

Membrane Technology
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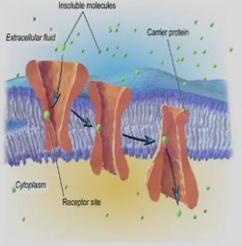
Lecture-34
Mechanism, Coupled Transport, Carrier Agent, Active and Passive Transport,
Applications

Good morning students this is lecture 34 under module 12 as you know this is the last module and we have three lectures in this and today's lecture is dedicated to facilitate transport to understand what is the mechanism of facilitated transport, what is a carrier, what are the different types of carriers available and what is active and passive transport and a few applications. So, let us now understand what is actually facilitated transport means.

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Facilitated Transport

- Facilitated membrane transport is a process where a carrier agent interact specifically with a substrate in the feed mixture and the substance-carrier complex diffuses across the membrane.
- Also known as 'carrier-mediated' transport.
- The carrier dissociates at the end of the membrane, and finally returns to its original position.
- The exterior substrate concentration has no effect on the rate of transport.
- Usually, a carrier with high association and dissociation rate constants, which are similar in magnitude, is desirable.



Facilitated transport

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So it is a membrane transport process where there is a carrier agent which interacts specifically with the substance in the feed substrate in the feed and the substance carrier complex diffuses across the membrane. As you can see in this particular figure this is a facilitated transport mechanism so this is also known as a carrier mediated transport because there is a carrier inside the membrane which is actually binding to the substance or a substrate or the solute which we want to separate through the membrane.

And then takes it across through the membrane and finally dispose it up at the permeate side. So, the carrier dissociates at the end of the membrane and finally returns to its original position the exterior substrate concentration has no effect on the rate of transport. Usually a carrier with high association in dissociation rate constants which are similar in magnitude is desirable. So, if I just try to draw something let us say a small example.

Let us say this is the membrane this is the membrane and there is a solute X which I want to transport through the membrane using this carrier mediated transport and there is a carrier which is inside this membrane. Now what will happen in this particular mechanism this solute this solute will bind to the carrier, so this is carrier Delta is carrier which is inside the membrane. So, the solute will come and sit here on the surface of the membrane and that is the interface of the membrane and the aqueous medium then it will bind this.

So once it binds it becomes a complex right then it moves to the opposite the membrane on the perimeter side once it comes here by virtue of the; here a concentration difference of the solute which you want to transport here it will dissociate itself so X comes to the permeate side and that carrier becomes free. Now again carrier is being recycled so this is how the facilitated transport or carrier mediated transport happens.

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Facilitated Transport

- For the transport to be selective, the membrane is permeable to the flow of certain substances and impermeable to the flow of others including the carrier molecule.
- Substances such as amino acids, organic acids, NaOH, NaCl, carbon dioxide, oxygen, metals, and various ions, such as Cd(II), Cu(II), Co(II), and Fe(III), can be separated by using suitable carrier agents in liquid or solid composite membranes.

Facilitated Transport in Liquid Membranes

Covatta: Vapor Density, Membrane Transport, Nonequilibrium Thermodynamics (Third Edition), (2014), 433-434

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Established: 1958

So we will understand the mechanism and the other aspects in detail further transport to be selective the membrane is permeable to the flow of certain substances and impermeable to the flow of others including carrier molecule. The carrier should be in such a way that its association and dissociation rate should be very high for the solutes and it should remain inside the membrane it should not come out in out of the membrane.

So substances such as amino acids organic acids sodium hydroxide sodium chloride carbon dioxide oxygen metals and various ions such as cadmium copper cobalt and iron can be separated by using suitable carrier agents in liquid or solid composite membranes. So, this is an example of a facilitated transport in a liquid membrane is very easy to impregnate carrier molecules inside the liquid membranes because in that liquid membranes are always so if you recall the liquid membrane structure.

So let us say this is pores this is another part so the pore is already filled with the liquid membrane. So, you can impregnate your carriers here in a very easy way it can be done so you can see how it is happening here so the carriers this is the carrier which is impregnated inside the membrane liquid membrane this is a membrane this is the membrane phase this entirely the solute that is going to be separated is coming to the liquid and this is the liquid membrane and the bulk interface you can say the feed interface.

Then it is crossing the membrane and it is getting bound to the carrier. So, you can see this is a carrier and substance this one your solute complex now by virtue of the concentration difference here so this carrier complex moves across the membrane one way here this reaches here this side receiving feed side so your solute will be getting dissociated and your carrier again gets back or it get gets renewed basically right so this is how this happens well the this facility transport happens.

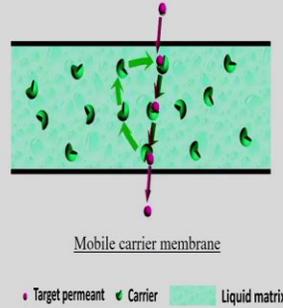
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Facilitated Transport Membranes

Three types:

(i) *Mobile Carrier Membrane*

- The carrier can diffuse freely through the membrane.
- Usually liquid membranes.
- The major ingredient is often carrier solution or carrier-bearing liquid compounds, such as ionic liquid.
- The carrier serves as a “ferryboat” plying between the two sides of membrane.



Courtesy: Yifan Li et al., Chem.Soc.Rev., 2015,44,109–118

So are three types of facilitated transport membranes are available so first one is mobile carrier membrane. So, here the carrier can diffuse freely through the membrane you can see here how it actually looks like so this is the membrane actually right so this is the liquid matrix in the case of the pores filled with liquids. This is your carrier and this is what easier target permeant or you can say the solute right.

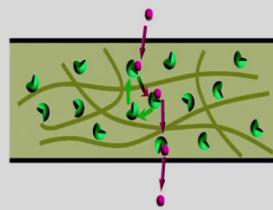
So usually this type of membranes are liquid membranes so the major ingredient is open carrier solution or carrier bearing liquid compounds such as ionic liquids so ionic liquids are a class of green solvents which are very famous for their various excellent properties or you can say that fine and tunable properties we can prepare a particular ionic liquid to suit a target or operate a particular application.

So the carrier here serves as a ferryboat plying between the two sets of the membrane. so, it is just moving here and there you can see this carrier is moving here again then it moves back to the other side after releasing the permeate.

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(ii) *Semi-mobile Carrier Membrane*

- Usually are solid-state membranes of which polymer materials are often utilized as the hosting matrix.
- The mobility of carrier lies in between a mobile carrier and a fixed-site carrier.
- The carrier can migrate elsewhere at a cost of high diffusional activation energy.



Semi-mobile carrier membrane

● Target permeant ● Carrier — Polymer chain
■ Polymer matrix

Courtesy: Yifan Li et al., Chem.Soc.Rev., 2015, 44, 103–118



So, this is one the second one is semi mobile carrier membrane. So, here it is the membrane is a polymeric membrane you can see this is the polymer chains these are polymer since this is your carrier and this is again your permeate or you can say the solute. So, these are solid-state polymeric membranes of which are you upon here or utilize as the hosting matrix that mostly polymeric membranes.

