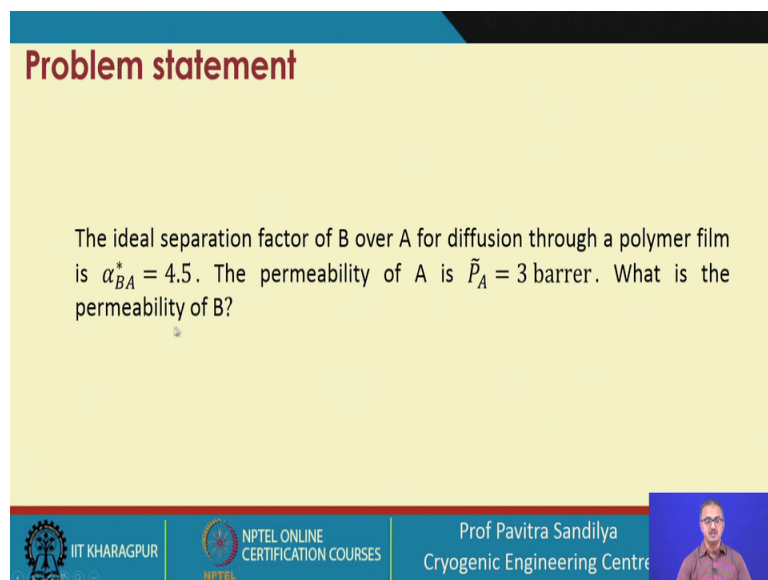


**Upstream LNG Technology**  
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**Lecture – 40**  
**Tutorial on membrane gas separation**

Welcome, after learning about some fundamentals about the membrane gas separation in the natural gas systems, now we shall be looking into some of the applications of these fundamentals to solve the real life problems in the membrane gas separation.

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**Problem statement**

The ideal separation factor of B over A for diffusion through a polymer film is  $\alpha_{BA}^* = 4.5$ . The permeability of A is  $\tilde{P}_A = 3$  barrer. What is the permeability of B?

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Which is first is the, first problem in this problem we have to separate 2 components A and B. And we are given the ideal separation factor alpha BA, as 4.5. The permeability of the component a is given as 3 barrer and we have been asked to determine the permeability of component B.

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**Solution**

Given:

$$\alpha_{BA}^* = 4.5$$
$$\tilde{P}_A = 3 \text{ barrer}$$

To Find:

$$\tilde{P}_B$$
$$\alpha_{BA}^* = \frac{\tilde{P}_B}{\tilde{P}_A}$$
$$\tilde{P}_B = \tilde{P}_A \times \alpha_{BA}^*$$
$$\tilde{P}_B = 3 \times 4.5 = 13.5 \text{ barrer}$$

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So, here we have that we first write what data are given to us, and then we write what we need to find out; then we go to the definition of the ideal separation factor, in this case alpha b a star and this is the ratio of the permeabilities. And then we find that PB is equal to PA tilde into alpha BA star, and then from this we find the permeability of component B as 13.5 barrer. So, this is a very simple problem in which, we find that how to determine the permeability of a component from the permeability of another component and the value of the ideal separation factor.

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**Problem statement**

Carbon dioxide is separated from a mixture of 10% CO<sub>2</sub>(A) and 90% CH<sub>4</sub> (B) using a membrane at 35°C and 10 atm total pressure. An asymmetric polysulphone membrane of 1 micron skin layer thickness is used. The permeate side is continuously swept with nitrogen gas.

Determine

- CO<sub>2</sub> flux through the membrane
- Average diffusivity of CO<sub>2</sub> in polysulphone and
- Permeance of CH<sub>4</sub> in polysulphone.

(Permeation of the sweep gas (N<sub>2</sub>) through the membrane may be neglected.)

Given : Ideal separation factor CO<sub>2</sub> of CH<sub>4</sub> over ( $\alpha_{AB}^*$ ) = 22  
Henry's law constant for solubility of CO<sub>2</sub> at 35°C in polysulphone ( $S_A$ ) = 2.1 cm<sup>3</sup>(STP)/(cm<sup>3</sup>)(atm)  
Permeability of CO<sub>2</sub> ( $\tilde{P}_A$ ) = 5.6 barrer

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Next we come to this problem, in this problem we have been given that carbon dioxide is to be separated from a mixture of 10 percent carbon dioxide and 90 percent methane, using a membrane at 35 degree centigrade and 10 atmosphere total pressure. In this we are using a asymmetric polysulphone membrane, with my one-micron skin layer thickness.

