

Membrane Technology
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Lecture-32
Basic Principle of Gas Separation, Transport Mechanism, Factors Affecting Gas Separation

Good morning students and this is lecture 32 under module 11 in today's lecture we will discuss about gas separation. As you know one of the most important applications of membrane technology is gas separation and we will discuss about it we will try to understand the principles and different types of membranes and as well as modules that is being used for gas separation and what is the transport mechanism for gas separation and the factors affecting the gas separation as well as 3 or 4 different applications.

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Gas Separation

- Over the past few decades, gas separation using polymeric membranes has drawn a great deal of interest from researchers due to many advantages.
- These include inherent simplicity, ease of control, compact modular nature, lower capital cost, higher energy efficiency and high selectivity.
- The stream to be separated is fed to the membrane device at an elevated pressure, where it passes across one side of the membrane.
- The opposite side of the membrane is held at a lower pressure.
- The pressure difference across the membrane provides the driving force for the diffusion of gas across the membrane.
- Separation is achieved because of the differences in the relative transport rates of the feed components.

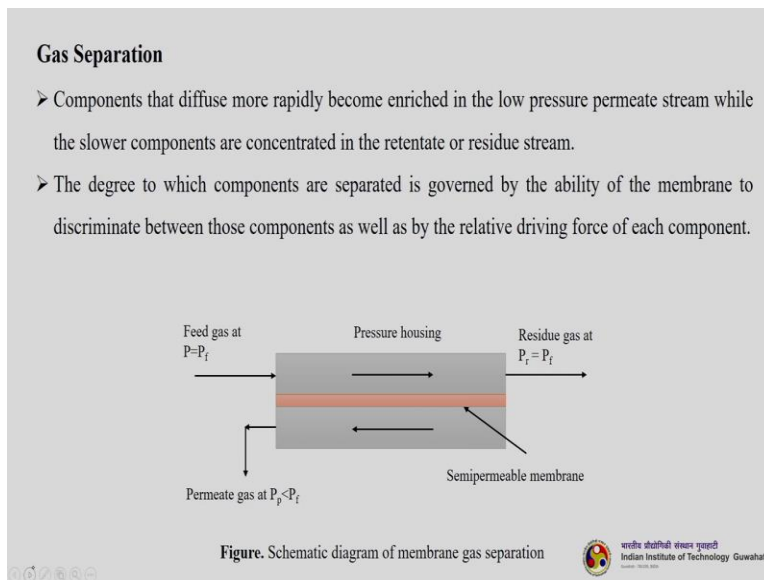


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So, let us begin as you know about the past few decades gas separation using polymeric membranes I have drawn a great deal of interest from researchers due to its various advantages. The advantages include inherent simplicity, ease of control, compact modular nature lower capital cost, higher energy efficiency as well as high selectivity. Now the stream to be separated is fed to the membrane device at an elevated pressure where it passes across one side of the membrane the usual membrane separation principle.

The opposite side of the membrane is held at a lower pressure the pressure difference across the membrane provides the driving force for the diffusion of gas across the membrane. Little more a similar to that of what we discussed during pervaporation. So, separation is achieved because of the differences in the relative transport rates of the feed components.

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Components that diffused more rapidly become enriched in the low pressure permeate stream while the slower components are concentrated in the retentate or residue stream. So, every a component has a particular diffusivity so if diffusivity is very high then and apart from their size and other factors then they will pass through the membrane and it will be collected in the permeate side if the deposited diffusivity is very low and along with their molecular weight so there will be mostly retained on the surface of the membrane.

So the degree to which the components are separated is governed by the ability of the membrane to discriminate between those components as well as by the relative driving force of each component. So, you can see this is the schematic basically feed gas at P equals to P_f , f is the feed gas pressure, so a residue guess what you are getting out equals to P_r equals to P_f and permeate gas is P_p less than P_f .

So this is the this is one of the measured thing is that the pressure of the permeate gas should be lower than that of the feed gas.

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Membrane for Gas Separation

- Industrial gas separation membranes are generally categorized as cellulosic and non-cellulosic.
- Amorphous (nanocrystalline) polymeric membranes used for gas separations are in either in glassy or rubbery state.
- When the temperature is above the glass transition temperature (T_g), polymer is in rubbery state.
- In the rubbery state, polymers tend to be soft and more flexible.
- When the temperature is lower than the glass transition temperature of the polymer, the polymer is at glassy state.
- In the glassy state, polymers are rigid and often brittle.
- There is low level of molecular movement and the rate of diffusion of large molecules is small.
- Properties that change around T_g include density, specific heat, dielectric coefficient, rates of gas/liquid diffusion through the polymer, and conductivity or charge mobility.



So, industrial gas separation membranes are generally categorized as cellulosic and non cellulosic, amorphous or nano crystalline polymeric membranes used for gas separation either in glossy or rubbery state. Now when the temperature is above the glass transition temperature that is T_g polymer is in rubbery state. Now if you recall we have already discussed what is glass transition temperature what is its importance and how the polymers behaves when you actually heat it and during our discussion of the membrane materials.

So, in rubbery state polymers tend to be soft and more flexible when the temperature is lower than glass transition temperature of the polymer the polymer is at glassy state. So, in the glassy State polymers are usually they are rigid and often brittle, so there is a low level of molecular movement and the rate of diffusion is very small. So, properties that change around the gas transition temperature include the density, specific heat, dielectric coefficient, rates of gas liquid diffusion through the polymer and conductivity or charge mobility membrane for gas separation.

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Membrane for Gas Separation

- The gas sorption capacity of the polymer depends on its free volume and its physical affinity for the gas.
- The mobility of sorbed molecules depends on the free volume of the polymer and on the degree of rigidity of the chains.
- Ideal gas separation membranes are of two types: *selective* and *permeable*.
- Selective membranes produce high purity gas and permeable membranes provide large flux.
- But both are inversely related, as selectivity increases, flux decreases and the vice versa.
- Permeability and selectivity are somewhat antinomic properties, especially when the selectivity is of a diffusional type, i.e. when the polymer acts as a molecular sieve.

So the gas separation capacity of the polymer depends on its free volume and its physical affinity for the gas. The mobility of the salt molecules depend on the free volume of the polymer and on the degree of rigidity of the chains. Ideal gas separation member and set of two types either their selective membranes or their permeable membranes. So, selective membranes produces high purity gas and permeable membranes provide larger flux.

So there is a trade-off between this high purity of the gas yield as well as the high permeability. So, you need to balance between these two right so you need to choose a membrane in such a that and basically what you are looking for you are you looking for extremely high permeability or you are looking for a very high purity product so depending on that you need to choose your membrane. So, you can either go for a selective membrane or a permeable membrane.

So, both are inversely related so a selectivity increases flux decreases and permeability and selectivity are somewhat antinomic properties especially when the selectivity of a diffusional type when the polymer acts as a molecular sieve. So, when the diffusional transport is happening so the polymer material itself is behaving just like a molecular sieve so some sort of sieving mechanism is happening.

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Membrane for Gas Separation

- The majority of industrial membrane processes for gas separations utilize glassy polymeric membranes because of their high gas selectivity and good mechanical properties.
- Glassy polymers like polyimides are used for CO_2/CH_4 separation; polysulfones are used in H_2 separations; and cellulose acetate membranes are used for the removal of CO_2 and H_2O from natural gas.
- In the area of rubbery polymers, polyurethanes possess high permeability and are being applied in O_2/N_2 separation.

So the majority of industrial membrane processes for gas separation utilized glassy polymeric membranes because of their high selectivity and good mechanical properties so mostly their glassy polymeric material. Material such as like poly mites which are used for the carbon dioxide methane separation one of the most important application of the gas separation, polysulfones are used for hydrogen separation. Then cellulose acetate membranes used for the removal of carbon dioxide and water from natural gas.

So there are a lot many applications are and this one examples of such membranes for different gas phase application. So, in the area rubbery polymers polyurethanes possess high permeability and are being applied for oxygen nitrogen separation.