So, the mobility of carrier lies in between a mobile carrier and a fixed side carrier. The carrier can migrate elsewhere at a cost of high diffusional activation energy. So, the next one is fixed side carrier membrane so here also again the membrane is a polymer matrix you can see the polymer chains here these are your career this is the solute or permeate. So, usually solid state membranes carrier can only vibrate within a confined nano space rather than my creative's because you can see here the carrier is fixed to the polymeric matrix.

You can see it is fixed you can see something like this the structure, so this is fixing structure right. So, the target molecular ion passes through the membrane by carrier to carrier hoping. So, this mechanism is called hopping mechanism we can let us say how it will happen. So, let us say this it comes here the solute. Now it comes here and binds here right once it binded after some time and then it hops again here then it hops again here then it comes in get dissociated in the opposite side. So basically it is a hopping mechanism that takes place in a fixed site carrier membrane.

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Facilitated Transport Mechanism

- If 'A' is a species moves through the membrane and 'C' is the carrier species, 'C' reversibly react or bind with 'A' in the feed side of the membrane to form the permeate-carrier complex 'CA'.
- The complex 'CA' diffuses through the membrane, reaches the permeate side where it decomposes and releases the permeant 'A'.

Membrane

Feed side Permeate side

CA CA

A + C A + C

Facilitated Transport of 'A'

Courtesy: B. K. Dutta, Mass Transfer and Separation Processes, PHEI, 2007

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So let us understand the mechanism how the facilitated transport actually happens. So, let us take an example of a species A which moves through the membrane and see is the carrier species. So, A is the solute which you want to remove or transport using the membrane and C is the carrier. Now what is happening to see is reversibly reactor bind with A in the feed side of the membrane to form a permeate carrier complex.

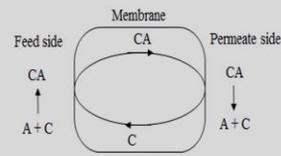
So this is the membrane and this is the membrane feed interface so here this reaction is happening so $A + C$ is giving CA, so CA is your it is a intermediate complex right so then this moves across the membrane in this direction because of the concentration gradient you can say. So, once it reaches the permeate side now it releases and this reaction happens so CA because it will give you A and C.

So A is written here and C is a recycled back to the membrane. So, the complex CA diffuses through the membrane reaches the permeate side where it decomposes and releases the permeate A.

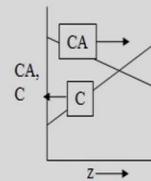
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Facilitated Transport Mechanism

- The carrier 'C' gets freed and diffuses back to the feed side where it again binds to a fresh permeant 'A'.
- 'C' acts as a 'shuttle' within the membrane.
- The concentration of 'CA' decreases across the membrane; that of the carrier has a concentration gradient in the opposite direction.
- Both 'CA' and 'C' diffuses across the membrane under their respective concentration driving force.



Facilitated Transport of 'A'



Concentration distribution

Courtesy: B. K. Datta, Mass Transfer and Separation Processes, PHI, 2007



So the carrier C gets freed and diffuses back to the feed side where it again binds to permeant A, so CA has a subtle within the membrane so it is settling only C, C is free inside the membrane matrix so it is shuttling between the feed side and the permeate side so the component CA decreases across the membrane under the outer carrier and that of the carrier is a concentration gradient in the opposite direction.

You can see that CA is this is the gradient here this is CA it is decreasing and this one with respect to across the thickness of the membrane you can say whereas the carrier is in the concentration profile or gradient is in the opposite direction. So, both CA and C diffuses across the membrane under their respective concentration driving force.

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Facilitated Transport Mechanism

- The polymer matrix can also contain a functional group that act as a carrier called as 'fixed' carrier.
- For this case, the solute transport occurs by a 'hopping mechanism', very similar to that of surface diffusion.
- Facilitated transport is much faster than passive transport because of the higher effective solubility of the CA complex in the membrane.

So, the polymer matrix can also contain a functional group that act as a carrier called as a fixed carrier right. We have just discussed about a fixed carrier membrane so for this case the solute transport occurs by hopping mechanism very similar to that of a surface diffusion facilitated transport is much more faster than passive transport because of the higher effective solubility of the CA complex in the membrane.

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Facilitated Transport Mechanism

- If the fluid in the permeate side contain another species 'B' that relieves 'A' from the complex 'CA', the flux of 'CA' further increases by this phenomenon.
- The complex 'BA' does not diffuse through the membrane.
- The phenomenon can be expressed as:



- The species 'A' is recovered by decomposing the complex 'BA' leaving from the permeate unit.
- 'B' is again recycled to the permeate-side fluid.
- The concentration of 'A' in the form of 'BA' in the permeate side may be higher than that of feed side.
- For such cases, the facilitated transport of 'A' occurs against its 'apparent' concentration gradient.

So, if the fluid in the permeate side contents another species B so we had just discussed previously about one component and the feed contains only one solute that is let us say which we discussed a solute A it is binding to C The carrier and it is getting associated then the complex

passes through the membrane matrix then dissociated itself in the permeate side. Let us now understand that if there is a component B another solute which is present in the permeate side.

Then what will happen, that releases A from the complex CA the flux CA further increases by this phenomena that means what is happening the complex BA does not diffuse through the membrane though B and A is forming a complex it is not diffusing back to the membrane. So, you can see that the X and feed side is basically $A + C$ is giving AC then this complex is moving through the membrane then once it reaches the permeate side.

So this complex AC plus is reacting $AC + B$ is giving $BA + C$, so but BA is not diffusing back but the C is again recharged or renewed so it is free now to bind with another solute of A. So, the species A is recovered by decomposing the complex BA living from the permeate unit B is again recycle to the permeate side fluid. So, the concentration of A in the form of BA in the permeate side may be higher than that of the feed side.

For such cases facilitate transport of A of course against a temperate concentration gradient however we do not have to provide any extra energy for this to happen.

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Three important characteristics of facilitated transport are:

- 1) Solute's flux is larger and more selective.
- 2) At low solute concentration, the flux varies linearly with solute concentrations, however, reaches a limiting value and gets saturated at high solute concentration.
- 3) Flux of one solute may be easily poisoned by another solute or may be strongly influenced by the gradient of another solute.



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So, let us understand the three important characteristics of facilitated transporter. The first important thing is that solute flux so solute flux would be larger and it should be highly selective

or more selective. Second is that at what happens at low solute concentration usually the flux varies linearly with solute concentration. However once it reaches a very high solute concentration and it gets saturated after reaching a limiting value. So, third one is that flux of one solute may easily be poisoned by another solute or may be strongly influenced by the gradient of another solute.

So these are the three things that need to be considered while we designed some facilitated membrane system.

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Facilitated Transport Applications

Facilitated transport of oxygen through the lungs membrane

- The carrier hemoglobin binds to the permeant oxygen to form oxy-hemoglobin complex.
- The presence of hemoglobin significantly increases the solubility of oxygen and boost its rate of transport through the membrane.

