

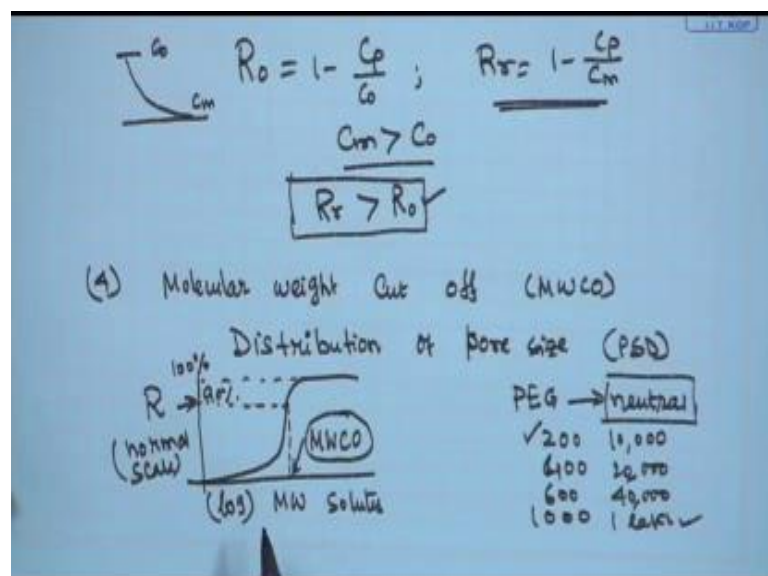
**Introduction to Process Modeling in Membrane Separation Process**  
**Prof. Sirshendu De**  
**Department of Chemical Engineering**  
**Indian Institute of Technology, Kharagpur**

**Lecture – 04**  
**Fundamentals of Separation Processes and Introduction of Membrane System**  
**(Contd.)**

Welcome to this session of the class. So, we have basically looking into the various properties of the membrane based systems and various definitions which will be quite useful for the process modeling.

So, we have looked into the permeability, we have looked into the retention, we have looked into the osmotic pressure, we have seen how the osmotic pressure of the solution will be really measured and connect it to the concentration of the solute into the system. And then how the permeability of the membrane and the retention of the membrane are defined, and how they are really you now connected to the throughput of the process and the selectivity of the membrane. And then we have looked into the definition of the various you know difference of real retention, and observe retention, how they are measured and how they will be you know can be really measured it to a accurately by conducting a separate set of experiments.

(Refer Slide Time: 01:20)



Next definition that will be quite important in our case is molecular weight cut off. So, sometimes you will be seeing these MWCO of the membrane is really, really very important in order to specify a membrane. Now, in a membrane there cannot be a you know unimodal pore size or I should not say unimodal it should there should be it should not be a uniform pore sized membrane; that means, membrane cannot have a unique pore size throughout its whole matrix. So, therefore, there only be existing actually what is existing is that there will be a distribution of pore size that will be existing into the membrane. This is known as pore size distribution or PSD. So, there therefore, if you would really look for a membrane you cannot have a uniform pore size a membrane if there will be a distribution of pore size; although, one can have an average pore size. So, if you remember there whenever we are discussing about the categories of different membrane based processes we have specified some we know pore size of the membrane.

Now, these pore size is basically an average pore size of the membrane. Now, this average of the pore size is basically obtained by the averaging the pore size distribution. Now, these if you how the pore size distribution is calculated this is be they will be calculated by measuring the retention versus molecular weight of solutes. Now, if the so what we do we conduct in experiment by using molecular of several solutes of different molecular weights. For example, but this solutes have to be neutral solutes. For example, an example of neutral solutes this polythene glycol you already mention polythene glycol during our, I know steps of (Refer Time: 03:43) discussed as steps of casting.

So, polythene glycol is basically a polymer which is a neutral polymer that is very, very important. We have to take the neutral polymers, for example, polythene glycol, polyvinyl, pyrrolidone etcetera. And this polythene glycol polymer is available with different molecular weights; that means, in market the PEG is available with different molecular weights starting form 200, 400, 600, 1,000, 10,000, 20,000, 40,000 Dalton, 1 lakh Dalton so on and so forth. So, we take the different polythene glycol of various molecular weight at a particular concentration prepare a solution, and then we measure you conduct the experiment in a small laboratory experiment in filtration cell and measure its permeability.