(Refer Slide Time: 05:47)

Membrane Materials

❖ Ceramic and Zeolite membranes

- Ceramic- and zeolite-based membranes have begun to be used for a few commercial separations.
- These membranes are all multilayer composite structures formed by coating a thin selective ceramic or zeolite layer onto a microporous ceramic support.
- Ceramic membranes are prepared by the sol-gel technique.
- Zeolite membranes are prepared by direct crystallization, in which the thin zeolite layer is crystallized at high pressure and temperature directly onto the microporous support

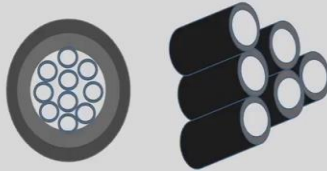


Figure. Schematic representation of ceramic hollow fiber membranes

So, let us now understand the membrane materials so ceramic and zeolite membranes. Ceramic and zeolite membranes have begun to be used for a few commercial applications just for a few years back. So, these membranes are all multi-layer composite structures formed by coating a thin selective ceramic or geo like layer into the micro porous support layer. So, this we have already discussed many a times what is ceramic member and how they are being prepared.

And the ceramic membranes are prepared by the sol-gel technique, zeolite membranes are prepared by direct crystallization in which the thin zeolite layer is crystallized at high pressure and temperature directly onto the micro porous support. So, these are some of the pictures of the ceramic hollow fiber membranes.

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Membrane Materials

❖ Composite membrane with very thin Pd layer

- Thin layer of palladium on tantalum or vanadium support film and porous substrate, such as ceramic or stainless steel is used.
- Tantalum and Vanadium are quite permeable to hydrogen, so possibility of getting more H_2
- These membranes are quite permeable at high temperature.
- Reduced materials cost.
- Improved mechanical strength.

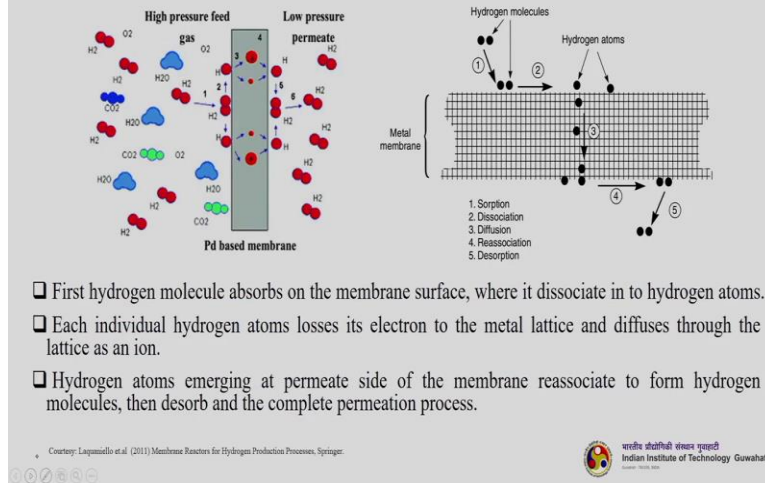
So composite membrane with a very thin palladium layer to thin layer of palladium on tantalum or vanadium support film and porous substrates such as ceramic or stainless steel is being used for many applications of gas separation, tantalum and vanadium are quite permeable to hydrogen so possibility of getting more hydrogen that is why they are being used. So, these membranes are quite permeable at high temperature reduced materials cost and improved mechanical strength.

Because of the use of stainless steel and other things so metallic membranes again only palladium membranes are dense metallic membranes have typified by palladium or silver membranes. Palladium membranes are for hydrogen permeation and silver membranes for oxygen permeation because their permeability inside these membrane materials is very high. So, usually they are preferred they are prepared by cold rolling than the electroless plating then you have electroplating then CBD which is called chemical vapour decomposition then magnetron sputtering etcetera.

There are various methods to prepare it they are highly selective their mechanical and thermal stability is good and we can use it for long term. So, that life is actually more and applications in membrane reactors and get separation.

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❑ Hydrogen permeation through metal membrane is shown below.



So, hydrogen permeation through metal membrane is shown below so you can see how it is happening actually. So, the first the hydrogen molecules so hydrogen molecules will observe on the membrane surface where it dissociates into hydrogen atoms right. So, and this is the Palladium based membrane you can see how it is happening and here the hydrogen is coming it is first initially getting solved on the surface of the membrane right this part.

So in the two it is getting dissociated, so once in dissociates then it will start diffusing through the membrane. Then once it comes to this almost tail end of the membrane so they are again getting re-associated then the desorption is happening here. So, this is how it happens sorption, desorption and dissociation, diffusion, reassociation and desorption. The five different steps so each individual hydrogen atom loses its electron to the metal lattice and diffuses through the lattice as an ion.

So this you need to take care of hydrogen at as itself is not getting diffuses it is getting separated into ions and then ions are getting hydrogen ions are getting are diffused or you can say to permeate it through the membrane or the Palladium lattice you can say. So, hydrogen atoms emerging at the permeate side of the membrane re-associates to form hydrogen molecules then desorb and complete permeate process this is how hydrogen separation happens using a palladium based membrane.

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Membrane Materials

- Pd membranes shows high solubility and permeability for hydrogen.
- In some earlier works, Pd membranes showed 99.9% pure hydrogen separation through a 25 μm thick membrane.
- **Advantages:** high H_2 selectivity and long term use.
- **Disadvantages:** expensive (100 times more expensive than polymeric membranes) and brittle.
- **Pd/Ag alloy** used to reduce cost and increase toughness.
- Pd/Ag shows the low permeability.
- To avoid all these problems, composite metallic membrane is prepared.



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So, palladium membranes so high solubility and permeability for hydrogen in some earlier works palladium membranes saw 99.9% pure hydrogen separation using a 25 micron thick membrane. So, you can see extremely high pure hydrogen can be obtained using palladium membranes. So, advantage is of course a hydrogen selectivity and long term use disadvantage is expensive 100 times more expensive than polymeric membranes and they are brittle.

And palladium and silver alloy is used to reduce the cost as well as the roughness and increase the roughness. Palladium silver alloys so low permeability compared to only palladium to avoid all these problems composite metallic membranes and repairs.

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Membrane Materials

❖ Polymer materials

- Most gas separation processes require that the selective membrane layer be extremely thin to achieve economical fluxes.
- Composite membranes with glassy thin selective layers with high-flux are good.
- The microporous support layer can be a tough glassy material to provide strength.

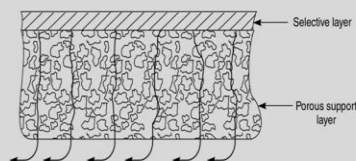


Fig. Two-layer composite membrane formed by coating a thin layer of a selective polymer on a microporous support that provides mechanical strength



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So, let us not talk about polymer membranes so most gas separation processes require that selective membrane layer be extremely thin to achieve economic flux. So, this is the selective layer and this is the layer which is giving its supposed some sort of composite structure. So, composite membranes with glassy thin selective layers with high flux are good the micro porous support layer can be tough glassy material to provide strength so this basically this layer.

So it is a two layer composite membrane formed by cutting a thin layer of selective membrane or a selective polymer and micro porous support that provides mechanical strength. Now you can go for a three layer also it is possible we have discussed earlier how it happens right. So, here this in this case it is also on a two layer or a bilayer composite membrane.

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Membrane Module

- In gas separation process, hollow fiber and spiral wound systems are used extensively.
- Cellulosic membranes have either spiral wound or hollow fiber configurations, while most of the non-cellulosic membranes have hollow fiber configurations.
- Hollow fiber module has the advantage of very large surface to volume ratios.
- The hollow fibers can have an I.D. up to 200 microns.
- The larger the I.D., the lower the pressure drop inside the tubes, but the lower is the area to volume ratio.
- The wall thickness can vary from 25 to 250 microns depending upon the pressure which must be withstood.