Facilitated transport of oxygen by hemoglobin

$O_2 + \text{hemoglobin} \rightleftharpoons \text{Oxy-hemoglobin (complex)}$

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So let us understand few application some real-life applications like this facilitated transport of oxygen through the lungs of the membrane. You know the hemoglobin the carrier is the hemoglobin here it binds to the permeate oxygen to form oxyhemoglobin complex. Now this oxyhemoglobin complex it diffuses through the membrane and once it reaches the permeate side it will release the oxygen to the opposite side and again it is free now to bind to another molecule of oxygen.

So the presence of hemoglobin significantly increases the solubility of oxygen and boost its rate of transport through the membrane. So, increasing the solubility of oxygen in the presence of oxygen is something very important so this is how it happens actually the oxygen is getting transported inside the cells.

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Separation of olefin from a gas mixture by Ag^+ as carrier:

- Ag^+ reversibly binds to the olefin

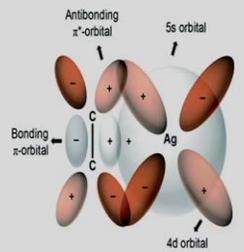
Feed side (higher pressure): $Ag^+ + \text{olefin} \rightarrow Ag^+-\text{olefin}$

- The silver-olefin complex diffuse to the permeate side (lower pressure) and decomposes there to release the olefin.

Permeate side (lower pressure):

$$Ag^+-\text{olefin} \rightarrow Ag^+ + \text{olefin}$$

- The regenerated Ag^+ diffuses back to the feed side through the pore membrane filled with a solution of silver salt.



Schematic illustration of the π complexation bond formed between olefin and $Ag(i)$.

Courtesy: Junjun Hou et al., J Membr Sci, 2010, 348-355

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Another example is it is a chemical industry example separation of olefin from a gas mixture by silver as carrier using silver as carrier. So, silver reversibly binds to olefin so you can see the reaction so silver plus olefin gives a silver olefin complex. Now the silver olefin complex diffuse to the permeate side which is present in the lower pressure and decomposes there to release the olefin. So, in the permeate side what is happening that complex is again dissociates to silver and olefin.

Now the regenerated metal silver diffuses back to the feed side through the pore membrane filled with a solution of silver salt. So, this is the schematic illustration of how the PI complex is unbound from between olefin and silver. So, you can see how this reaction is happening it is not a reaction basically you can say the bonding between silver and olefin.

Another example is separation of carbon dioxide from air by amine functional group carrier. Now carbon dioxide capture has become a global concern due to the anthropogenically forced carbon emission and climate change 2 mole of polyethyleneamine absorb one mole of carbon dioxide so this is the membrane basically or membrane material you can say. So, by using PI numerous NH functional groups which are already present in the membrane matrix it reacts with carbon dioxide to form carbonate or bicarbonate under humid conditions.

So humid condition is the necessary requirement so carbonate will be hydrolyzed by water to degenerated amine on the opposite side you can see how it is happening so this is the schematic of carbon dioxide and nitrogen transport mechanism in a PI facilitated transport membrane. So, you can see the dashed lines these lines so it is actually the pathway for nitrogen gases. So, the nitrogen is getting transported whatever amount which is much lesser than that of the carbon dioxide of course.

And the mechanism for this transport is solution diffusion whereas carbon dioxide is getting transported through the facilitated transport by combining or by binding with the NH groups already present in the membrane. So, one it says here the carbon dioxide will be will dissociate from the NH groups and amine will be regenerated.

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Possible reactions of CO₂ with PEI

$$2RNH_2 + CO_2 \rightarrow RNHCOO^- + RNH_3^+$$

$$RNHCOO^- + H_2O \rightarrow RNH_2 + HCO_3^-$$

$$2R_2NH + CO_2 \rightarrow R_2NCOO^- + R_2NH_2^+$$

$$R_2NCOO^- + H_2O \rightarrow R_2NH + HCO_3^-$$

$$R_3N + H_2O \rightarrow R_3NH^+ + OH^-$$

$$CO_2 + OH^- \rightarrow HCO_3^-$$

● CO₂ → CO₂ pathway
● N₂ - - - N₂ pathway

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So these are the various reactions you can just go through later on and see understand what are the different reactions that is going through when carbon dioxide is getting transported through the membrane using a facilitator mechanism right. So, now let us understand what is coupled transport?

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Coupled Transport

- It resembles facilitated transport except that a complex BC forms on the downstream surface of the membrane by reaction with a species present on the permeate side liquid.
- A kind of active transport across a biological membrane in which a transporter protein couples the movement of an ion (typically Na^+ or H^+) down its electrochemical gradient to the uphill movement of another molecule or ion against a concentration/electrochemical gradient.
- Energy stored in the electrochemical gradient of an ion is used to drive the transport of another solute against a concentration or electrochemical gradient.
- The free energy needed to perform active transport is provided by the concentration gradient of the driving ion.

Course: Physiology



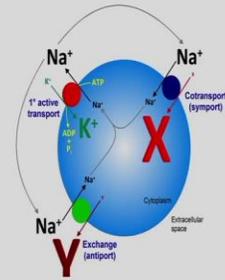
So coupled transport resembles facilitated transport except that a complex BC forms on the downstream surface of the membrane by reaction with a species present on the permeate side liquid. Now kind of active transport across a biological membrane in which the transporter protein couples the movement of an ion usually or you can say typically sodium or hydrogen down its electrochemical gradient to appeal the movement of another molecule or ion against a concentration or electrochemical gradient.

So energy stored in the electrochemical gradient of an ion is used to drive the transport of another solute against a concentration or electrochemical gradient. The free energy needed to perform active transport is provided by the concentration gradient of the driving ion.

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Coupled Transport

- Sodium is the driving ion for many cotransporters and exchanger.
- These transport proteins may also be referred to as sodium-coupled co-transporters.
- **Na⁺/glucose co-transporter**, found in the small intestine and kidney proximal tubules, simultaneously transports 2 Na⁺ ions and 1 glucose molecule into the cell across the plasma membrane.
- In exchange, the driving ion and driven ion/molecule move in opposite directions.
- For example, the **Na⁺/Ca²⁺ exchanger**, found in cardiac muscle cells and elsewhere in the body, transports 3 Na⁺ ions into the cell in exchange for 1 Ca²⁺ ion transported out of the cell.



Coupled transport or secondary active transport. X and Y represent transporter substrates.

Country: Physiolgym



So, sodium is the driving ion for many core transporters and exchangers these transport proteins may also be referred to as sodium coupled Co transporters. So, this is a classic example of a coupled transport or secondary active transport here you can see that there is a these X and Y's. X and Y here so X and Y represent transporter substrates that is getting transported. So, an example is sodium plus glucose co transporter found in small intestine and kidney proximal tubules simultaneously transports two sodium ions and one glucose molecule into the cell across the plasma membrane.