Similarly, we do experiments with different molecular weights of the solutes and measure the retention and then plot the retention as a function of molecular weight it in a log scale. So, this is basically same log semi log scale these a log scale in a molecular weight because you are looking for we are covering a wide molecular weight starting from 200 to 1 lakh and then these in a normal scale. So, if you really do that then you will be getting an S shaped curve some something like this, where R is 100 percent. So, as we have talking about once you generate this retention versus molecular weight curve of the solutes for this particular membrane, I am coming close to whatever I am trying to talk about the molecular weight cut off.

So, therefore, since there is a there exists a distribution of pore size in a membrane it is very difficult to measure the pore size distribution. There are instruments for measuring the pore size distribution for example; porometer and so on so forth, but this instrument itself will be costing minimum 45 lakhs, 40 to 45. So, instrument is very, very expensive. In fact, some of the research units or you know an institution is very difficult to procure that instrument. So, it is very difficult to measure the pore size distribution even if you measure a pore size distribution then ultimately you will be talking about you will be specifying a membrane by its average pore size.

So, if you have a pore size distribution which will be ultimately it will be converting to an average pore size, then it is very difficult to identify these particular average pore sized membrane will be good for what purpose. So, whether the let say will be will be learning up with a membrane which will be having an average which will be there will be existing a pore size distribution in this membrane and we have measure an average pore size of the membrane. Let say the average pore size is around 40 angstroms or so or let say you know 4 nanometer is 40 angstroms, so for particular this membrane with average forces 40 angstroms these will be used for separation of which solute it is very, very difficult to understand that.

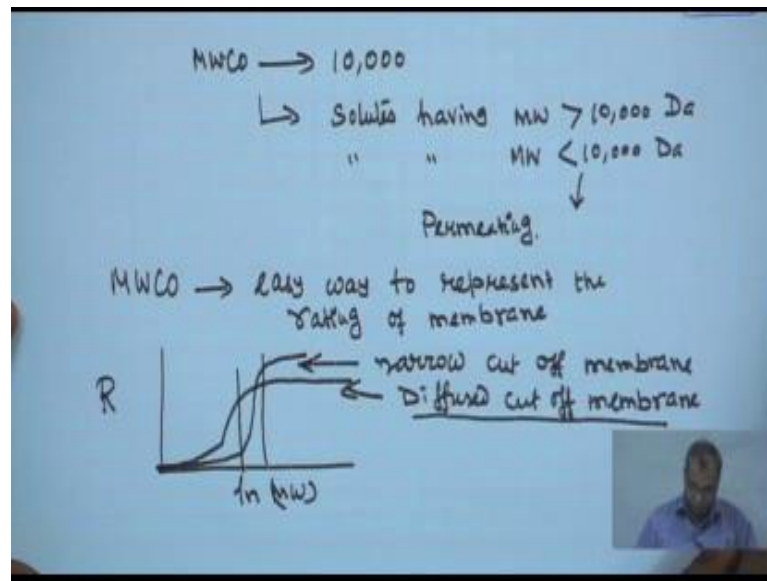
Therefore, a concept has come out that instead of pore size can we just relate that what is that typical molecular weight of the solute it will be I mean this for separation of typical molecular weight of solutes this membrane will be effective. In order to answer this question the concept of molecular cut off has come up. So, therefore, how this molecular

weight cut off will be measured. We generate a curve by measuring the retention of solutes of different molecular weights, but the neutral solutes are very, very important. We have to select a neutral solute, because otherwise there will be a charge-charge interaction if we take a protein there will be protein so can be charged depending on the pH of the solution and the isoelectric point of the protein. So, there you can be charge-charge interaction between the membrane surface and the protein and actual retention capability of the protein will be of the membrane can be must.

