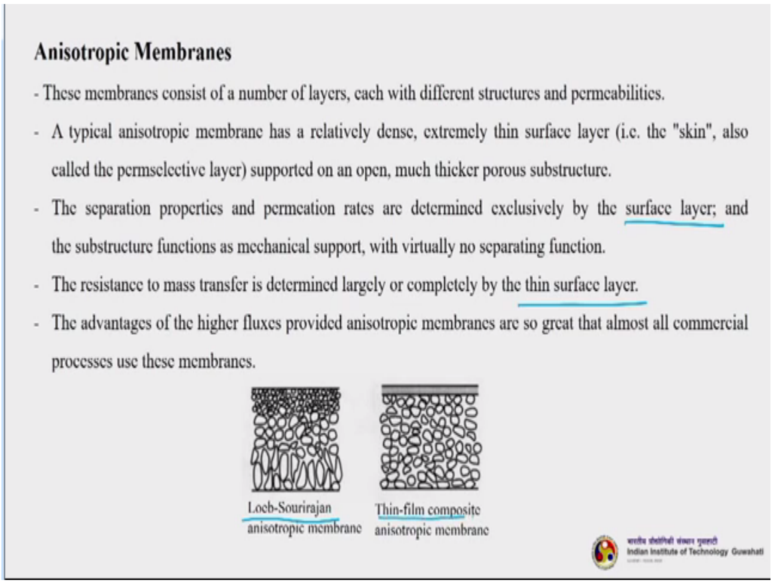

Let us understand water and anisotropic membranes. So these membranes consist of a number of layers, each with different structures and permeability. So a typical anisotropic membrane has a relatively dense extremely thin surface layer which is skin just I just draw in the previous slide . So to make you understand the skin layer which is also called as palm selective layer supported on an open much thicker porous sub structure. So the separation properties.

And permeation rates are determined exclusively by the surface layer. So the surface layer of the skin layer is doing the separation the below layer which is mostly porous then the surface layer is providing the mechanical support and virtually it has nothing to do with the separation. The resistance to mass transfer is determined largely and completely by the thin surface layer the skin layer. So the advantages of higher fluxes provided anisotropicmembranes are so great.

That means the flux are very high that almost all commercial processes nowadays are using this type of membranes. So the first membrane here you can see this is the Loab and Sourirajan anisotropic membrane okay and the next one is the thin film composite membrane in which there is a separate thin film fabric repair and then fused with this porous layer.

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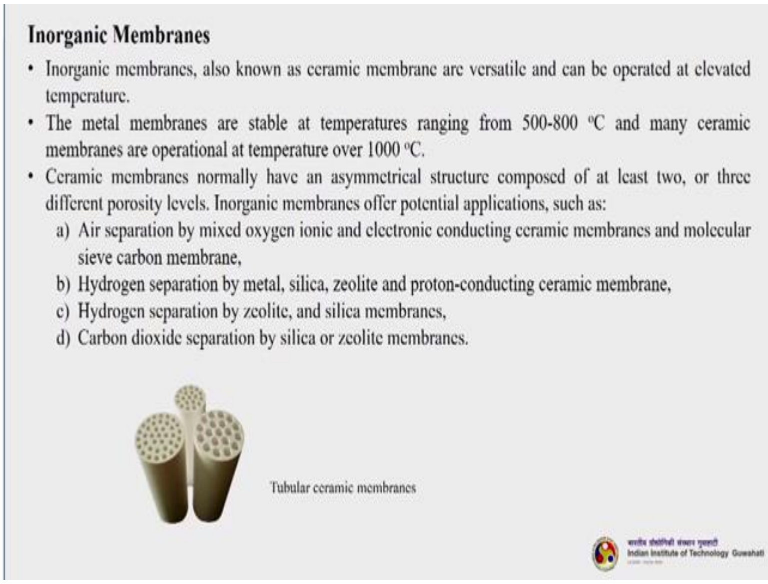

The next membranes are inorganic membranes are also called ceramic membranes. So they are very versatile and can be operated at elevated temperature that is the beauty of this ceramic membranes, then they can withstand higher temperature, almost close to thousand degree centigrade and they can withstand higher pH, their high chlorine resistance their mechanical stability and chemical and thermal stability is very good.

So ceramic membranes normally have an asymmetric structure composed of at least two or three different porosity levels. So inorganic membranes suffer potential application such as air separation by mixed oxygen ionic and electronic conducting ceramic membranes and molecular sieve Carbon membrane, then hydrogen separation by metal silica zeolite and proton conducting ceramic membrane hydrogen separation by zeolite and silica membranes.

Carbon dioxide separation by silicon gel equipments.. So these are all commercialized processes you can see these are actually tubular ceramic membranes in this figure shows.