So this is how it happens you can see here how it is happening by different mechanism one is called antiport another is called symport this antiport and this symport this we will discuss at the end up our today's lecture. So, here you can see that sodium is binding and then getting transported inside the cytoplasm and here sodium is again binding to the X and getting transported to the cytoplasm and here sodium and potassium.

So the sodium is coming out of the cytoplasm whereas potassium is getting inside the cytoplasm by supply of certain energy in the form of certain energy so it can be ATP or it is ADP right. So, another example is Na⁺ and Ca²⁺ exchanger cation and calcium exchangers. So, found in cardiac muscle cells and elsewhere in the body transport three sodium ions into the cell in exchange for one calcium ion and transported out of the cell.

So that means what is happening in this; in the exchanger mechanism of sodium and calcium. So, sodium is getting inside the muscle cells cardiac muscle cells whereas calcium is getting out of the muscle cells. So, let us now understand the couple transport mechanism.

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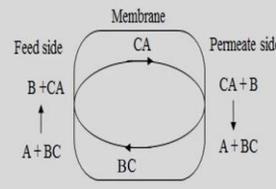
Coupled Transport Mechanism

- In coupled transport, a species 'B' present in the downstream side of the membrane form a complex 'BC' by reacting with the complex 'CA' present in the permeate side.

Permeate side: $CA + B \rightarrow BC + A$

- 'BC' diffuses through the membrane and reaches the upstream surface, where it react with the species 'A'.
- By this process the complex 'CA' is formed on the upstream side that diffuses through the membrane to permeate side.

Feed side: $A + BC \rightarrow AC + B$



Coupled transport of A and B

Courtesy: B. K. Datta, Mass Transfer and Separation Processes, PSE, 2007

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So, in copper transport SPC's be present in the downstream side of the membrane form a complex BC by reacting with the complex A present in the permeate side so you can see that A + BC this is the reaction A + BC is giving you B + CA so the CA is getting transported across this membrane in this side across the length of the membrane then once it comes to the permeate side CA is binding to B which is already present in the permeate side thereby releasing A and forming another complex BC.

Now this BC is moving in the opposite direction so this is called couple mechanism. So, BC diffuses through the membrane and this is the upstream surface where it again reacts to the surface species A by forming a complex CA and releasing B this is how it happens so what is happening here so the transport of A is happening here transport of B is happening this side. So, in the by this process the complex CA is formed on the upstream side that diffuses through the membrane to the permeate side so A + B, BC giving AC + B.

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- The species 'CA' and 'BC' diffuses through the membrane in opposite direction.
- In overall, the species 'A' travels from the feed side to the permeate side and species 'B' travels from the permeate side to the feed side, because of which the phenomenon is called coupled transport.

Coupled transport of A and B

Concentration distribution


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The species CA and BC diffuses through the membrane in opposite direction overall the species A travels from the feed side to the permeate side and species B travels from the permeate side to the feed side because of which the phenomenon is called the coupled transport. So, it is a coupling effect basically so the concentration of CA is the gradient is in this side and concentration of BC is gradient is in this side so that is why it is moving BC is moving in this side this, this direction and CA is moving in this direction.

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Coupled Transport Applications

Copper recovery from waste liquor using microporous membrane:

- The membrane used is microporous polypropylene of Hoechst-Celanese called 'Celgard' impregnated with a solution of LIX-64.
- LIX-64 contains an oxime dissolved in an organic medium immiscible with water.
- On the feed side (pH 2.5), the oxime (carrier) forms a complex $\text{Cu}^{++} \cdot \text{oxime}$ by binding with Cu^{++} .

Feed side: $\text{Cu}^{++} + \text{oxime} \cdot \text{H}^+ \rightarrow \text{Cu}^{++} \cdot \text{oxime} + \text{H}^+$

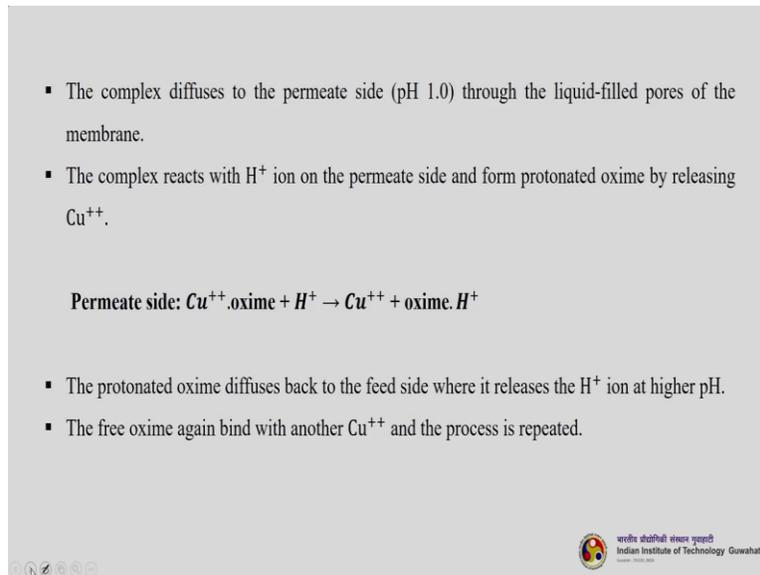

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So, now a few applications the first one is copper recovery from waste liquor using a microporous membrane. So, the membrane used in this particular replication is a microporous polypropylene of Hoechst Celanese membrane called Celgard impregnated with the solution up

LIX 64, so celgard is the membrane LIX 64 is the carrier. So, LIX 64 contains an enzyme dissolved in an organic medium immiscible with water so oxime is the carrier.

So in the feed side where the pH is maintained is 2.5 the oxime that is the carrier from some complex see you covered oxime complex by Cu^{++} binding with copper. So the copper two-plus and oxime H^+ is binding to a giving you copper oxime complex plus hydrogen.

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- The complex diffuses to the permeate side (pH 1.0) through the liquid-filled pores of the membrane.
- The complex reacts with H^+ ion on the permeate side and form protonated oxime by releasing Cu^{++} .

Permeate side: $\text{Cu}^{++}.\text{oxime} + \text{H}^+ \rightarrow \text{Cu}^{++} + \text{oxime}.\text{H}^+$

- The protonated oxime diffuses back to the feed side where it releases the H^+ ion at higher pH.
- The free oxime again bind with another Cu^{++} and the process is repeated.

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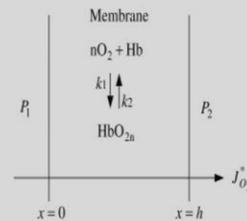
So, the complex diffuses to the permeate side where the permeate pH is maintained is 1 through the liquid filled pores of the membrane the complex reacts with hydrogen ion on the permeate side and form protonated oxime by releasing the copper so the copper oxime complex plus proton or hydrogen which will give you the copper as well as oxygen hydrogen complex which will again diffuse back. The protonated oxime diffuses back to the feed side where it releases the hydrogen ion at the higher pH.

The free oxime again bind with another copper and the process is repeated and it is get it is continued.