And the permeate side is continuously swept with nitrogen gas so that; there is no accumulation of the permeate gas on the permeate side, because if there is a accumulation of the permeate gas, what will happen? That it will reduce their driving force by increasing it is partial pressure. So, the nitrogen is used so that; their partial pressure of the particular component in this case carbon dioxide can be kept minimum.

So, that is how we are sweeping the permeate side with nitrogen gas, and we are asked to determine the carbon dioxide flux through the membrane. The average diffusivity of carbon dioxide in polysulphone and the Permeance of methane in the polysulphone and these are the data given to us and we have been asked that, we can neglect the permeation of the nitrogen through the membrane, because if nitrogen also permeates the membrane it will change the driving force, it will change the resistance to the mass transfer.

So, in this case we are neglecting the permeation of the nitrogen through the membrane. So, we have to use this particular data ideal separation factor carbon dioxide 2 CH 4 is 22, then henrys law constant is given here and this is the permeability of carbon dioxide.

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### Solution

Given:  
 $\alpha_{AB}^* = 22$   
 $S_A = 2.1 \text{ cm}^3(\text{STP})/(\text{cm}^3)(\text{atm})$   
 $\bar{P}_A = 5.6 \text{ barrer}$   
 $l_m = 0.15 \text{ }\mu\text{m} = 1 \times 10^{-4} \text{ cm}$   
 To Find:  
 $J_A, D_A, \bar{P}_B$

(a)  $J_A = \frac{\bar{P}_A(p_{A1} - p_{A2})}{l_m}$   
 $p_{A1} = 0.1 \times 10 \text{ atm} = 1 \text{ atm}$   
 $p_{A2} = 0$

Substituting these values in the equation we get,  




$$J_A = \frac{5.6 \times 10^{-10} \frac{\text{cm}^3(\text{STP})\text{cm}}{(\text{cm}^2)(\text{s})(\text{cmHg})} (76\text{cmHg} - 0)}{1 \times 10^{-4} \text{ cm}}$$

$$= 4.26 \times 10^{-4} \text{ cm}^3(\text{STP})/(\text{cm}^2 \cdot \text{s})$$

$$= 1.9 \times 10^{-4} \text{ gmol}/\text{m}^2 \cdot \text{s}$$

(b)  $\bar{P}_A = S_A \times D_A = 5.6 \times 10^{-10} \frac{\text{cm}^3(\text{STP})\text{cm}}{(\text{cm}^2)(\text{s})(\text{cmHg})} D_A = 2.1 \frac{\text{cm}^3(\text{STP})}{\text{cm}^2(\text{atm})} D_A$   
 $D_A = 2.02 \times 10^{-8} \text{ cm}^2/\text{s}$

(c)  $\alpha_{AB}^* = 22 = \bar{P}_A/\bar{P}_B$   
 $\bar{P}_B = \bar{P}_A/22 = 5.6/22 = 0.254 \text{ barrer}$   
 $\bar{P}_B = \bar{P}_B/l_m = 0.254 \times 10^{-10}/10^{-4}$   
 $= 2.54 \times 10^{-7} \text{ cm}^3(\text{STP})/(\text{cm}^2 \cdot \text{s})(\text{cmHg})$

Now, for solution what we first do? We list out all the data given to us the value of the ideal separation factor. Then this SA then PA and this thickness of the membrane and we have to find out these values the flux diffusivity and the permeance. First for the flux we write this equation, in this equation we need to know the partial pressures so on the detected side the partial pressure is given by the product of the mole fraction and the total pressure and that is coming to 1 atmosphere.

And as we learnt earlier that, when the composition is in given terms is in given in terms of some fraction if there is nothing mentioned for gas we assume it to be mole fraction or the volume fraction. So, that is why we are taking this point one as the 0.1 as the mole fraction, and on the permeate side because of the nitrogen swept we are assuming that there is no accumulation of the gas on the permeate side. So, the partial pressure is almost kept to 0.

So, with these values, what we do we? Plug in the values in this expression for the flux and after plugging in we find this is the value of the flux, please mind it that use the appropriate units. So, when you are starting to solve these problems initially, always write their units so that; you do not commit any mistake in getting the final result. So, after that we find this is the value of the flux.

Next we come to this value of the permeance, which is nothing but the SA into DA and this we have taking the values of a SA and BA. And we find that this is the value we get

and we permeance value has been given to us 5.6 barrer, and from this a diffusivity is found to be  $2.02 \times 10^{-8}$  cm<sup>2</sup>/s. So, this is a diffusivity value of the component CO<sub>2</sub> through the membrane.

