BioMEMS and Microfluidics

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Lecture-11

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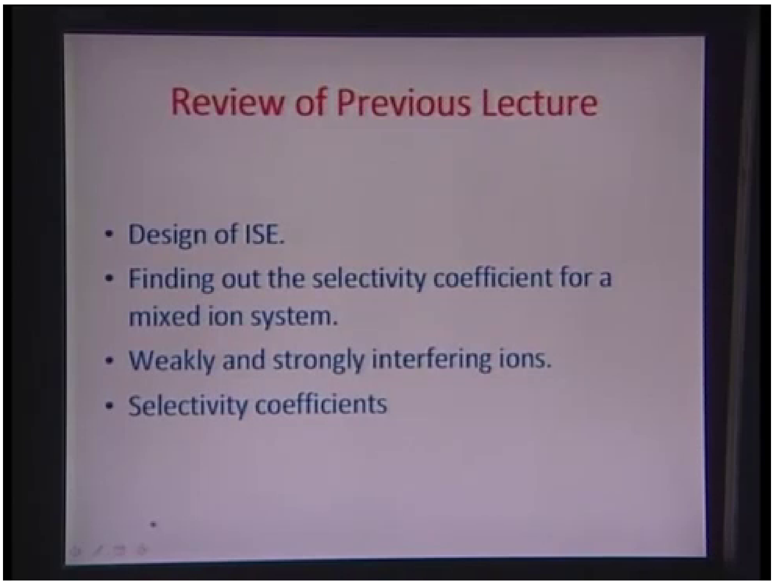

Review of Previous Lecture

- Design of ISE.
- Finding out the selectivity coefficient for a mixed ion system.
- Weakly and strongly interfering ions.
- Selectivity coefficients

Will just like to do a brief review of a, what we covered last time, we talked in details about designing of the ion select electrodes. We also try to find out you know the Debye-Huckel equations and how you know we can be use for solved it ion transport. Basically, we looked at the interaction of a primary ion of interest in an environment of the counter ion cloud. And try to derive something called the activity coefficient, which is also important for determining the participation really off an electrode light of interest of an ion of an interest an electro light over the several other competing ions.

We try to also define, then equal a sky as in many equations, where you know the selectivity of a particular ion of interest over the other interfering ions. And their contribution to the measure EMF worth certain details you know for both the weakly and strongly interfering ions, so we kind of compare how this EMF variation would take place and we try to solve several in might examples to look at you know the different practical aspects of design of such electrodes.

Today, will be starting a new topic on why this sensing protocols are really needed and how this can be used detect some of the analyzed of interest you know as we go by we will finally, converts into something, which is very, very important the area BioMEMS, which is surface driven flows in all these a micro as says. Typically, as discussed in my previous lectures BioMEMS devices to use a lot of microfluidics.

Essentially microfluidics also is defined as a flow of fluids the microscope scale this flows can sometimes be totally driven by charged surfaces this force can be electro-kinetic force, electrostatic force, electroplating force so and so forth. And, so we will make a detailed analyzes of such flows and then, find you apply them to make now will mechanical devices like micro pumps, micro waves, micro mixers etcetera. So, this would reform a small part of the curriculum on this Bio Micro electrode chemical systems.

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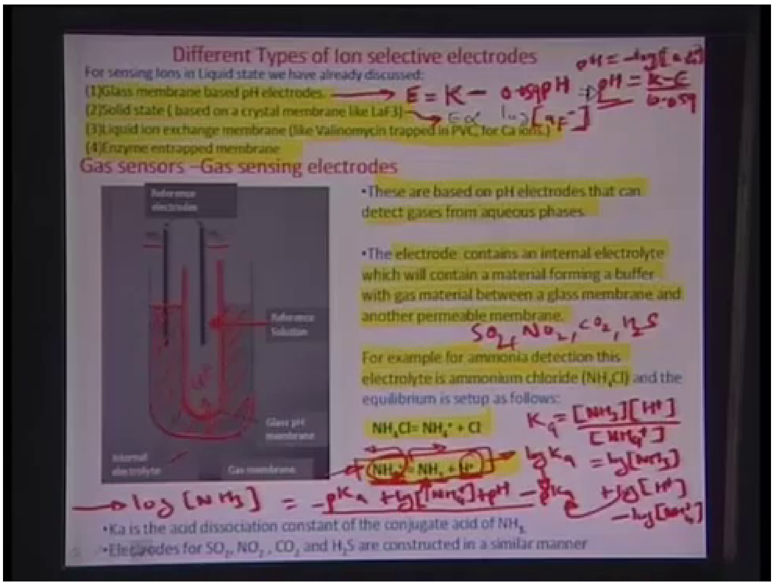

Different Types of Ion selective electrodes

For sensing Ions in Liquid state we have already discussed:

(1)Glass membrane based pH electrodes. → $E = K - 0.059pH \Rightarrow pH = \frac{K-E}{0.059}$

(2)Solid state (based on a crystal membrane like LaF3) →

(3)Liquid ion exchange membrane (like Valinomycin trapped in PVC for Ca ions.)