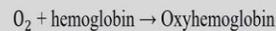
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Carrier Agent

- In facilitated transport in membranes, a carrier agent interacts specifically with a substrate in the feed mixture and form a substance-carrier complex.
- The complex diffuses across the membrane, and the carrier dissociates at the end of the membrane, and finally returns to its original position.
- Example: A red blood cell membrane transports oxygen with the hemoglobin as the carrier.



Facilitated transport of oxygen by hemoglobin



Now a carrier is not so carrier since this is a facilitated or carrier mediated transport so carrier what is a carrier, how to choose a carrier and what are the properties of carrier this plays a very important role. So, in facilitated transport in membranes interact specifically with a substrate in the feed mixture and form a substance carrier complex. Now this complex diffuses across the membrane and the carrier dissociates at the end of the membrane and finally returns to its original position.

So just to have discussed again oxygen transport through the cells oxygen in the presence of hemoglobin, so oxygen plus hemoglobin is from any oxyhemoglobin complex this complex diffuses through the membrane this is the complex right. And then it releases oxygen here and the hemoglobin is back to business right.

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Carrier Agent

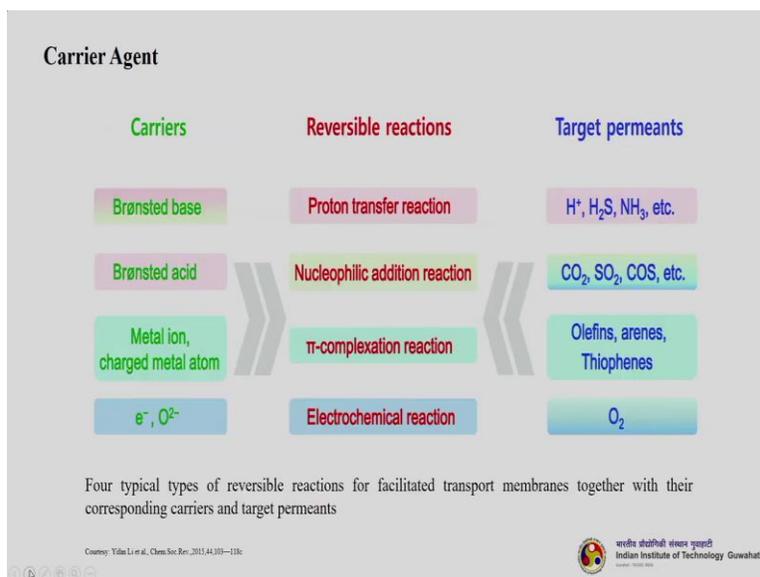
- The carriers are basically classified based on several specific target permeants, e.g. O_2 , CO_2 , olefin, and sugar, etc.
- Four basic types of reversible reactions includes are:
 - 1) proton transfer reaction,
 - 2) nucleophilic addition reaction,
 - 3) π -complexation reaction and
 - 4) electrochemical reaction
- Carriers and the corresponding target permeants are therefore closely connected with reversible reactions as the ligament.

Courtesy: Yilin Li et al., Chem Soc Rev, 2015, 44, 103–116



So, the carriers are basically classified based on several specific target permeants as for example whether it is carrying oxygen it is a oxygen permeate carrier or the carbon dioxide transporter or carrier olefin sugar etcetera four basic types of reversible reactions happens so those are proton transfer reaction nucleophilic addition reaction, pi complexes and reaction an electrochemical reaction. Now carriers and the corresponding target permeates have therefore closely connected with reversible reactions and the ligament.

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So these are four types of four typical types of reversible reactions which is listed here right for facilitated transport membranes together with their corresponding carriers and target permeates. So, in a proton transfer reaction a bronsted base is the carriers then target permeates can be

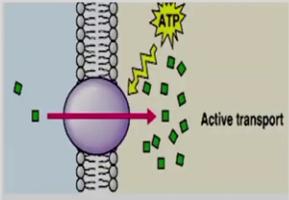
hydrogen, hydrogen sulfide, ammonia etcetera. In a nucleophilic addition reaction a bronsted acid is the carrier then carbon dioxide, sulfur dioxide, COS etcetera can be permeants can be transported.

So if in case of a PI complexes in reaction metal ion or charged metal atoms are basically their carriers so olefins, arene's, thiophenes etcetera are the permeance. So, in case of electrochemical reaction so this oxygen 2 minus are electron they are the carriers and usually the oxygen is the permeants.

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Active Transport

- Active transport, also known as uphill transport is a process of transporting molecules from a low-concentration region to a high-concentration region.
- Active transport must couple to another spontaneous process to transport substrates against their thermodynamic forces.
- It is a very important process for biological systems.
- Various artificial membranes are used for the active transport of substrates.



Courtesy: Yusef Demirel, Membrane Transport, Nonequilibrium Thermodynamics (Third Edition), (2014), 43-44

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So, let us now understand what is active transport? Now active transport also known as uphill transport is a process of transporting molecules from a low concentration to a high concentration regime. So, active transport must coupled to another spontaneous process to transport substrates against their thermodynamic forces it is a very important process for most of the biological systems various artificial membranes are used for the active transport of substances.

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- Since the process is not spontaneous, an sufficient amount of input energy is required so that active transport can happen.

- Examples:

- 1) Transport of Na^+ and K^+ ions through the cell membrane of red blood cells (RBCs) against their respective concentration gradients.

- 2) Transport of glucose from blood (lower concentration) to liver cells (higher concentration).

- 3) Transport of minerals in soils (lower concentration) to the root tissues of the plants.

- The mechanism of such transport is very complex.

- The mechanism may be resemble to the pumping of a liquid by squeezing the silicon tubing of the peristaltic pump by its rollers.

- Energy required for such transport is supplied by ATP (Adenosine triphosphate).



Since the process is not spontaneous and sufficient amount of input energy is required so that active transport can happen. Now there are a few examples I have just listed down so the first one is transport of sodium and potassium ions to the cell membrane of the red blood cells against their respective concentration gradients. The second is transport of glucose from blood so usually it is in the large concentrations blood to that to the liver cells where glucose is already presented in higher concentration.

So it is against the concentration gradient. The transport of minerals in the soil which is present in the large concentration to that of the root tissues of the plants where the minerals are present already in higher concentration again against the concentration gradient. So, the mechanism of such transports are very complex the mechanism may be resemble to the pumping of a liquid by squeezing the silicon tubing of a peristaltic pump by its roller.

So how it happens now in peristaltic pump let us say this is our pedestal take pump okay. The roller so the silicon tubing is coming like this right and then again there is another roller and again so you are pumping here some material so it will come here and again it will the two rollers will be here, so it will squeeze here it is getting squeezed. So, you can see something some structure something like this.

So you know what will happen in this so this is the schematic whatever the flow is getting that is squeezed and it is getting squeezed then it will be expanded. So, basically again it is a throwing mechanism squeezing out squeezing in squeezing it squeezing in squeezing out something like that. So, energy required for such transport is supplied by ATP which is adenosine triphosphate may be ATP, ADP also.