Next we come to the ideal separation factor, which is given as the ratio of the permeabilities or permeance. This is given as 22 and so from here we find the value of this may for component B the permeability comes to about 0.254 barrer. And once we get this value we get the permeance like this; that we put this value of  $\tilde{P}_B$  and divided by the thickness of the membrane and this is the result for the permeance we get for the component B. So, we can see that how this particular problem can be solved to find out the flux, the diffusivity and the permeance of the various solutes.

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**Problem statement (effect of membrane defect)**

An asymmetric polysulphone gas separation membrane has a skin thickness of  $l_m = 0.15 \mu\text{m}$ . Since it has pinholes, a Polydimethylsiloxane (PDMS) coating of thickness  $l_c = 0.3 \mu\text{m}$  is applied on it. The coating also fills the pinholes. The cross section of the pinholes occupies a fraction  $\zeta = 5 \times 10^{-6}$  of the membrane surface. Oxygen enriched air is to be prepared using this membrane. Permeability of the oxygen(A) and Nitrogen(B) in the membrane material are  $\tilde{P}_{mA} = 1.2$  and  $\tilde{P}_{mB} = 0.19$ ; those in the coating are  $\tilde{P}_{cA} = 781$  and  $\tilde{P}_{cB} = 351$  (all in barrer). Determine

- the overall permeability and
- the ideal separation factor of O<sub>2</sub> in the composite membrane.

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Next we come to a problem which is very common in the membrane, and in this case we have taken a problem, which tries to analyze that what would be the effect of any kind of defects like in terms of the pinhole on the membrane. So, here we have the problem, we are again considering some asymmetric polysulphone gas separation membrane with a skin thickness of about 0.15 micron.

And there is a pinhole, now what happens in the pinhole; we to cover the pinhole against some other kind of polymer is used and one of them is polydimethylsiloxane, and this is in short called PDMS. So, this particular polymer is coated on the skin to cover up the

pinhole and this particular coating will also have its own thickness that is about 0.3 micron.

Now, because this thickness is more than the thickness of the particular membrane, so, this particular coating will also offer its resistance to the mass flux, but we have to do it to save the membrane so that; we do not have to go for a new membrane. So, for some initially we may use such kind of coating to cover up any kind of pinhole. The coating also fills the pinhole and, and then what we find? That the cross section of the pinhole occupies about that this 5 into 10 to the power minus 6 of the membrane surface that is, this zeta represents; the ratio of the cross section area of the pinhole to the cross section area of the actual membrane surface.

Now, we have Oxygen enriched air to be prepared, and what we are doing that we have oxygen Nitrogen mixture, oxygen is represented by A and nitrogen by B, and we have all these value of the permeability is given here, and we are also given this on the for the coating we are given. So, this represents the permeabilities through the membrane, this m represents membrane and these are the probabilities to the coating c represent the coating. And all in the barrier these are spelling mistake here this is in barrer. So, we have to determine the overall permeability and the ideal separation factor of oxygen in the composite membrane.

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The slide illustrates the structure and resistance of a composite membrane. At the top left, a cross-section shows a PDMS layer, a pinhole, and a skin. Below this, a circuit diagram shows a resistor  $R_c$  in series with a parallel combination of two resistors,  $R_{c,m}$  and  $R_m$ . The text 'Series ( $R_c$  &  $R_{eq}$ )' and 'Parallel ( $R_{eq}$ )' is placed above the circuit. To the right, another circuit diagram shows a resistor  $R_m$  in series with a parallel combination of two resistors,  $R_{c,m}$  and  $R_m$ . At the bottom left, a schematic of the composite membrane shows a top layer of thickness  $l_c$  and a bottom layer of thickness  $l_m$ . The bottom layer contains a pinhole. The slide is part of an NPTEL lecture from IIT Kharagpur.

So, here we are representing in the pictorially, how it is looks like; that here we have this membrane and on this we have the skin, the skin is represented by these black things. So, there and these hollow things the white ones are the pinholes, and to prevent the pinholes what we are doing we are using this PDMS layer.

So, what we find that whenever their permission is occurring, one permissions is occurring through this and one is occurring through this. Now in this case what if we just magnify this thing, we find their different the resistances are coming into picture one resistance is due to the resistance through the particular PDMS coating, and one resistance is coming through the membrane and this particular pinhole.

Now, as we learned that the, this PDMS coating is also filling up the pinhole. So, whenever the solute is passing, this particular region and this is a pinhole region and the membrane region through this the flux is occurring in parallel whereas, through these 2 parallel resistances are in series with the resistance through the particular coating.