So, in order to avoid that it is very, very, important to select a neutral solute and measure its concentration its retention at different molecular weight levels. So, we generate this curve and the value of molecular weight corresponding to 90 percent of retention this value is 90 percent of retention and the molecular weight corresponding to that is known as the molecular weight cut off of the membrane. So, we define molecular weight cut off of the membrane is that molecule which will be molecular of the solute which will be molecular weight of the solute which will be retained by 90 percent of the membrane. So, this is a typical definition of molecular weight cut off of the membrane and from this is a typical method by which molecular weight cut off of the membrane is defined.

So, therefore, all the membranes are manufactured based on the molecular weight cut off only because it is very difficult to get the pore size distribution and average pore size even if you get an average pore size it is very difficult to connect it to its utility in order to separate a particular solute. On the other hand, if you can directly specify this particular membrane is qualified enough to separate this molecular weight of the solute then it will be very useful.

(Refer Slide Time: 09:25)



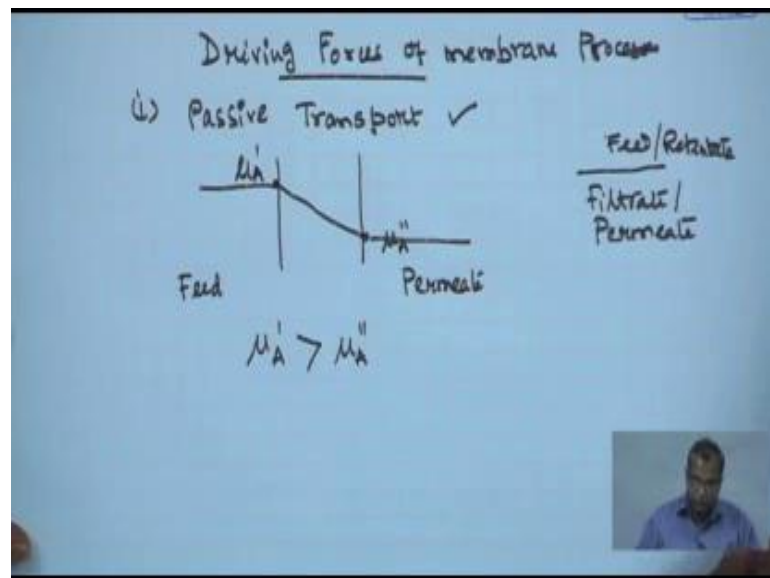
So, therefore, the molecular weight solutes is defined and if molecular weight cut off of the membrane is 10,000 that means, this particular membrane will be retained solutes having molecular weight beyond 10,000 solutes having molecular weight less than 10,000 Dalton they will be permeating through the membrane. So, therefore, 10,000 cut off membrane means it will allow it will it will retains solutes having molecular weight more than 10,000 and it will permeate solutes which will be having a molecular weight less than 10,000. So, if you go to a manufacture he will not supply you the membrane based on its average pore size he will supply you the membrane based on the molecular weight cut off. One has to place an order that I would like to have 10 pieces of 10,000 molecular weight cut off, 10 pieces of 1 lakh molecular weight cut off, 10 pieces of 10,000 or 2000 molecular weight cut off, so will be supplying the material to you.

So what is the molecular weight cut off is therefore molecular weight cut off an easy way to represent or quantify the rating of the membrane. And the principle based on this molecular weight cut off is defined is that molecular weight of the solute is directly proportional to the size of the solute. So, if the size is more, its molecular weight is more. So, therefore, in order to separate that you have to get a large of pore size membrane or larger molecular weight cut off membrane; if the size of solute you want to would like to separate is less its molecular weight is less so you would like to have a molecular weight

cut off low molecular weight cut off membrane. So, one has to one can identify a particular membrane by looking into the molecular weight of the solutes to be separated and the molecular weight cut off value will be helping in identify that particular membrane for the particular purpose or application.

Now, if the distribution of retention versus molecular weight is very sharp, then it is called a narrow cut off membrane or because actually the variation is very small and if it is bite then this is known as the diffused cut off membrane. Therefore, it is desirable to have a narrow cut off membrane in order to have a particular application, but sometimes because of the very complex phenomena involving with the de-mixing processes then that of narrow cut off membrane is very difficult to obtain most of the cases one land up with the diffused cut off membrane. And perform the molecular weight cut off as defined as 90 percent intention of the solute is an easy way to identify a particular membrane for a particular operation.