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Active Transport of Cations

- Two types: *Symport* (co-transport) and *Antiport* (exchange)
- The transport proteins responsible for coupled transport are referred as co-transporters (also known as symporters) and exchangers (also known as antiporters).
- In symport, the direction of transport is the same for both the driving ion and driven molecule/ion.
- In antiport, the driving ion and driven ion/molecule are transported in opposite directions.

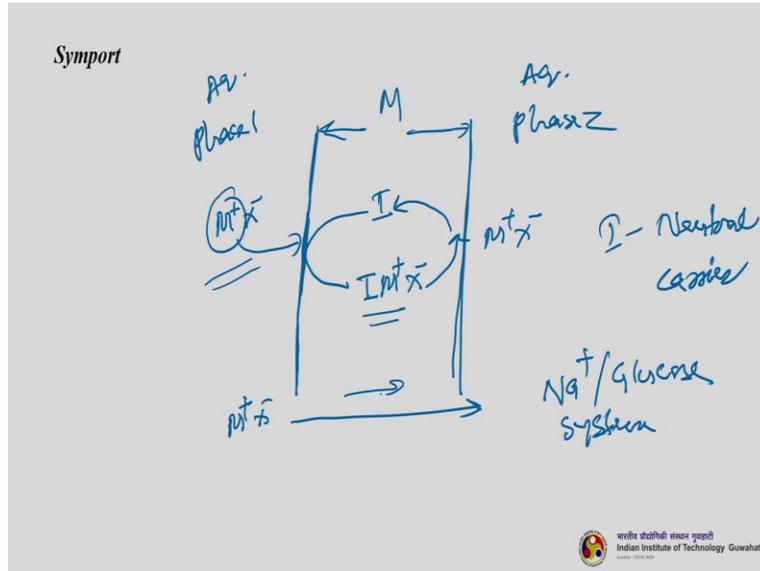
The diagram illustrates two types of active transport proteins embedded in a lipid bilayer membrane. In the top diagram, labeled 'Symport', a yellow protein channel is shown with two particles, A and B, being transported in the same direction (downwards) across the membrane. In the bottom diagram, labeled 'Antiport', a yellow protein channel is shown with particle A being transported upwards and particle B being transported downwards. The IIT Guwahati logo is visible at the bottom right of the slide.

So now let us understand how the cation strands what happens is as I told our you earlier about symport and antiport here we will try to understand actually what is symport and antiport, so two types of mechanism for cation transport one is symport which is also called a core transport another is called antiport which is called exchange there is something called uniport. So, uniport in the case in which one per minute is actually getting transported in a proper in a single direction inside a membrane.

But we will try to understand what is symport and antiport now you can see the basic differentiation in the diagram itself in symport what is happening the transport proteins responsible for copper transport are referred to as core transporters also known as symporters and exchangers also known as antiporter's. So, in symport that direction of transport is the same for both the driving ion and driven molecular ion.

So here both A and B are driving in the same direction but in antiport it is the reverse that is why the name antiport actually that driving ion molecule and driven ion molecule are transported in opposite direction.

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So, we will try to understand actually how symport happens. So, I will try to draw a schematic so let us say this is your membrane right and this is a phase aqueous phase 1 phase 2 here I have a phase 2 we can say aqueous phase of course it is a aqueous phase right. And we will talk about how the cation transport is happening in a symport so initially what will happen so salt plus X minus it will bind it will come to the interface here the phase one the interface of the membrane in aqueous phase one.

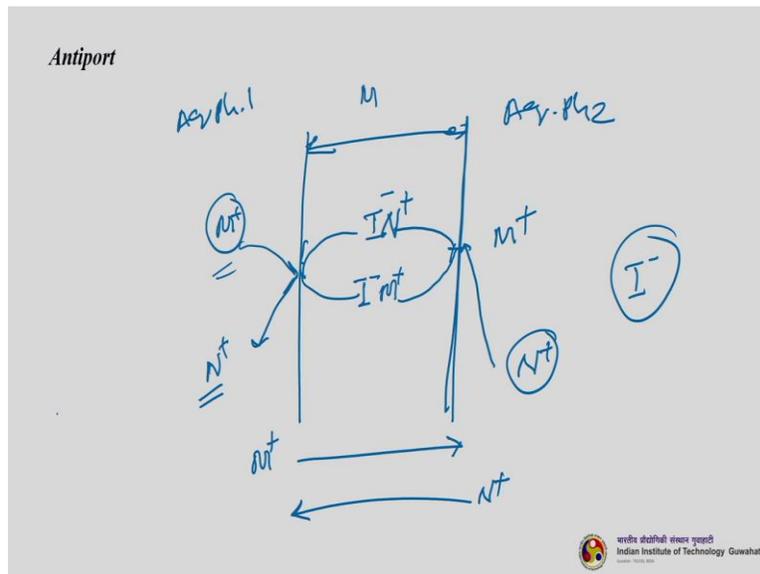
And it is it will complex here right so once it is complex here complex with the carrier basically here we will talk about a carrier which is usually neutral so I is a neutral carrier right. So, what will happen so this I is coming here and it is binding, binding to what binding to M, so now it is forming a complex which is called $IM^+ X^-$ complex. Now once it reaches here right it reaches here to the opposite side of the membrane so the phase 2, so the phase 2 interface it will release the salt $M^+ X^-$ and the I is getting renewed.

So here $M^+ X^-$ both are getting transported in the same direction whereas I is bounding only to the cation. So, this is how it happens in case of here Na plus glucose system. So, your sodium is

bound to one of the carrier protein and along with that glucose is getting transported. So, it is very this one common in most of the cells a human cells animal cells. So, once the carrier leaves the complex sorry releases the salt that side.

So it gets renewed and comes back to the membrane side inside the membrane and again get associate itself with another molecule of the salt form a complex and again the process continues. So, this is in case of symport.

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So in case of antiport let me try to explain again by drawing another image so this is your membrane, so this is aqueous phase 1 this is aqueous 2 so here we can have a negatively charged this one here a carrier, let us say that is negatively charged carrier I minus and there is a salt which this one a cation which I want to transport as when there is a another cation also. We are talking about antiport so in the opposite side.

So what will happen this M it will complex with the I and form a complex I - M + then it moves across the membrane due to the concentration gradient once it reaches the aqueous phase interface 2 here it will release your M plus right and it will bind to this N thereby from another complex called I- N+ complex. Now this I- M+ complex will reach here and it will release here N+, so I hope you will understand how it is happening.

So here M^+ is moving in this direction right whereas N^+ is moving in this direction and please try to remember that they are binding to one particular negatively charged carrier molecule one single type of carrier that is binding to first the cation that is present in the phase one releases it in the opposite side again bind to the cation which is present in the opposite side of the permeate side from the complex brings it back to the upstream side or feed side or aqueous phase one side dissociates again binds to the cation present here this M^+ .