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So, in gas separation process hollow fiber and spiral wound systems are basically used we are talking about modules now. So, cellulosic membranes have either spiral wound or hollow fiber configurations it suits best to them and while most of the non cellular membranes have hollow fiber configurations. The hollow fiber you know all of fiber has the advantage of very large surface to volume ratio right. So, that is why hollow fibers is being commercially adapted more.

So the hollow fibers can have an ID or internal diameter up to 200 microns the larger the ID the lower the pressure drop inside the tubes but the lower is the area to volume ratio. So, if you have a high area to volume ratio in a small area we can have more surface right generated for air

separation or mass transfer so the wall thickness can vary from 250 to 225 to 250 microns depending upon the presser which must be withstood.

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Membrane Module

- The skin is from 0.1 to 1.0 micron thick and is formed on the outside of the hollow fiber.
- The hollow fiber systems are currently being used commercially for the recovery of hydrogen and carbon dioxide and for the separation of nitrogen from air.
- Spiral wound configuration, on the other hand, has the advantages of a lower pressure drop in the direction of flow, and the technology to build the system is less complex, but volume ratio is lower.

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So, the scheme is from 0.1 to 1 micron thick and is formed on the outside of the hollow fiber. The hollow fiber systems are currently being used commercially for the recovery of hydrogen or carbon dioxide and for the separation of nitrogen from a spiral wound configuration of the under hand has the advantage of a lower pressure drop in the direction of flow and the technology to build the system is less compressed but volume ratio is lower.

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Mechanism of Gas Transport

- Three general transport mechanisms are commonly used to describe gas separations using membranes.
- They are *Knudsen diffusion*, *molecular sieving*, and *solution-diffusion*.

Knudsen Diffusion

- In Knudsen diffusion, separation, is achieved when the *mean free paths* of the molecules are large relative to the membrane pore radius.
- A gas molecule 'A' at partial pressure P_{A1} at the entrance to the capillary is diffusing through the capillary having a diameter of d m.
- The total pressure P is constant throughout.
- The mean free path λ is large compared to the diameter d .
- As a result, the molecule collides with the wall and molecule wall collisions are important.
- This type of diffusion is known as Knudsen diffusion.

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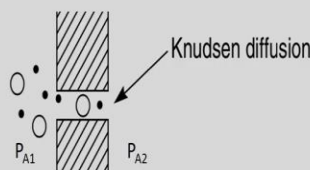
So, let us now understand the mechanism of gas transport the three general transport mechanisms are commonly used to describe gas operations using membranes they are not strained diffusion molecular shipping and solution diffusion mechanisms. So, briefly we have discussed this solution diffusion we have discussed in detail. So, let us now go ahead and discuss again about Knudsen diffusion little. So, in Knudsen diffusion the separation is achieved by mean free paths of the molecules.

So if the mean free path of the molecules are larger relative to the pore radius then Knudsen diffusion happens. So, mean free path is something we can define the mean free path is the distance between the two successive collisions of the molecules. Now the collision of the path so collision of the molecules itself among themselves otherwise our here in the case collision of the walls also in which they are traveling basically.

So if I guess molecule a at A partial pressure P_{A1} at the entrance to the capillary is diffusing through the capillary having a diameter of D . So, the total pressure P is constant throughout the mean free path λ is large compared to the diameter D . So, once λ is greater than D then Knudsen diffusion will come into picture. So, as a result the molecule collides with the wall and molecule wall collisions are important this is called Knudsen diffusion.

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- The separation factor from Knudsen diffusion is based on the inverse square root ratio of two molecular weights, assuming that the gas mixture consists of only the two types of molecules.
- The process is limited to systems with large values for the molecular weight ratio, such is found in H_2 separation.
- Due to their low selectivities, Knudsen diffusion membranes are not commercially attractive.




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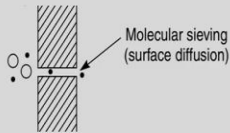
So, the separation factor from Knudsen diffusion is based on the inverse square root of that molecular weights; assuming that gas mixture consists of only two types of molecules so the process is limited to systems with large values for the molecular weight ratio such is found in hydrogen separation due to their low selectivities. Knudsen and diffusion membranes are not commercially attractive, let us say this is something like this is your d and this is a molecule which comes and travels so it will collide something like this no molecules.

So this is basically the mean free path we can call it and the λ if the λ is greater than d then the Knudsen diffusion will be prevalent. However due to the low selectivities Knudsen diffusions are not commercially being given importance.

(Refer Slide Time: 13:51)

Molecular Sieving

- The molecular sieving mechanism describes the ideal condition for the separation of vapor compounds of different molecular sizes through a porous membrane.
- Smaller molecules have the highest diffusion rates.
- This process can happen only with sufficient driving force.
- In other words, the upstream partial pressure of the faster gas should be higher than the downstream partial pressure.
- The main limitation is that condensable gases may cause fouling and alter the structure of the membrane.
- Therefore, it is only feasible commercially in robust systems such as those that use ultra microporous carbon or hollow fiber glass membranes.





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So, molecular sieving so the molecular sieving mechanism describes the ideal condition for the separation of vapour compounds of different molecular sizes through a porous membrane. Smaller molecules have the highest diffusion rates this process can happen only with sufficient driving force so in other words upstream partial pressure of the faster gas should be higher than the downstream partial pressure otherwise the molecular diffusion will not happen, molecular sieving will not happen.

The main limitation is that condensable gases may cause fouling and alter the structure of the membrane so this is a disadvantages. So, when you are dealing with a condensable gas then we

need to be very careful and choose the polymer or the material of the membrane in such a way that we avoid the fouling otherwise swelling of the membrane. So, therefore it is only feasible commercially in robust systems such as those that use ultra micro porous carbon or hollow fiber gas membranes.

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Solution-Diffusion

- In gas permeation, the permeating gas is made to pass through the membrane by applying a pressure difference on either side of the membrane.
- This pressure difference causes a difference in dissolved gas concentration between the two faces of the membrane and hence a diffusional gas flows through the membrane.
- Solution-diffusion separation is based on both solubility and mobility factors.
- Gas permeation can be seen as a three-stage process in the solution-diffusion model:
 - ❑ Adsorption and dissolution of gas at the polymer membrane interface
 - ❑ Diffusion of the gas in and through the bulk polymer
 - ❑ Desorption of gas into the external phase



Now see if solution diffusion we have discussed in detail along with the equations and all just quickly will go through it. So, in gas permeation the permitting gas is made to pass through the membrane by applying a pressure dependence on either side of the membrane now this is true for any mechanism. Now this pressure dependent causes the different difference in dissolved gas concentration between the two phases of the membrane and hence a diffusional gas flows through the membrane.

A solution diffusion is based on the solubility and mobility factors so it can be a three-step process, so first adsorption and dissolution of gas at the polymeric membranes interface. Then diffusion of the gas in and through the bulk of polymer then desorption into the external space. So, these are the three necessary steps that happens during the solution diffusion.

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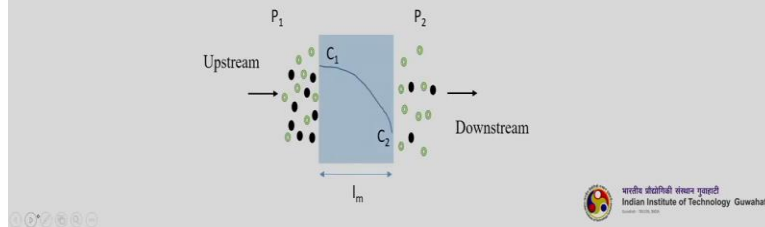
- Permeation is used to describe the overall mass transport process, and diffusion refers only to the movement of gas molecules inside the polymer membrane.
- The model assumes that the pressure within a membrane is uniform and the chemical potential gradient across the membrane is expressed only as a concentration gradient.
- Koros et al. (1988) gave a thorough review on polymeric membranes for solution-diffusion based permeation separations.
- Koros and Fleming (1993) suggested that solution-diffusion is achieved via penetrant species undergoing random jumps in the polymer matrix due to a concentration difference between membrane upstream and downstream, resulting in a diffusion flux travelling downstream.