(Refer Slide Time: 13:13)

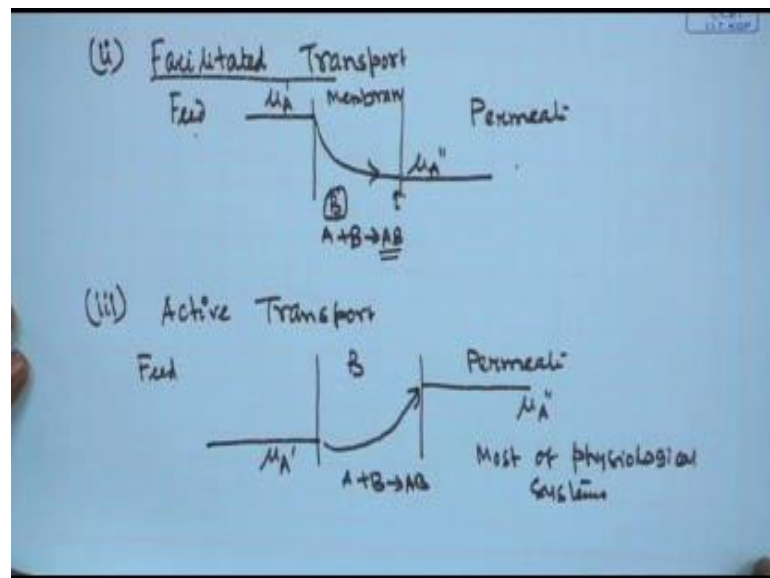


So, we have looked into the various applications of the membranes and various properties that will be really looking into the membranes which will be really useful for our modeling purposes. Now, let us look into the details of the various driving forces of membrane separation processes. The basic driving forces of the transport process is the

passive transport, they are category is under this. In case of passive transport, the chemical potential in the feeds stream more than the chemical potential in permeate. So, let us say this feed or retentate stream and these are the filtrate or the permeate string. By the way now in case of a membrane the feed stream is also called as the retentate stream because that is retained by the membrane and the filtrate is also known as the permeate stream or permeate side because the that has been permeated by the from through the membrane.

So, in the feed stream, if the chemical potential or particular component A is higher than the chemical potential in the downstream,  $\mu_A$  prime is the chemical potential in the feed and  $\mu_A$  double prime is the chemical potential in the permeate and if  $\mu_A$  prime is greater than  $\mu_A$  double prime then there will be solute transport through the membrane from the feed side to the permeate side and this is known as the passive transport.

(Refer Slide Time: 15:06)



Second transport mechanism is known as the facilitated transport. Now, in this case, the transport has been facilitated by an agent that is present within the membrane barrier. So, this is the feed side, this is the permeate side. And you have chemical potential  $\mu_A$  prime of the species A in the feed side; and in the permeate side you are having the

chemical potential  $\mu_A$ , but in this case it is not a straight listing the solute will be present in the membrane matrix. So, this is the membrane, in the membrane matrix. And there is another species B there is present in the membrane matrix it will be making a complex with the solute, so A plus B will be given to AB. So, there will be a species that has been present within this membrane. So, these species will be taking up will be taking up will be reacting with a forming a complex AB whenever A is desorbed into the membrane matrix or the polymer matrix.

Now, AB is formed the complex AB is formed and AB is not allowed to come out of the membrane either in the feed side or into the permeate side, but AB does not have any concentration in the permeate side. So, therefore, because of the concentration gradient, it will be transported by diffusion through the permeate side. And it facilitates transport of A from the feed side to the permeate side. Then again it will be dissociated and in this side and A will be you know desorbing to the permeate side. So, in this case, what is happening that the agent B is facilitating transport of from the feed side to the permeate side therefore, this process is called the facilitated transport.