(4)Enzyme entrapped membrane

Gas sensors –Gas sensing electrodes

- These are based on pH electrodes that can detect gases from aqueous phases.
- The electrode contains an internal electrolyte which will contain a material forming a buffer with gas material between a glass membrane and another permeable membrane.

SO_2, NO_2, CO_2, H_2S

For example for ammonia detection this electrolyte is ammonium chloride (NH_4Cl) and the equilibrium is setup as follows:

$NH_4Cl = NH_4^+ + Cl^-$

$NH_4^+ = NH_3 + H^+$

$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$

$\log K_a = \log[NH_3] + \log[H^+] - \log[NH_4^+]$

$\log[NH_3] = -pK_a + \log[NH_4^+] + pH$

- Ka is the acid dissociation constant of the conjugate acid of NH_3
- Electrodes for SO_2, NO_2, CO_2 and H_2S are constructed in a similar manner

So, let us try to understand why these electrodes are used to design selective electrodes are used for sensing various analyzed of interest. And most of these metabolites of interest are essentially found within the human body and very important go let us to try to design something, which can take up various gases, which are generated and try to identify some an alight of interest metabolite of interest in the human blood on the bases on this measured gasses.

So, let us a look at what we have covered, so for in as regards the very important component of ion selective electrode; that is the membrane. So, we have looked into glass membranes based pH electrodes, we have also looked into solid state based on crystal membranes like Lanthanum fluoride. We have typically also looked into liquid ion exchange membranes like Valinomycin, if you remember this was a reason ten from the extract of a tree was an organic reason.

Also it is found in cell walls and there used as molecules, which furnish the transportation of calcium and potassium ions. And then, we also talked about enzyme entrapped membranes particularly if you remember about the glucose oxidase case we described details how and enzyme entrap membrane can be able to pick up an interest. So, just to did you know of few mathematical details about how pH electrodes are calibrated.

So, essentially if you look at the Nernst equation for such a electrode in the EMF measured by the pH electrode would really be equal to the inter set financial interest, which is K minus of the slope 0.059 mind in this case we talking about hydrogen plus 1. So, you have n equal to 1 here times pH, pH as we know is the negative log of hydrogen ion concentration the negative log of the hydrogen ion activity of the hydrogen ion concentration in extremely high background electrolytes, where there is a huge charge in the background we can consider the activity to be same as the concentration as we remember from before.

So, E is equal to K minus 0.059 pH and pH here can we identify as K minus E by 0.059. So, that is how you can find out the pH in a the case of glass membrane pH electrodes for the crystal membrane electrodes like let say lanthanum fluoride, which detects fluorine ions of fluoride ions as minus the EMF in this case potential metric will be proportional to the logarithmic of logarithm of activity of florid ions. And similar in a similar kind of situation the activity can be the concentration are we can assume the gamma to be equal to 1 in that particular case.

So, let us talk about gas sensors gas sensing electrodes at the outside to kind of know, what is the basic kinetic, which is involve in such electrodes and this would be kind of followed with the detail analysis of why they are required as I pointed out again and again before. So, here in this electrode if you look at you have essentially at glass pH membrane and this is a pH electrode.

So, this right here in this region is the glass pH membrane you also have a gas membrane here especially for dissolving the gasses, which would be measured or which are internet, which measured in pH change we have a reference solution here inside this particular concentrate tube, so this is essentially is a concentrate tube. So, we have separating this tube filling it up with the reference solution or reference electrolyte and this portion here is permeable to only hydrogen ion.

So, this is the, the typically the if my you recall them silicates of group in smells, which are able to select specifically hydrogen ions over the other interfering ions. So, here also we have another reference solution in this particular zone, so you have a solution inside the glass membrane for the hydrogen ions and we have a solution out sided and we have two electrodes here R E1 and R E2, which are both reference electrodes and they would able to sense any transfer of H plus ions into this particular solution here into the internal electrolyte here.

So, essentially you are trying to detect the change in pH and how that is related to the an alight of interest is being reflect here below and the following you know area this light. So, essentially these are based on pH measurement they can detect gases from aqueous phases the electrolyte contains the electrode contains a internal electrolyte, which will contain a material forming a buffer with the gas material between the glass membrane the permeable are the selective membrane.

So, essentially this is the concept of buffering, so you have definitely trying to select something, which would create a buffer material and would equilibrate with the particular gas that is been taken up from in this particular electrode. Let suppose we have try to detect the ammonia NH_3 the system is trying to detect ammonia gas. So, electrolyte in that case would be ammonium chloride NH_4Cl on the way it equilibrates with the ammonia is given in these set of equations here.