So, permeation is used to describe the overall mass transport process and diffusion refers to the movement of gas molecules inside the polymeric membrane. So, the model assumes that pressure within a membrane is uniform and the chemical potential gradient across the membrane is expressed only as a concentration gradient in 1988 Koros Quebec thorough review on polymeric membranes for solution diffusion based permanent separations anybody interested may refer this.

So Koros and Fleming again in 1993 suggested that solution diffusion is achieved via penetrant species undergoing random jumps in the polymer matrix due to a concentration difference between member and upstream and downstream resulting in a diffusion flux traveling downstream.

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- Varying the chemical nature of the polymer allows control of the relative extent of solution and diffusion of different gases through the polymer matrix.
- The upstream gas which has a pressure of P_1 comes in contact with the membrane interface.
- With a driving force (e.g. chemical potential, concentration gradient, etc.), the permeate gas forms a concentration profile across the membrane with respect to membrane thickness l_m .
- The normalized flux is gas flow rate divided by the membrane surface area and it is denoted as N_A .



So, varying the chemical nature of the polymer allows control of relative extent of solution and diffusion of different gases through the polymer matrix. Now the upstream gas which is a pressure of p_1 comes in contact with the membrane interface with a driving force that is chemical potential concentration gradient whatever it is, the permeate gas forms a concentration profile across the membrane with respect to the membrane thickness l_m .

So, that normalized flux is gas flow rate divided by the membrane surface area and it is denoted by N_A and N is the molar flux rate.

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- Separation of the gas mixture is achieved when one of the components interacts more strongly with the membrane material or, in other words, diffuses faster through the membrane.
- Among the three solution-diffusion stages, the diffusion step is the slowest.
- Hence, it is the rate determining step in permeation.
- In general, the relationship between the linear flux J and the driving force is:

$$J = -D \frac{dc}{dx}, \text{ where } D \text{ is diffusion coefficient.}$$

- When the solubility of a penetrant gas in a polymer is sufficiently low, the concentration of the penetrant is proportional to the vapor pressure of penetrant in polymer.

And separation of the gas mixture is achieved when one of the components interact more strongly with the membrane material in other words diffuses faster through the membrane. so, among the three solution diffusion stages the diffusion step is the slowest so that is the rate determining step. So, whatever step is slowest that will be usually the rate determining step so in general relationship can be expressed the flux we can write minus $D \frac{dc}{dx}$ where D is the diffusion coefficient.

So when the solubility of a penetrant gas in a polymer is sufficiently low the concentration of the penetrant is proportional to the vapor pressure of the penetrated polymer.

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➤ This relationship is expressed as Henry's law,

$$C = S \cdot p$$

➤ S is the solubility coefficient (Henry's law constant) for the particular gas polymer pair, p is the partial pressure of A in gas and C is the equilibrium solubility of gas in the polymer.

➤ At steady state, the permeation of a pure gas A through a membrane of thickness l_m is characterized by a permeability coefficient P_A generally defined as:

$$P_A = \frac{N_A}{(p_1 - p_2)/l_m} = \frac{N_A}{\Delta P/l_m}$$

where, N_A is the normalized flux, P_1 and P_2 , are the upstream and downstream pressures and ΔP is ($P_1 - P_2$).

- The permeability of dense membranes is low because of absence of pores.
- The permeance of component A can be high if l_m very small, even though the permeability is low.
- Thickness of the perm-selective layer is typically in the range 0.1 to 10 μm for gas separations.
- The porous support is much thicker than this and typically more than 100 μm .


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So this relationship is expressed by Henry's law which is C is given by this C equals to S into p , S is the solubility coefficient that is Henry's law constant for the particular gas polymer pair and p is the partial pressure of A in gas and C is the equilibrium solubility of gas in the polymer. At steady state the permeation of the pure gas through the membrane thickness l_m is characterized by a permeability coefficient P_A generally written as P_A equals to N_A by $p_1 - p_2$ by l_m which is we can write N_A by ΔP by l_m .

So here N_A is normalized flux and p_1 p_2 at the upstream and downstream process and ΔP is $p_1 - p_2$, so the permeability of dense membrane is low because of absence of pores the permeation of component A can be high if l_m is very small. So, this we have I told you many

times whenever we have come across such discussion on membrane thickness the thickness layer which is doing the separation or permeation must be thin so as to avoid resistance. So, even though the permeability is low so thickness of the palm Selective layer is typically in the range of 0.1 to 10 micron for gas separation.

Porous support can be around 100 microns or even more than that it is fine its job is to provide mechanical support only.

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➤ When large difference in permeabilities exists among species, both high permeance and high selectivity can be achieved in asymmetric membranes.

➤ If Henry's law applies, then S is constant at a given temperature and so is D .

➤ The permeability coefficient, P_A , can also be defined as:

$$P = D \cdot S$$

➤ The diffusion coefficient, D , is a kinetic term governed by the amount of energy necessary for a particular penetrant to execute a diffusive jump through the polymer and the intrinsic degree of segmental packing in the matrix.

➤ The solubility coefficient, S , is a thermodynamic term that depends on factors such as condensability of the penetrant, interactions between the polymer and penetrant, and the amount of penetrant-scale non-equilibrium excess volume in glassy polymers.



So, any last difference in permeable it is exist among species both high permeance and high selectivity can be achieved in asymmetric membranes if Henry's laws applies then S is constant at a given temperature so is D a permeability coefficient also defined as P equals to $D S$, so D is the diffusion coefficient that is the kinetic term governed by the amount of energy necessary for a particular penetrant to execute diffusive jump through the polymer.

And the intrinsic degree of segmental packing in the matrix and solubility coefficient S is a thermodynamic term so your D is a kinetic term whereas S is the thermodynamic term that depends on factors such as condense ability of the penetrant interactions between the polymer and penetrant and the amount of penetrance scale non-equilibrium excess volume in glassy polymers.

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- For a binary gas mixture permeating through a polymer membrane, the selectivity of a polymer membrane towards two different penetrant gases, A and B can be commonly expressed in terms of the ideal selectivity or ideal perm-selectivity (down-stream pressure considered negligible)

$$\alpha_{AB} = P_A/P_B$$

- Expanding the permeability into diffusivity and solubility terms, the ideal selectivity can be

expressed by,

$$\alpha_{AB} = \left(\frac{D_A}{D_B}\right) \left(\frac{S_A}{S_B}\right)$$

Here, $\frac{D_A}{D_B}$ is the ratio of the concentration-averaged diffusion coefficients of penetrants A and B and

referred to as the membranes diffusivity and $\frac{S_A}{S_B}$ is the ration of solubility selectivity.



So for a binary gas mixture penetrating through a polymer membrane the selectivity of a polymer membrane towards two different penetrant gasses let us say A and B can be commonly expressed in terms of the ideal selectivity of ideal perm selectivity downstream pressure considered negligible so α_{AB} can be P_A by P_B so if you expand it then we can include diffusivity and solubility. So, D_A by D_B into S_A by S_B where D_A by D_B is the ratio of the concentration averaged diffusion coefficients and S_A by S_B is the solubility ratio solubility selectivity solubility basically.

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- High permeability and high selectivity are the most important criteria in evaluating a membrane.
- The two more important quantities that dictate the performance of membrane device are the *flux* and the *separation factor or selectivity*.
- If x is the mole fraction of A in the feed side and y that in the permeate side for a binary mixture of A and B (component A has the higher permeability), the separation factor is then given by:

$$\alpha_{AB} = \left(\frac{y/(1-y)}{x/(1-x)}\right) \quad \text{or} \quad y = \frac{\alpha x}{1 + (\alpha - 1)x}$$

- The permeability coefficient of dense film materials is commonly expressed in units of barrer:

$$1 \text{ barrer} = 1 \times 10^{-10} \frac{\text{cm}^3 (\text{STP}) \text{ cm}}{(\text{cm}^2 \text{ polymer}) (\text{s}) (\text{cm Hg})}$$

- Such a unit was originally defined for convenience because many polymer membranes had permeabilities around 1 barrer.