The third process is known as the active transport of species. In case of active transport, the solute is transported from the feed side to the permeate side by active transport. So, it is being transport against this potential difference. So, chemical potential of A in a feed side is  $\mu_A$  and that is in permeate side is  $\mu_A$ . So, there will be an agent here will be again making a complex with A, and then it will be transported and that will be give you the activation energy, and this will be transported against the driving force and then it will be desorbed to the permeate side. So, this active transport is generally occurring in most of the biological systems in physiological system, most of physiological system, we are having the active transport. And in our membrane based processes, whatever will be covering in this course will be basically getting into the passive transport and the facilitated transport.




(Refer Slide Time: 19:03)

Description of transport by  
Phenomenological equations.

Cause-effect relationship.  
Flux  $\propto$  Driving Force  
Proportionality const  $\Rightarrow$  System characteristic

Phenomenon Relation	Flux	Driving force	constant	
Fick's law	Mass	Concentration gradient	D	✓
Ohm's law	Electricity	Electric Potential gradient	R	✓
Fourier's law	Heat Flux	Temperature Difference	K	✓



Now, we will be looking into the various you know relationship between the description of transport process is using the phenomenological equation and description of transport by phenomenological equations. So, the transport of solute through the membrane can be described by the phenomenological equation. Let us first understand what is the phenomenological equation. These nothing but a natural phenomena which will be using which will be arising out of cause effect relationship. If there is a cause in a nature, there will be an effect, if there is a driving force, there is a gradient of driving force existing that will lead to flux or transport of species. So, the cause is the gradient of the driving force and the effect is the transport of species so this cause effect relationship is known as the phenomenological equation they are occurring as natural phenomena.

And by this phenomenological equations, permeate the flux is generally this is mathematical represented as flux is proportional to the driving force. So, they occur in the phenomena and the proportionality constant is the characteristic property of the system. So, where is proportionality constant, constant is basically the system characteristic. Now, there are several phenomenological equations of similar type of phenomena are happening and various famous laws are existing to describe this system. So, it has just had a summary of this which is quite common to us phenomena involved. Phenomenological relation, flux, driving force and the proportionality constant which

has taking about the first one is the Fick's law, law of mass transport through by diffusion we are talking about a mass flux. And what is the driving force concentration difference or concentration gradient, and what is the corresponding proportionality constant, it is the solute diffusivity.

The second one is known as Ohm's law for current. What is the flux? Flux is basically electricity or charge flux. What is a driving force potential gradient electric potential gradient? And what is the proportionally constant is basically conductance or inverse of resistance. The third common phenomenological equation is Fourier's law of heat conduction that we are taking about the heat flux, thermal heat flux. And what is the driving force temperature difference. And thermal conductivity is the proportionality constant. So, these well known three examples are the examples of phenomenological equations or relationship how a phenomena is relate to the driving force. So, the flux is the cause under the driving force is the cause and the flux is the effect or the result and various constants of these cause effect relationship proportionality constants are basically related to the various system properties.

(Refer Slide Time: 24:02)

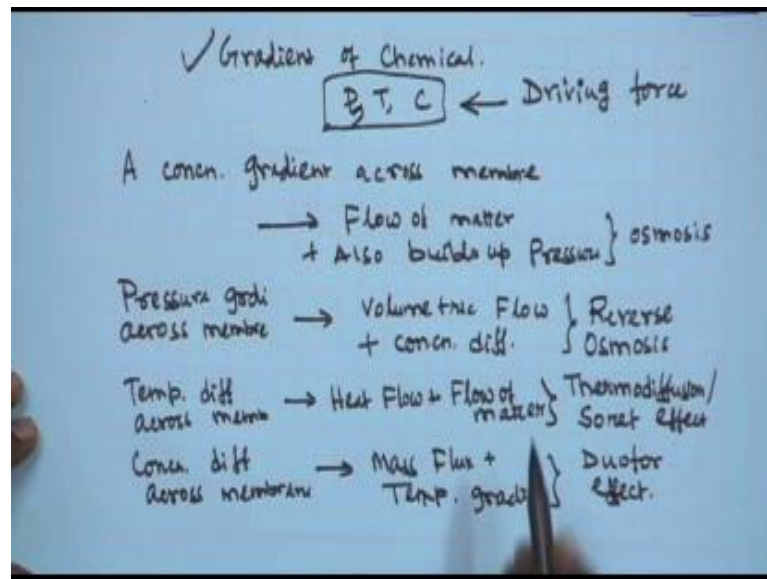
Volumetric Flux / Mass Flux  
 ↓ Driving force → Pressure Difference.  
 $v_w \propto \Delta P$   
 $v_w = L_p \Delta P$   
 ↓ Membrane Permeability.  
 $R_m = \text{Membrane (hydraulic) resistance}$   
 $= \frac{1}{\mu L_p}$   
 ↑ viscosity of permeating solution.  
 $[R_m] \rightarrow \underline{\underline{m^{-1}}}$