So, here actually it is you can note that so two molecules are transported in opposite direction so and you are using one anionic charged or negatively charged carrier or anionic carrier. So, that is very important if we are talking transport of cations. So, the single cation itself is a single anionic carrier is binding to both the cations and this is how here antiport reactions or transport happens.

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Examples of Active Transport systems

Permeant	Carrier	Membrane
Uranyl ions	2,3-epithiopropyl methacrylate-dodecyl methacrylate-methacrylamide propyl trimethyl ammonium terpolymer	Anion exchange membranes
Na^+ , K^+	Oxidative phosphorylation	Living cell mitochondria
Anion	Reversed bienzyme	Porous membrane
Amino acids: glycine, phenylalanine, lysine	2,3-epithiopropyl methacrylate-2-acrylamide-2-methyl propane sulfonic acid	Cation exchange membranes
d-lactate	(14C)-methylamine, (14C)-thiocyanate	Inverted membrane vesicles of <i>Escherichia coli</i>

Courtesy: Tapan Dasgupta, Membrane Transport, Nonequilibrium Thermodynamics (Third Edition), (2014), 433-484

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Now these are the examples of active transport systems so you can see the permeate carrier and membrane all are given here. So, if you want to talk about Uranyl ions so we will have a carrier this is a big name actually 2,3 epithiopropyl methacrylate dodecyl ok that is a big name actually so and we can have an anion exchange membrane. So, in case of transport of sodium and potassium so oxidative phosphorylation will be the carrier leaving cell mitochondria is the membrane.

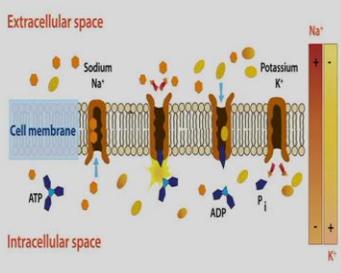
And in case of anions reversed by enzyme is the carrier porous membrane can be the membrane so similarly there are other examples also you can go through it later on right.

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Active Transport Applications

Sodium Potassium Pump

- Exchanges sodium ions for potassium ions across the plasma membrane of animal cells.
- Three Sodium ions bind with the protein pump inside the cell.
- The carrier protein then gets energy from ATP and changes shape.
- In doing so, it pumps the sodium ions out of the cell.
- At that point, two potassium ions from outside the cell bind to the protein pump.
- Potassium ions are then transported into the cell, and the process repeats.



The diagram illustrates the Sodium Potassium Pump mechanism. It shows a cross-section of a cell membrane separating the extracellular space (top) from the intracellular space (bottom). A protein pump is embedded in the membrane. On the intracellular side, three sodium ions (Na+) are shown binding to the pump. Simultaneously, two potassium ions (K+) are shown binding to the pump on the extracellular side. The pump is powered by ATP, which is converted to ADP and inorganic phosphate (Pi). A vertical bar on the right indicates the concentration gradient, with Na+ being higher in the extracellular space and K+ being higher in the intracellular space. The logo of the Indian Institute of Technology Guwahati is visible in the bottom right corner.

So, now understand the active transport applications so sodium potassium pump. Now what is this? This is for real life in real life cells so exchange exchanges what it does actually it exchanges sodium ions for potassium ions across the plasma membrane of animal cells ok right. So, how the mechanism happens actually it is very clear in the this particular image. So, sodium is getting transported in this side right where is here from potassium is getting transported in this side ok.

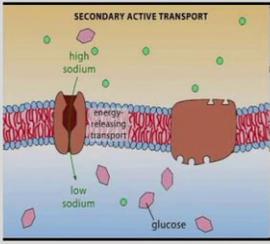
So this is how it is getting transported 3 sodium ions bind with the protein pump inside the cell right then what happens the carrier protein gets energy from ATP and it changes its shape. So, in doing so it pumps the sodium ions out of the cell right. So, here these are the pumps you can call these are the pumps right so at that point 2 potassium ions from outside the cell bound bind to the protein pump. Then potassium ions are then transported into the cell and the process repeats.

So you can; but that again this is something like that this antiport mechanism which we have just discussed that three sodium's are getting exchanged with two potassium ions right. So, the energy that is required for doing this transport it comes usually from the ATP's the adenosine triphosphate or ATP adenosine triphosphate and the P i's.

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Sodium Glucose transport protein

- The protein binds to two sodium ions, which “want” to move into the cell, and one glucose molecule, which “wants” to stay outside of the cell.
- The diffusion of the sodium into the cell allows the glucose to also be carried into the cell without the transport protein expending ATP.
- ATP must be expended by the sodium-potassium pump elsewhere in the cell to keep up the sodium gradient that allows the sodium-glucose transport protein to function.



SECONDARY ACTIVE TRANSPORT

high sodium

low sodium

glucose

energy releasing transport

Courtesy: www.medicalartlib.com/2008

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Source: 2008-2009

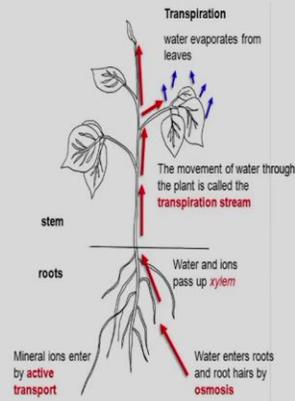
So another example is the sodium glucose transport protein this we have discussed little earlier but just for another time. So, this is a secondary active transport system the protein binds to two sodium ions which want to move into the cell and one glucose molecule which wants to stay outside of the cell. So, the diffusion of the sodium into the cell allows the glucose to also be carried out into the cell without the transport protein expending ATP.

So ATP must be expended by the sodium potassium pump elsewhere in the cell to keep up the sodium gradient that allows the sodium glucose transport protein to function. This would be at the end of sodium otherwise sodium would not at all move so this is how the sodium and glucose transport happens.

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Mineral transport from soil to inside root of plant

- During the active absorption of minerals, ions from the outer space of the cell move into the inner space and it generally occurs against the concentration gradient.
- These move into the roots by using energy in the form of ATP.
- Specific proteins present in the membrane of the root hair cells actively pump ions from the cell to the cytoplasm of the epidermal cells.
- These proteins act as control points for the type and quantity of solutes that reach the xylem.



Courtesy: Agricultural Study Blog



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So, another example which is very classic is of course their mineral transport from soil to inside root of a plant so what is happening here you can see this particular figure actually. So, during the active absorptions of mineral so ions from the outer space of the cell move into the inner space and it generally occurs against the concentration gradient. Now this move into the roots by using energy in the form of ATP specific proteins present in the membrane of the root hair cells actively pump ions from the cell to the cytoplasm of the epidermal cells.

Now these proteins act as a control points for the type and quantity of the solutes quality quantity of the solutes that is the xylem. So, you can see the mineral and center by active transport water enters the roots and root hair by osmosis water and ions pass up through xylem and then transportation and all these things happens.