So, high permeability and high selectivity are most important criteria in evaluating a membrane the two more important quantities that dictate the performance of membrane devices at the flux

and separation factor or selectivity. Now if x is the mole fraction of A in the feed side and y is that up in the permeate side for a binary mixture of A and B. So, let us assume that component A has higher permeability the separation factor then we can write α_{AB} equals to $\frac{x}{y} \cdot \frac{1-y}{1-x}$ or we can write $\alpha_{AB} = \frac{x}{1-x} \cdot \frac{1-y}{y}$.

So the permeability coefficient of dense filling material commonly explained in terms of barrer so 1 barrer equals - 1 into 10 to the power -10 centimeter cube into STP cm centimeter square polymer s centimeter Hg on Mercury. So, such a unit was originally defined for convenience because of many polymer membrane said permeability is a now 1 barrer.

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Factors Affecting Gas Permeation

Temperature

- Gas diffusion coefficients generally increase with increasing temperature when the polymer does not undergo thermally induced morphological rearrangements such as crystallization over the temperature range of interest.
- Both diffusivity and solubility coefficients are temperature dependent.
- The selectivity also sensitive to changes in temperature.
- The increased segmental motion at higher temperatures reduces the ability of polymer to discriminate between penetrants of different physical dimensions, thereby resulting in a diffusivity selectivity loss.



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So, let us now understand the different factors that actually affect the gas permeation let us discuss its temperature. So, gas diffusion coefficients are generally increased with increasing temperature right when the polymer does not undergo thermally induced morphological rearrangement such as crystallization about the temperature range of interest. So, both diffusivity and solubility coefficients are temperature dependent the selectivity also sensitive to change in temperature.

The increased segmental motion at higher temperature reduces the ability of polymer to discriminate between the penetrance of different physical dimensions thereby resulting in a diffusivity selectivity loss.

(Refer Slide Time: 21:26)

Pressure

- Large variation of permeability may occur with the change in the pressure of permeant contacting with the polymer.
- A few typical patterns of response can be observed in permeability versus pressure relationships.
- For the permeation of an organic vapour into a rubbery polymer, permeability increases linearly with increasing pressure.
- For low sorbing penetrants, such as He or N₂ in rubbery or glassy polymers, diffusion and solution become independent of gas pressure.
- A decreasing trend of permeability with increasing pressure is typically observed with highly soluble gases such as CO₂ in glassy polymers.



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Next is pressure so large variation of permeability may occur with the change in pressure of permeant contacting with the polymer. A few typical patterns of response can be observed in permeability versus pressure relationship for the permeation of an organic vapor into rubbery polymer permeability increases linearly with increasing pressure. For low serving penitence such as helium or nitrogen in rubbery or glassy polymers diffusion and solution become independent of gas pressure.

So a decreasing trend of permeability with increasing pressure is typically observed with highly soluble gases such as carbon dioxide and glassy polymers.

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Plasticization Pressure

- The plasticization pressure is the pressure at which an increase in permeance occurs.
- At such feed pressure, the gas concentration in the polymer material disrupts the chain packing.
- The polymer matrix swells and the segmental mobility of the polymer chain increases.
- This results in an increase in gas diffusivity and induces increase in permeability.
- The polymer is highly plasticized by the penetrant, the diffusion coefficient may become a function of time.
- This non-ideal behaviour is explained by free volume theory.
- Free volume theory of diffusion suggests that *molecules can only diffuse through free volume in a molecule matrix.*

Then plasticization and pressure so plasticization and pressure is usually defined as the pressure at which an increase in permeance occurs so at such feed pressure the gas concentration in the polymer material disrupts the chain packing. The polymer matrix swells and the segmental mobility of the polymer chain increases this results in an increase in gas diffusivity and induces increase in permeability the polymer is highly plasticized by the penetrant the diffusion coefficient may become a function of time.

Now this non-ideal behavior is experience explained by the free volume theory. Free volume theory of diffusion suggests that molecules can only diffuse through free volume in a molecular matrix. So, this is what is the free volume theory.

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Permeant Condensability

- In general, gas solubility in polymers increases with increasing gas condensability.
- Condensability can be measured as the gas critical temperature, or the normal boiling point.
- Diffusion coefficients of permeants are found to decrease with increasing size of the permeants.
- Diffusion coefficients in polymers are also sensitive to permeant shape.
- Linear or oblong permeant molecules such as CO_2 exhibit higher diffusivities than those of spherical molecular shape of equivalent molecular volume such as CH_4 .
- Specific interactions between gas and polymer molecules also affect gas solubility.
- Gases such as CO_2 which has a quadrupole moment are generally more soluble in polar polymers.

And then permeant condensed ability so in general gas solubility and polymers increases with increasing gas condensability, so, condensability can be measured as the gas critical temperature or the normal boiling point diffusion coefficients of permeants are found to decrease with increasing size of permeates. So, diffusion coefficient in polymers are also sensitive to permeant shape also plays a very important role right.

So a linear or oblong permeant molecule such as carbon dioxide exhibit high diffusivity than those of spherical molecular shape of equivalent molecular volume such as methane. Specific interactions between gas and polymer molecules also affect gas solubility gases such as carbon dioxide which has a quadrupole moment are generally more soluble in polar polymers.

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Polymer Crystallinity

- Crystallinity in polymers tends to reduce both permeant solubility and diffusivity, thereby reducing permeability, which is generally undesirable.
- Polymer crosslinking reduces polymer segmental mobility; therefore, diffusion coefficients of the penetrant gas typically decrease with an increasing degree of crosslinking in the polymer.
- In lower molecular weight polymers, chains are more mobile and penetrant diffusivity decreases with increasing molecular weight.
- At higher molecular weights, when the concentration of chain ends is low, diffusivity is relatively independent of molecular weight as is solubility.

Polymer crystallinity, so crystallinity and polymers tends to reduce both permeant solubility and diffusivity thereby reducing permeability which is usually undesirable. And polymer cross-linking reduces polymer segmental mobility therefore diffusion coefficients of the penetrant gas typically decreases with an increase in the degree of cross-linking of the polymer. So, in lower molecular weight polymers chains are more mobile and penetrant diffusivity decreases with increasing molecular weight.

At higher molecular weights when the concentration of chain ends is low diffusivity is relatively independent of molecular weight as its solubility.

(Refer Slide Time: 24:08)

Applications of Gas-separation

Production of Hydrogen

- Examples: Separation of hydrogen from nitrogen in ammonia purge gas stream, hydrogen/methane separation in refinery off-gases and hydrogen/carbon monoxide adjustment in oxo-chemical synthesis plants.
- Hydrogen is a small, non condensable gas, which is highly permeable compared to all other gases.
- The glassy polymers are primarily used to make hydrogen-selective membranes.
- Early hydrogen membrane gas separation plants used polysulfone or cellulose acetate membranes, but now a variety of specifically synthesized materials, such as polyimides (Ube, Praxair), polyaramide (Medal) or brominated polysulfone (Permea) are used.

Now let us discuss few applications of gas separation. So, the first one is production of hydrogen so example is separation of hydrogen from nitrogen in ammonia pores gas stream, hydrogen methane separation in refinery of gases and hydrogen carbon monoxide adjustment in Oxo chemical synthesis plants. So, hydrogen you know is a very small non condensable gas which is highly permeable compared to all other guesses. This is the reason why hydrogen is separated using this guess separation technique.

The glassy polymers are primarily used to make hydrogen selective membranes early hydrogen membrane get separation plants used solvent polysulfone or cellulose acetate membranes but now a variety of specifically synthetic material such as polyimides, polyaramide, brominated polysulfone all these materials are being used.