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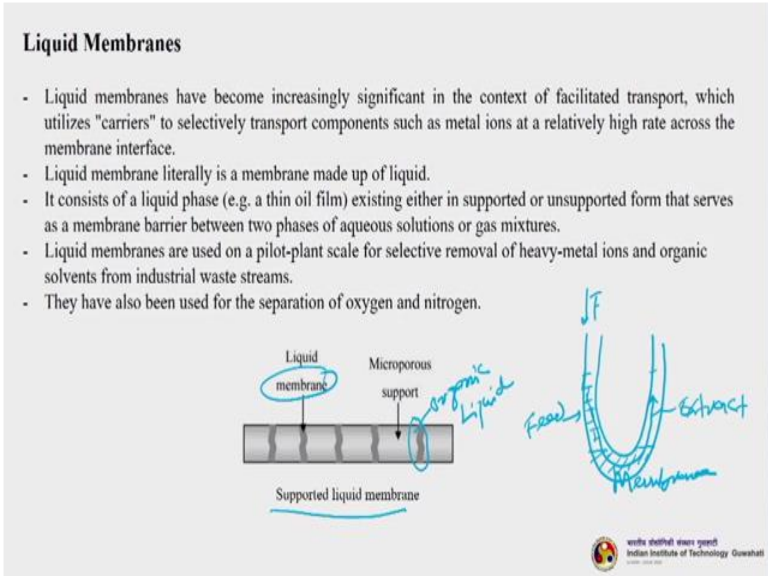

Then the next membrane type of membrane is liquid membranes the liquid membrane is a latest addition to the membrane group. So it is significantly its application is increasing after the facilitated transport came into picture. So utilizes carriers to selectively transfer components such as metal lands at a relatively high rate across the membrane interface. So what is a liquid membrane. So liquid membrane literally is a membrane which is made up of a liquid.

So it consists of a liquid phase that is a thin oil film existing either in supported or on supported form that serves as a membrane barrier between two phases of ecosolutions or gas mixtures. So liquid membranes are used on a pilot plant scale for selective removal of heavy metal ions and organic. Solvents from industrial waste streams they have also been used for separation of oxygen and nitrogen what you are seeing here.

The students, in this picture is that supported liquid membrane where you can see this is one particular pore now this pore is filled with organic liquid which is membrane path. So this is a organic liquid which is the membrane pet and this is that support. So we can in it is very easy to prepare a liquid membrane you know you if you have a u-tube manometer type of thing in the glass. So you can have something like this.

So you can in one limb you can pour your liquid membrane okay. From here, let us say you pour from here okay and it comes and deposited here. So it will be here, So from here you can pass your feed okay. So and here the feed contents here okay and here we can have an extract patch and this is feed press and this is the membrane. So the component that we want to transport will eventually come through the membrane purpose.

Then it will go to the extra path this extract path will help in holding the solutes. And will thereby limiting the BEC diffusion of the solutefrom the extract phase to the feed phase So this is the simplest form of liquid membrane that we can help mister

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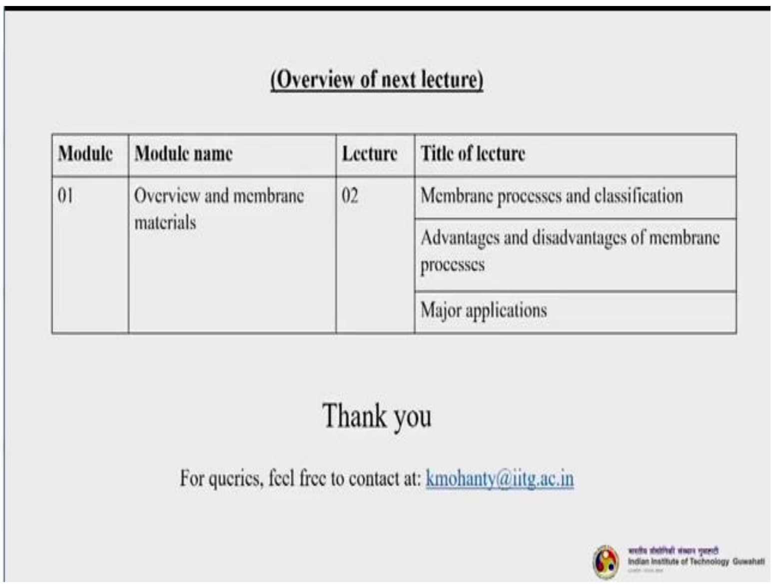

Students today we understand what is a membrane and what are the types of membrane as well as we understand what is flux and we understand what is this different separation processes also. In our next lecture under the same module, we will discuss the different types of membrane processes and their classification and what are the various advantages and disadvantages of different membrane processes and their major applications.

So thank you very much if you need any clarification you can always write to me at this email id kmohanty@itg.ac.in thank you very much.