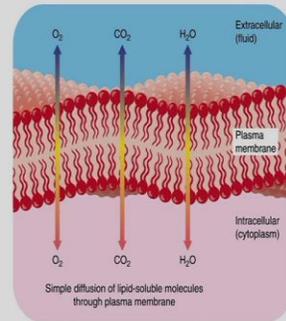
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Passive Transport

- In Passive transport, compounds are able to move freely across the membrane based only on a favorable concentration gradient.
- Requires no energy for transport of compounds.

Three types:

- *Simple diffusion*
- *Facilitated diffusion*
- *Osmosis*



Courtesy: SC-12



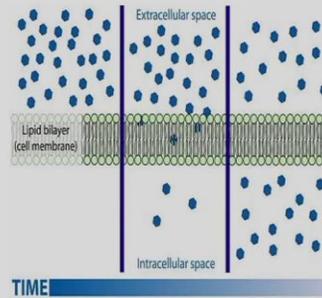
So, now let us understand what is passive transport? Now we have understood what is active transport now let us discuss what is specific as put in passive transport compounds are able to move freely across the membrane based only on a favorable concentration gradient it requires no energy for transport of compounds. So, basically three types simple diffusion facilitated diffusion and osmosis you can see how it is happening here.

So this is simple diffusion of lipid soluble molecules through plasma membranes. So, oxygen is moving in this direction and carbon dioxide is also moving in this direction water is also moving in these direction. So, this is actually in both sides it is happening so this is a simple diffusion mechanism.

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Simple diffusion

- Molecules move from an area of high concentration to an area of low concentration.
- Molecules naturally flow down their concentration gradient.
- Diffusion proceeds without an input of energy.
- Molecules that are small and uncharged can freely diffuse across a cell membrane.
- *Example:* Movement of oxygen from lung cells to blood due to concentration gradient.



Simple diffusion of ions

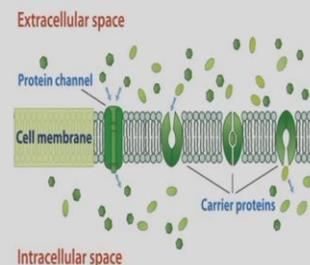
Content: 05-12

So, in simple diffusion the molecules move from an area of high concentration to area low concentration so that is how it is only happening than using the concentration gradient so molecules naturally flow down their concentration gradient diffusion proceeds without an input of energy molecules that are small and uncharged can freely diffuse across the cell membrane. So, one example is movement of oxygen from lung cells to blood due to concentration gradient.

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Facilitated diffusion

- Involve the passive movement of molecules along their concentration gradient, guided by the presence of another molecule – usually an integral membrane protein forming a pore or channel.
- Does not directly involve high-energy molecules like adenosine triphosphate (ATP) or guanosine triphosphate (GTP), since the molecules are moving along their concentration gradient.
- *Example:* sodium ion crosses the membrane through a channel protein specific for sodium ions.



Protein channels and carrier proteins involves in passive transport

Content: 05-12

So the next is facilitated diffusion here it involves the passive movement of molecules along their concentration gradient guided by the presence of another molecule usually an integral membrane protein forming a pore or channel. This is how you can see the pore channel is formation happens right and how it binds to the carrier proteins and then getting transported so it

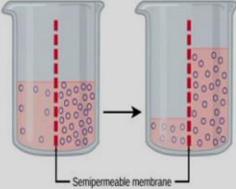
does not directly involve high energy molecules like adenosine triphosphate or guanosine triphosphate GTP.

Since the molecules are moving along their own concentration gradient. So, example is sodium ion crosses the membrane through a channel protein specific part.

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Osmosis

- Diffusion of water through a semipermeable membrane according to the concentration gradient of water across the membrane.
- Only water is transported across a membrane and the membrane limits the diffusion of solutes in the water.
- If water has a concentration gradient in this system it will diffuse down its concentration gradient, crossing the membrane to the side where it is less concentrated.
- Osmosis continue until the concentration gradient of water goes to zero.



Osmosis of water

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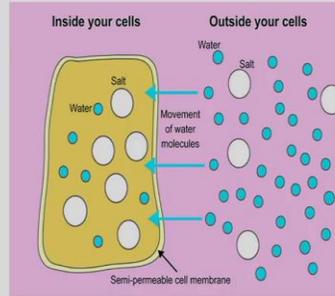
The next is osmosis you know what is osmosis? We have discussed osmosis, reverse osmosis in great details. So, diffusion of water through a semipermeable membrane according to the concentration gradient of water across the membrane only water is transported across the membrane and water limits the diffusion of solute in the water. If water has a concentration gradient in the system it will diffuse down its concentration again crossing the membrane to the side where it is less concentrated.

So osmosis continued and led until the concentration gallon of water goes to zero. This is how your osmosis phase is happening.

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Osmosis: Examples

- Both animal cells and plant cells lose and gain water by osmosis
- Cells gain water through osmosis and recover their salt-water equilibrium.
- Water moves from an area of high concentration (outside the cell), through the cell membrane to an area of low concentration (inside the cell).



Osmosis in animal cell

Courtesy: Osmosgen

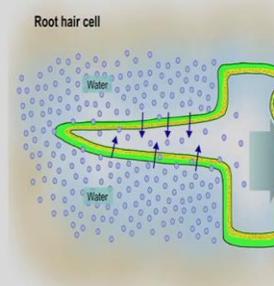
So, I think we will just discuss one example osmosis example, so both the animal cells and plant cells lose and gain water by osmosis. This is how osmosis is very important phenomena for all the living things. So, inside your cells and outside yourselves what is happening you can say it is a semi permeable cell membrane this is the membrane this one and water this is water this is the big one is salt so movement of water molecules is happening from outside of the cell to inside of the cell and along with that of the salt.

So water moves from an area of high concentration that is the outside the cell through the cell membrane to an area of low concentration inside the cell.

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Osmosis: Examples

- Plants rely on osmosis to take in water through their root hair cells.
- These cells have a large surface area that efficiently absorb water and minerals.
- When a plant is watered, the water is absorbed, moves from an area of high concentration (the soil) to an area of low concentration (the root hair cells) before being transported to the rest of the plant.



Osmosis in plant cell

Courtesy: Osmosgen

So, plants rely on osmosis to take in water through their root hair cells these cells have a large surface area to efficiently absorb water and other different types of minerals. So, in a plant protein a plant is water the water is observed moves from an area of high concentration that is soil to an area of low concentration that is the root hair cells before being transported to the rest of the plant. So, this is how osmosis is taking place in root hair cell.

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So I think with this will conclude this today's lecture most of it is being taken from K. Nath book and B.K. Dutta's book and some other this one reports or this one papers from literature so you can refer them later. So, in this I thank you very much in case you have any query please feel free to write to me at kmohanty@iitg.ac.in. Our next lecture that is lecture 35 under module 12 will focus on different types of gas liquid and liquid-liquid contactor devices.

But then I will discuss little about membrane reactor and bioreactors and PEM hydrogen fuel cell. Thank you very much.