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Table. Hydrogen separation membranes

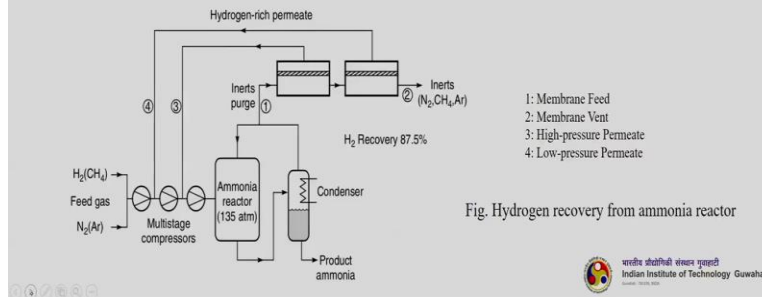
Membrane	Selectivity			Hydrogen pressure-normalized flux 1×10^{-6} $\frac{\text{cm}^3 (\text{STP}) \text{ cm}}{(\text{cm}^2 \text{ polymer}) (\text{s}) (\text{cm Hg})}$
	H ₂ /CO	H ₂ /CH ₄	H ₂ /N ₂	
Polyaramide	100	> 200	> 200	-
Polysulfone	40	80	80	100
Cellulose acetate	30-40	60-80	60-80	200
Polyimides	50	100-200	100-200	80-200

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So you can see this table tells us about the selectivity of various membranes. So, if you see four hydrogen carbon monoxide the polyaramide membrane is gives 100% selectivity whereas the same membrane is giving more than 200% selectivity for hydrogen methane as well as hydrogen nitrogen separation. So, selectivity of polysulfone membrane is actually lower for all these cases where as you can see a polyimides and ploysulfone acetate there fairly good for hydrogen methane as well as hydrogen nitrogen separation.

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- During the production of ammonia from nitrogen and hydrogen, argon enters the high-pressure ammonia reactor as an impurity with the nitrogen stream and methane enters the reactor as an impurity with the hydrogen.
- Ammonia produced in the reactor is removed by condensation, so the argon and methane impurities accumulate until they represent as much as 15% of the gas in the reactor.
- To control the concentration of these components, the reactor must be continuously purged.



This is an example of hydrogen recovery from an ammonia reactor. Let us see how it is being done. So, during the production of ammonia from nitrogen and hydrogen, argon enters the high-pressure ammonia reactor as an impurity with the nitrogen and methane enters the reactor as an impurity with the hydrogen atoms. So, what is happening here so with hydrogen methane is entering with nitrogen argon is entering.

Now they are being pushed to some multi-stage compressors so the three is basically the stream 3 is high-pressure permeate and 4 low-pressure permeate. So, usually, at this pressure, two different multi-stage compressors. So, ammonia is produced in the reactor then it spreads to the ammonia reactor so ammonia is produced in the reactor needs to be removed by condensation so you would get product ammonia here after the condensation.

So the argon and methane impurities they accumulate until they represent as much as 15% of the gas in the reactor then to control the concentration of these components the reactor must be continuously purged. So, when we are purging it we have to take it to a two-stage membrane system where two different gas separation membranes are used and where you are purifying it in the first test so you are getting the low-pressure permeate here the low-pressure permeate.

In the second stage you are getting that a hydrogen-rich permeate that is a high-pressure permeate and you are getting here all sorts of inerts like nitrogen, methane and argon all you are getting in

the permeate side from the second membrane stage and hydrogen is being recirculated so this is how hydrogen is recovered from ammonia reactor, so you are basically enriching hydrogen.

(Refer Slide Time: 27:10)

➤ The hydrogen lost with this purge gas can represent 2-4% of the total hydrogen consumed.

➤ These plants are very large, so recovery of the hydrogen for recycle to the ammonia reactor is economically worthwhile.

	Stream Composition (%)			
	Membrane feed, 1	Membrane vent, 2	High-pressure permeate, 3	Low-Pressure permeate, 4
Hydrogen	62	21	87.3	84.8
Nitrogen	21	44	7.1	8.4
Methane	11	23	36	4.3
Argon	6	13	2	2.5
Pressure (atm)	135	132	70	28
Flow (scfm)	2000	740	830	430

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The hydrogen lost with this purge gas can represent usually 2 to 4% of the total hydrogen consumed these plants are very large so the recovery of hydrogen for recovery to the ammonia reactor is economically worthwhile. So, you can see this is a stream composition membrane feed membrane vent high pressure permeate and low pressure permeate. So, this is actually if you go back and see again so this is 1 this is 2 this is 3 and this is 4.

So you can see the composition how it is varying at different stages so you can get in fair idea that how hydrogen is getting enriched when the low pressure permeate with the high pressure permeate as well as in the low pressure permeate after passing through two membrane stages.

(Refer Slide Time: 27:58)

Production of Nitrogen from Air

- The permeabilities and selectivity of some of the membrane materials that have been used for this gas separation is given below.
- There is a strong inverse relationship between flux and selectivity.
- Membranes with selectivity of 6-7 are found to be economical.

Polymer	Oxygen permeability (Barrer)	Nitrogen permeability (Barrer)	Oxygen/Nitrogen selectivity
Poly(1-trimethylsilyl-1-propyne) (PTMSP)	7600	5400	1.4
Teflon AF 2400	1300	760	1.7
Silicone rubber	600	280	2.2
Poly(4-methyl-1-pentene) (TPX)	30	7.1	4.2
Poly(phenylene oxide) (PPO)	16.8	3.8	4.4
Ethyl cellulose	11.2	3.3	3.4
6FDA-DAF (polyimide)	7.9	1.3	6.2
Polysulfone	1.1	0.18	6.2
Polyaramide	3.1	0.46	6.8
Tetrabromo bis polycarbonate	1.4	0.18	7.5

So, the next example is production of nitrogen from air. So, the permeability and selectivities of some of the membrane materials that have been used for this gas separation is given below. There is a strong inverse relationship between flux and selectivity membranes with selectivity of 6 to 7 are found to be economical. So, you can see from here so you can go for a polyamide or polysulfur or polyamide membranes to have a better flux as well a higher selectivity.

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- This selectivity/permeability trade-off is very apparent in the plot of selectivity as a function of oxygen permeability.

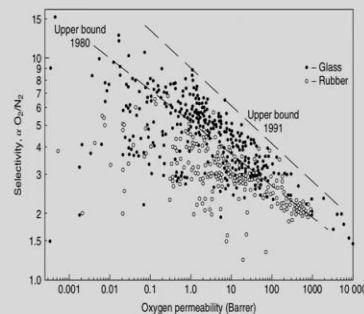
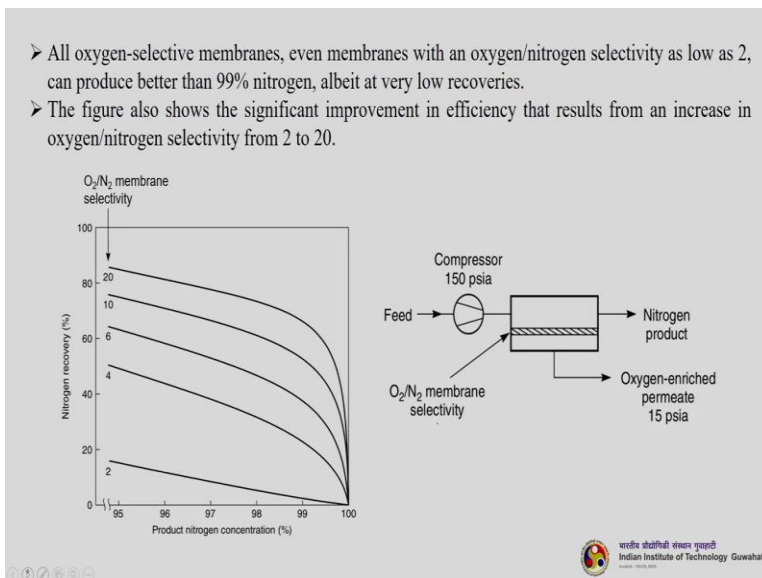


Figure. Oxygen/nitrogen selectivity as a function of oxygen permeability

So, the selectivity and permeability trade off is very apparent in the plot of selectivity as a function of oxygen permeability. You can see this, this is the selectivity of oxygen nitrogen here it is oxygen permeability given in barrer so you can see this is for the glassy polymers and whereas the rubbery polymers are represented here you can see there is a trade-off between these

two different class of membrane materials whether it is glassy and rubbery. So, the selectivity is better for the glassy materials and little low for the rubbery materials.