So, NH4Cl while you put it in a solvent typically aqua base solve immediately the converted into NH4 plus as and Cl minus. And then, if we assume that there is a equilibrium relationship between NH4 plus that is formed and the NH4 plus concentration that is there with in this electrolyte and the ammonia NH3 an hydrogen ions and NH plus in this following manor NH4 plus is an equilibrium with NH3 and plus NH plus.

So, what would happen if there is an increase decrease on the concentration of a NH3 there would be a shift the equilibrium either way. And this shift can be detected in terms of what is the pH of the medium, what is the negative log of hydrogen ions in the medium we are done with our measurements. So, we can find out what is the concentration of NH3 based on studying the equilibrium properties here in this particular reaction how it shifts both ways with respect to the production of H plus.

So, essentially we can also write all this down in terms of an equation we should be able to directly read the concentration of NH3 how, so let us look at lets frame the equation. So, you have a case here where the equilibrium constant Ka of this particular reaction can be return down in the manor Ka equals the concentration of the products, which is NH3 times H plus raise to their coefficient stoichiometric coefficients, which have one in this case divided by NH4 plus the ionic phase in the liquid electrolyte or the ammonium chloride solution.

So, essentially if we take logs the both sides we have log of Ka equals log of NH3 concentration plus log of hydrogen plus minus log of NH4 plus. And, so therefore, log of NH3 here really would be defined as this here is minus PKa if you many call it is the that is the way the P Ka would be define, so it is minus pKa. So, you have minus p Ka plus log of NH4 plus, which is actually the concentration of NH4 plus and you have plus pH, pH again is negative log of hydrogen and concentration this is transferred to the left side has a negative portion and this becomes minus P Ka plus log of NH4 plus p H.

So, you have a direct read out of NH 3 concentration logarithm of NH3 concentration if we can measure these different parameters as the equilibrium constant the NH4 plus concentration on the pH. So, K of course, is also known as the asset the situation constant if you major is we call little bit of fundamental chemistry this is essentially a gives as it has capability of the photometer. So, NH4 plus gets protonated are in donated and its generates hydrogen ion and it converts into NH3.

So, the electrodes for the other gases there is sulphide dioxide, nitrogen dioxide and these are essentially sometimes polluting the gas of atmosphere also carbon dioxide or hydrogen sulphide so and so for are measured by identical techniques using one of the other equilibrium process just as you saw in the case of ammonia here and there constructed pretty much in similar manor. So, let us look at what these gas and electrodes could do.

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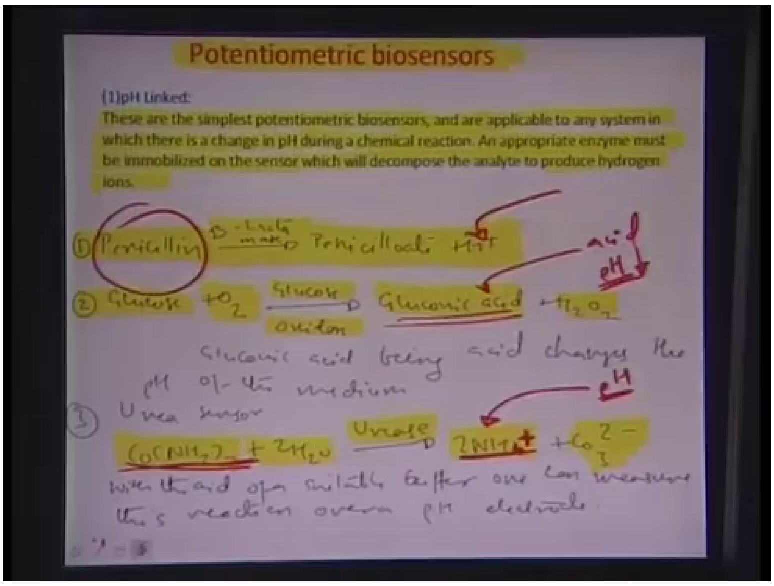

Potentiometric biosensors

(1)pH Linked:

These are the simplest potentiometric biosensors, and are applicable to any system in which there is a change in pH during a chemical reaction. An appropriate enzyme must be immobilized on the sensor which will decompose the analyte to produce hydrogen ions.

① Penicillin $\xrightarrow{\beta\text{-lactamase}}$ Penicilloate $+ H^+$

② Glucose $+ O_2$ $\xrightarrow[\text{oxidase}]{\text{Glucose}}$ Gluconic acid $+ H_2O_2$

Gluconic acid being acid changes the pH of the medium

③ Urea sensor

$CO(NH_2)_2 + 2H_2O \xrightarrow{\text{Urease}} 2NH_4^+ + CO_3^{2-}$

With the aid of a suitable buffer one can measure this reaction over a pH electrode

So, essentially one thing that they that they could be use as very appropriately is actually as a potentiometric bio sensor. So, essentially if you recall potentiometric is again form electrochemistry, where the voltage of the EMF is proportional to the concentration of the particular solution or concentration of the analytes of interest at of course, ZERO current. So, here essentially limiting the current to ZERO and trying to measure how the EMF of a system could varied with change in concentration of the analytes.