So, if we draw an electrical analogy to this, we find that there is this coating resistance which is the  $R_C$  and then we have the parallel resistances, one through the membrane and one through the coating which is in the membrane side. So, that is this  $R_{cm}$  represents resistance offered by the coating material on the membrane side, and these particular resistance and the membrane resistance they are in parallel and these 2 resistances are in series with the resistance through the coating. So, that is how we draw this diagram on electrical analogy.

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**Solution**

Given:

$$l_c = 3 \times 10^{-7} \text{ m}$$

$$l_m = 1.5 \times 10^{-7} \text{ m}$$

$$\zeta = 5 \times 10^{-6}$$

$$1 - \zeta = 1$$

To Find:

$$\tilde{P}_A \quad \tilde{P}_B \quad \alpha_{AB}^*$$

(a)

$$\hat{R}_A = \frac{l_c}{\tilde{P}_{cA}} + \frac{1}{\frac{(1-\zeta)\tilde{P}_{mA}}{l_m} + \frac{\zeta\tilde{P}_{cA}}{l_m}} = \frac{l_c}{\tilde{P}_{cA}} + \frac{l_m}{(1-\zeta)\tilde{P}_{mA} + \zeta\tilde{P}_{cA}}$$

$$\hat{R}_A = \frac{3 \times 10^{-7}}{781 \times 10^{-10}} + \frac{1.5 \times 10^{-7}}{(1.2 \times 10^{-10}) + (5 \times 10^{-6})(781 \times 10^{-10})} = 1.25 \times 10^3 (\text{cm}^2 \cdot \text{s}) / (\text{cmHg}) / \text{cm}^3$$

$$\hat{R}_B = \frac{l_c}{\tilde{P}_{cB}} + \frac{1}{\frac{(1-\zeta)\tilde{P}_{mB}}{l_m} + \frac{\zeta\tilde{P}_{cB}}{l_m}} = \frac{l_c}{\tilde{P}_{cB}} + \frac{l_m}{(1-\zeta)\tilde{P}_{mB} + \zeta\tilde{P}_{cB}}$$


$$\hat{R}_B = 7.74 \times 10^3 (\text{cm}^2 \cdot \text{s}) / (\text{cmHg}) / \text{cm}^3$$

$$\tilde{P}_A = \frac{l_m + l_c}{\hat{R}_A} = \frac{(0.3 + 0.15)10^{-6}}{1.25 \times 10^3} = 3.6 \times 10^{-10} = 3.6 \text{ barrer}$$


$$\tilde{P}_B = \frac{l_m + l_c}{\hat{R}_B} = 0.581 \text{ barrer}$$

(b)

$$\alpha_{AB}^* = \frac{\tilde{P}_A}{\tilde{P}_B} = \frac{\hat{R}_B}{\hat{R}_A} = \frac{7.74 \times 10^3}{1.25 \times 10^3} = 6.2$$




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Now, what we do that; we put all these values which are given to us. And we find that the 1 by zeta is 1; that means, zeta represents the fraction of the coating and 1 by zeta represents the fraction the membrane, we find the value is so small that we can assume that almost even, with in the presence of the pinhole almost every surface of the membrane is occupied by the membrane. And we have to find out this the permeability values and the ideal separation factor.

Now, in this case what we do we go by the calculation of the resistances. So, as per our figure we find these are the resistances through the coating and the membrane together, and these are resistance through the coating. So, this resistance is in series with these 2 resistances these are parallel resistances, and we just do the mathematical rearrangement to get this particular equation.

After getting this equation we have put the various values given in the problem to get the resistance here. And then we find the resistance through the for the another component B, this is component A and this is component B that is oxygen nitrogen. And here we have the values of these permeances from these resistance values, and this is the value of for nitro oxygen this is for the nitrogen.

So, that is how we find the permeabilities of these 2 components from the given data. And what we find here that; this oxygen is passing at a much higher rate than nitrogen by looking at this data.



Next we come to find the ideal separation factor, and we find that by taking the ratios of the permeabilities or the inverse of ratios of the resistances, we find that this is the value of the ideal separation factor. This shows that this particular membrane is selectively separating oxygen by letting oxygen to pass through it, while by retaining the nitrogen over it. So, that is how we are able to take care of the pinhole in our analysis of the membrane separation.

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**References**

- Dutta BK. Principles of Mass Transfer and Separation Processes. PHI Learning Pvt. Ltd. 2007 .
- Seader JD. and Henley EJ. Separation Process Principles. John Wiley & Sons, Inc. 1998.

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Further details may be found from these 2 references.

Thank you.