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And all oxygen selective membranes even membranes with oxygen nitrogen selectivity as low as 2 can produce better than 99% nitrogen. So, albeit at very low recovery the recovery will be low because of the low selectivity but purity will be very high. So, this figure particularly which you can see a nitrogen recovery versus product nitrogen concentration at different oxygen nitrogen membrane selectivity.

As you can see the selectivity increases you have recovery increases oxygen nitrogen selectivity about 2 you can see the almost you can get a 99% pure also however the recovery is very less you can see that recovery is less than 20%. So, you increase the selectivity your purity as well as recovery both increases.

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Separation of Natural Gas

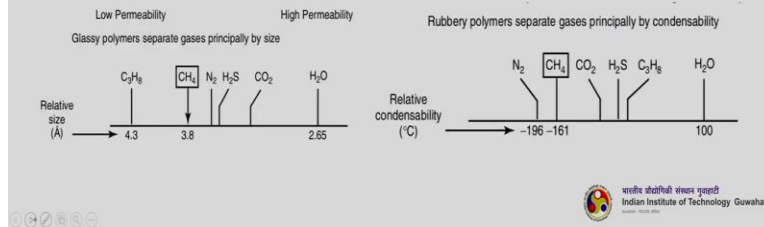
- Natural gas is usually produced from the well and transported to the gas processing plant.
- Natural gas contains methane, ethane, some propane and butane, and 1-3% of other higher hydrocarbons.
- Raw natural gas varies substantially in composition from source to source.
- In addition, the gas contains undesirable impurities: water, carbon dioxide, nitrogen and hydrogen sulfide.
- Water is small and condensable, it is easily separated from methane by both rubbery and glassy polymer membranes.
- Both rubbery and glassy membranes can also separate carbon dioxide and hydrogen sulfide from natural gas.

So, now the next example separation of natural gas, so natural gas is usually produced from the well and transported to the gas processing plant natural gas contains methane ethane some propane and butane and about 1 to 3% of other hydrocarbons. Here own natural gas varies substantially in composition from source to source. In addition the gas contains undesirable impurities so they are water carbon dioxide nitrogen and hydrogen sulfide provided what is the source of the natural gas actually so hydrogen sulfide presence varies.

So water is small and condensable and it is easily separated from within by both rubbery and glass polymeric membranes so not an issue at all. And both robbery and glassy membranes can separate carbon dioxide and hydrogen sulfide from natural gas.

(Refer Slide Time: 30:31)

- However, in practice carbon dioxide is best separated by glassy membranes, whereas hydrogen sulfide, which is larger and more condensable than carbon dioxide, is best separated by rubbery membranes.
- Nitrogen can be separated from methane by glassy membranes, but the difference in size is small, so the separations achieved are small.
- Finally, propane and other hydrocarbons, because of their condensability, are best separated from methane with rubbery sorption-selective membranes.



So, however in practice carbon monoxide is best separated by glass membranes whereas hydrogen sulfide which is larger and more condensable than carbon dioxide is best separated by a rubbery membranes. Now a nitrogen can be separated from methane by glassy membrane you can see this is a glassy polymers and this is rubbery polymers. So, the glassy polymers separate usually mechanism of separation is size separation of sieving mechanism whereas in rubbery polymers it is the separation is happening by the condensed ability factor.

The differences in incompressibility, so nitrogen can also be separated by methane by glassy membranes but the difference in size is very small so the separation which will get or achieved is very small. So, finally propane and other hydrocarbons because of their condensability are best separated from within with a rubbery substance selection membrane. So, you can see this methane sulfide carbon dioxide everything is being including this one year methane also will be removed using a rubbery polymer far, far better than using a glassy polymer okay.

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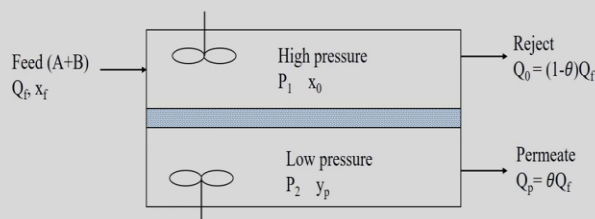
Table. Membrane materials and selectivities for separation of impurities from natural gas under normal operating conditions

Component to be permeated	Category of preferred polymer material	Typical polymer used	Typical selectivity over methane
CO ₂	Glass	Cellulose acetate, polyimide	10-20
H ₂ S ₂	Rubber	Ether-amide block copolymer	20-40
N ₂	Glass	Polyimide, perfluoro polymers	2-3
H ₂ O	Rubber or Glass	Many	> 200
Butane	Rubber	Silicone rubber	7-10

So, this table gives an idea about the membrane and materials and selectivities for separation of impurities from natural gas and the normal operating conditions. If we use cellulose acetate polyamide membrane you may get around selectivity is around 10 to 20 ok and etheramide will be will give us 20 to 40 polyamide so the selectivity is around 2 to 3 and there are many rubbery and glass materials are there so mostly you will get around more than 200 selectivity and silicon rubber will also give such a selectivity of 7 to 10 so you can choose depending upon your applications.

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Model for Gas-separation: Complete mixing model



- Q_f is the feed flow rate, Q_o is the reject flow rate and Q_p is the permeate flow rate
- A_m membrane area; l_m membrane area
- P'_A and P'_B permeabilities of A and B
- P_1 high pressure side and P_2 low pressure side
- x_o mole fraction of A in reject; y_p mole fraction of A in permeate

Now let us quickly discuss a small model for the gas separation this is called conflict mixing model please note please have a note on the different notations. So, the feed is a composition of

A and B and the feed flow rate is given by Q_f mole fraction is accept and the pressure inside or upstream side is P_1 and the mole fraction is X_0 pressure in the downstream side which is low is P_2 and the mole fraction is Y_p the reject or retentate mole this one flow rate is Q_r which is $1 - \theta$ into Q_f and permeate is Q_p equals to θ into Q_f .

So m is the membrane area and l_m is the thickness of the membrane thickness. So, P_A dash and P_B dash permeability's of A and B and P_1 is the higher pressure P_2 is the lower pressure so and more flux have already discussed.

(Refer Slide Time: 33:12)

➤ Q_p is the permeate flow rate, the flux of the components A and B through the membrane can be written as;

$$J_A = \frac{Q_p}{A_m} y_p = \frac{P'_A}{l_m} (P_1 x_0 - P_2 y_p)$$

$$J_B = \frac{Q_p}{A_m} (1 - y_p) = \frac{P'_B}{l_m} (P_1 (1 - x_0) - P_2 (1 - y_p))$$

$$\frac{J_A}{J_B} = \frac{\left(\frac{Q_p}{A_m}\right) y_p}{\left(\frac{Q_p}{A_m}\right) (1 - y_p)}$$

$$\frac{y_p}{1 - y_p} = \frac{\frac{P'_A}{P'_B} \left[x_0 - \left(\frac{P_2}{P_1}\right) y_p \right]}{(1 - x_0) - \left(\frac{P_2}{P_1}\right) (1 - y_p)}$$

Separation factor, $\alpha = \frac{P'_A}{P'_B}$



So, Q_p is the permeate flow rate the flux of the components A and B through the membrane we can write is there in terms of the flux J_A equals to Q_p by m into Y_p which is P_A dash by l_m into $P_1 X_0 - P_2 Y_p$ so similarly we can write for J_B also the flux up B also Q_p by A_m so this the flow rate by area into 1 minus the mole fraction of component B in permeate side that can be expressed in terms of X_0 and Y_p so if you do J_A by J_B so you would get this equation and we can write in terms of mole fraction we will get this equation. So the separation factor is given by Prime by P_A by P_B prime which is alpha.