Similarly, in our membrane based processed is also we are having a volumetric flux or mass flux if we just convert the volumetric flux by multiplying the density, you will be

getting the mass flux. And this volumetric flux or mass flux is generated by the driving force. What is a driving force in our case may be pressure difference pressure difference may be driving force. So, volumetric flux is proportional to  $\Delta P$ , if your pressure difference is driving force these are what the pressure driven membrane based processes and the proportionality constant is the membrane permeability. So, permeability is the proportionality constant. Sometimes, permeability is also related to the resistance of the membrane, hydraulic resistance of the membrane and this is related to the membrane resistance and sometimes which also call the hydraulic resistance of the membrane. And it is inversely proportional to the membrane permeability and  $\mu$  is the dense in viscosity of permeating solution. And typically most of the cases it is close to the water viscosity  $10^{-3}$  Pascal second.

So, if the permeability is measured or if the permeability is known, the membrane resistance can be evaluated. If membrane resistance is known, when permeability can be evaluated, if you are looking to the dimension of membrane resistance, if you put the value of you know dimension of  $\mu$  the viscosity it is Pascal second and permeability is meter by Pascal second by unit of membrane resistance hydraulic resistance will be typically in meter inverse. So, therefore, in case of membrane based processes and the normal conditions, we have the volumetric flux or the mass flux is the cause or the result and the pressure gradient is the driving force and with the proportionality constant is given by the membrane permeability.

(Refer Slide Time: 26:49)



Similarly, if as we have discussed in actual separation process the gradient of chemical potential is the real driving force, and it will be having a pressure, temperature and composition. So, any of these can be change, in any of this will be causing the flow of the flux of the solute. So, if you have a pressure so in membrane based processes the driving forces may be interdependent. So, gradient of any of these or many of these or to all of this or two of this will be causing a flux of the solute through the membrane, they can be interdependent. Thus a concentration difference, a concentration gradient across membrane leads to flow of matter also builds up pressure, the example is osmosis.

Pressure difference, pressure gradient across membrane leads to volumetric flow plus concentration difference this is the reverse osmosis. Temperature difference across membrane or temperature gradient across membrane leads to heat flow plus flow of matter. This is known as thermo diffusion or Soret effect. And next is concentration difference across membrane it may cause the mass flux plus temperature gradient, this is known as the Duofor effect.

So, therefore, we can see that the general gradient general driving forces gradient of chemical potential which will be having three component pressures - temperature and composition. Now, and these driving forces are interdependent; if one of them will

change, if two of them will be change, if three of them will be change, then there will be cause of flow of matter along with so with the temperature difference or also with the pressure difference. That means, in other words there driving forces are interdependent and if we have a temperature difference across the membrane. if there is no pressure difference then also there can be flow of matter or can be separation occur from the feed side to the permeate side.

So, these has been understood the actual driving force of the membrane separation is the gradient of chemical potential, which is a common driving force of in any separation process. Now, pressure, temperature, composition will be the independent driving for you know parameters which will be controlling the chemical potential if any one of them change, if two of them will change, if three of them will change, then they will be causing the flow of matter. And we are assuming that electro chemical potential difference is absent if that is present that will be another route cause of change in chemical potential.

So, in this class we have looked into the various difference is you know various definitions or very of parameters those will be important for our modeling course in membrane separation process. And also the nature of the driving forces those will be occurring in a membrane processes. Thank you very much. In the next class, we will be start will be starting the modeling of reverse osmosis system by defining first what is the difference between the osmosis and reverse osmosis.

Thank you very much.