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- To calculate membrane area, it is required to construct material balance equation for the complete mixing module.

$$\text{Overall material balance } Q_f = Q_o + Q_p$$

- We define a term stage-cut or fraction as: $\theta = \frac{Q_p}{Q_f}$

$$\text{Again, } \frac{Q_o}{Q_f} = 1 - \theta$$

- Now making a component material balance for A:

$$Q_f x_f = Q_o x_o + Q_p y_p$$

$$x_o = \frac{Q_f x_f - Q_p y_p}{Q_o} \quad y_p = \frac{x_f - x_o(1 - \theta)}{\theta}$$

To calculate the membrane area it is required to construct material balance equation for complete mixing module you can see what is Q_o actually here so Q_o is the reject flow rate and Q_p is the permeate flow rate so equals to the reject flow rate and the permeate flow rate so we can define a term which is called stage cut or fraction which is this θ is Q_p by Q_f , so again we can write Q_o by Q_f equals to $1 - \theta$. So, now making a component material balance for component for A so $Q_f x_f$ equals to $Q_o x_o + Q_p y_p$.

So you can write x_o like this from this particular equation and y_p from this particular equation something like this so you get the mole fractions basically.

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- Permeation rate of A at study state can be written as:

$$Q_p y_p = (\text{flux})(\text{area})$$

$$Q_p y_p = A_m \frac{P'_A}{l_m} (P_1 x_o - P_2 y_p)$$

$$\text{Substitute } Q_p = \theta Q_f$$

$$A_m = \frac{\theta Q_f y_p}{\left(\frac{P'_A}{l_m}\right) (P_1 x_o - P_2 y_p)}$$

Similarly for component B also it can be found out.

So, permeation rate of A at a steady state can be written as $Q_p \text{ into } Y_p$ equals to flux into area so you can write $Q_p \text{ } Y_p$ equals to area is A_m into flux is this so substituting Q_p equals to θ into a Q_f so you can write membrane area is $\theta Q_f Y_p$ divided by $P \text{ dash } A \text{ by } l_m$ into $P_1 \text{ } X_0 - P_2 \text{ } Y_p$ similarly for component B also it can be found out. So, this is how you will find out the membrane area are using this completely mixing model consider some.

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Gas Separation Problem

Q1: A membrane module for separation of a binary gas mixture with a partial recycle of permeate stream uses silicone-polycarbonate copolymer membrane to separate 150 m³ (STP) of air per hour to produce a permeate stream containing 30% oxygen. The stage-cut is 30% and 50% of the permeate is to be recycled into the feed stream. Permeability of N₂ in the 1*10⁻⁵ cm thick dense layer of the membrane is 40 barrer. The ideal separation factor is 5. The feed side pressure is 50 bar; that on the permeate side is 10 bar. Calculate the membrane area. Both the feed and permeate sides are well mixed.



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Now let us see a small numerical based on this particular membrane I am just reading out that text for the this one, so for the problem a membrane module for separation of a binary gas mixture with a partial recycle of permeate stream uses silicon polycarbonate copolymer membrane to separate 150 meter cube of air per hour to produce a permeate stream containing 30% oxygen so the stage cut the θ is given as 30% and 50% of the permit is to be recycled to the feed stream.

Permeability of nitrogen is given and in that 10, 1 into 10 to power of -5 centimeter thick dense layer of the membrane is 40 barrer so here l_m easier also given the ideal separation factor is also given as 5, feed side pressure is 50 bar and that on the permeate side pressure is 10 bar. So, you have been asked to calculate the membrane area. So, it is assumed that both feed and permeate sides are well mixed.

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$$\begin{aligned}
 Q_f &= 150 \text{ m}^3/\text{h} \\
 y_{PA} &= 0.3, \quad \theta = 0.5, \quad P_1 = 50 \text{ bar} \\
 P_2/P_1 &= 0.2
 \end{aligned}$$

O.M.B $Q_f = Q_0 + (1 - \xi) Q_p$, $\xi = \text{fraction of permeate stream}$

component A balance $Q_f x_{Af} = Q_0 x_{A0} + (1 - \xi) Q_p y_{PA}$

$$\theta = \frac{Q_p}{Q_p + \xi Q_p}$$

$$Q_p = \frac{0.3 \times 150}{1 - (0.3 \times 0.5)} = 52.94$$


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So let us now solve it so let us try to write down whatever it is being given so you know Q_f is given 150 meter cube per hour then here y_{PA} is 0.3 your θ equals to 0.5 P_1 equals to 50 bar P_2 by P_1 equals to 0.2 so if you take overall material balance so you can write Q_f equals to Q_0 plus $(1 - \xi) Q_p$ so here this ξ is fraction of permeate stream.

So component balance $Q_f x_{Af}$ equals to $Q_0 x_{A0}$ then here a plus 1 minus this ξ into $Q_p y_{PA}$ so $y_{PA} \theta$ you know θ equals to Q_p divided by $Q_p + \xi Q_p$ or Q_p equals to if you calculate Q_p it is 0.3 into 150 divided by $1 - 0.3 \times 0.5$ which is nothing but 52.94.

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$$\frac{y_P}{1 - y_P} = \frac{\frac{P_A'}{P_B} \left[n_0 - \left(\frac{P_2}{P_1} \right) y_P \right]}{(1 - n_0) - \left(\frac{P_2}{P_1} \right) (1 - y_P)}$$

$$\Rightarrow n_{0A} = 0.101$$

permeability of O_2 , $P_A' = \alpha P_B'$

$$\begin{aligned}
 &= 5 \times 40 \\
 &= 200 \text{ Bar}
 \end{aligned}$$


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So, P_2 by P_1 is also given so you can write Y_p into $1 - Y_p$ so please substitute that equation so it is P_A from the model equation which we have just discussed P_B into X_0 into $-P_2$ by P_1 and into Y_p so this whole divided by $1 - X_0 - P_2$ by P_1 into $1 - Y_p$ ok so here alpha is given separation factor is given as 5 simply substitute here all the values and you will get X_0 equals to 0.101. So, permeability of oxygen that is P_A dash is alpha P_B dash which is alpha is given as the separation factor is given as 0.5 and in case this is 40 so it is 200 barrer.

(Refer Slide Time: 39:28)

Handwritten derivation of membrane area A_m :

$$Q_p Y_p = \text{Flux} \times \text{Area}$$

$$A_m = \frac{Q_p Y_p}{(P_A' / l_m) (P_1 X_0 - P_2 Y_p)}$$

$$= \frac{\left(\frac{53 \times 10^{-6}}{3600} \right) (0.3 \times 10^{-5})}{200 \times 10^{-8} \left[(0.101 \times 50) - (0.3 \times 5) \right] \frac{76}{1.013}}$$

$$A_m = 82.5 \text{ cm}^2$$

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So we can find out this $Q_p Y_p$ equals to flux into area or A_m we can directly also write so it is $Q_p Y_p$ divided by this one P_A dash by l_m , l_m is the membrane thickness then $P_1 X_0 - P_2 Y_p$ so please substitute all these things and I think you will get this one so let me anyway write it so it is 53 into 10 power of -6 divided by 3600 hour to second conversion into 0.3 into 10 to the power of -5 whole divided by 200 into 10 to the power of -8 then it is 0.101 that is $P_1 X_0$ net and into 50 - 0.3 into 5 divided by 76 divided by 1.013.

So, anyway you substitute all these things you will get eighty two point five centimeter square so the membrane area which you will get is 82.5 centimeter square so this is how you can design and membrane for your gas separation of a particular application using this mixing complete mixing model from where you can find out your area of the membrane that is required to achieve a given separation.

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Text/References

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So with this I conclude today's lecture so mostly it is taken from Becker and little from other books also so please refer and read in case you have any query do feel free to write to me at kmohanty@iit.ac.in. In our next lecture we will discuss about membrane distillation this is a very interesting topic. So, we will discuss about the dismembered in this lesson its principle how it happens the mechanism the mass transfer and in different applications of membrane distillation so thank you very much.