So, potentiometric bio sensors are very useful, because pH sensor is essentially a potentiometric bio sensor. And, so as most of the cases you see there is a always either and addition for hydrogen plus ion r consumption of the hydrogen plus ions that is a shift equilibrium, because of that reason almost always you know the pH linked method can be used for measurement of some analytes. So, let us look at a some of the analytes, which are important from the bio perspective.

So, the before doing that, so we can define them as a simplest potentiometric electrodes applicable to any systems in which there is a change in pH during chemical reaction. So, an appropriate enzyme has to be mobilize some times on to the sensor, which is also known as a recognition element if you look at the sensor model, which to behavior, which we decompose the analyte of interest the produce hydrogen ion and an increase and hydrogen ion would mean reduction in pH.

Therefore, the you can according the measure what is the concentration of the analyte which is broken down. So, the first application is in terms of penicillin detection if you recall penicillin is an antibiotic and this administer in most of the times patients and sometimes. So, for if a right here different infections and there is a huge problem of a related to infection sometimes there are allergic behavior of the particular patient to penicillin.

So, therefore, where is a suppose to be some kind of a best side care which you have to provide to kind of a deduct suppose there is there is like the patient the first case which especially post surgical patients the first case is the doctor would have is my due to antibiotic like penicillin. And, so therefore, it kind of in the decipher the penicillin concentration of a the patient is example and then relate that to the energetic behavior the energetic response patients of a stormed. So, the way do it is a very simply design again a pH based electrode and use an enzyme here the beta lactose.

So, penicillin as you see here in the first equation here a first chemical reaction here in the presents of this catalyst beta lactamase converts into penicilloate, which is again such kind of a reduce form of penicillin and it actually elaborates hydrogen ion here. So, the penicilloate produce is essentially one charge less or one balance we less than the penicillin. So, it produces hydrogen ion carrying reduced by the beta lactamase and then, this nitrogen ion can be easily measured by use of the pH electrode which would give you a bases of the concentration of the penicillin at in the patients example a very often we also would like to measure several analytes of metabolites in the patients example.

One of them in glucose particularly people suffering with hypo and hypercalcaemia being we need through investigation probably on real times based sometimes of the blood glucose level and it is more. So, need a because sometimes there has to be there is a requirement of additional penicillin and system it could cyber either arise or a fall in the blood sugar level would accordingly legal result in though such are stop the dose from be released of the penicillin particular in patient.

So, suffer from this hyper and hypocalcaemia syndrome, so the way you deduct glucose is a very simple again we try to oxidize a glucose by another enzyme what look at oxidize this equation number to here we talks about how glucose has been broken down. So, glucose essentially in the presents of oxygen and in the presents of this catalyst glucose oxidize in enzyme would converted into gluconic acid and H2, O2 and gluconic acid being an asset would essentially change the pH of the medium, so this is an asset.

So, result in or decrease in the pH of a medium because of increasing the hydrogen ion concentration. And therefore, we can say for assume that if the glucose concentration can be decide by looking at the pH there is an formulation of mechanic asset similarly another very important metabolite of interest is blood urea is essentially indicated of human problems and the patient particularly in patient with kidney problem, it can be problem urinal problem in urinal system they have the sentence you have the blood urea level to be uncontrollably high sometimes.

So, therefore, it is important to try to find out what is the normal by looking at the urea concentration in the in the in the couple of the patient and, so therefore, one good way of looking at urease could be by again using a pH based electrode if you look at this particular equation here. It talks all about urea which is CONH2 whole twice, which actually kind of hydrolysis the presents of water and this enzyme here urease, which convert into NH4 as this is the asset, which is generate the leave assets which is generated CO3 minus 2.

So, therefore, an increase NH4 plus concentration would indicate again an increase in the a reduction in the pH because x essentially acidic. So, Lewis acid it has an additional hydrogen ion here it can actually go very well with the kind electrode that we have a discovering ah discussing earlier in the earlier slide by using ammonium chloride solution of the electrolyte. So, therefore, we know with the aid of a suitable buffer solution one can measure this reaction like buffer solution like NH4Cl as we saw in the last slide over a pH electrode a pH measurement here would be indicated of what is the urea concentration in the patient's blood. So, these are some of the illustrations of how potentiometric measurements can be made effectively bio sensing particularly of metabolites of a biological importance, let where in human body.

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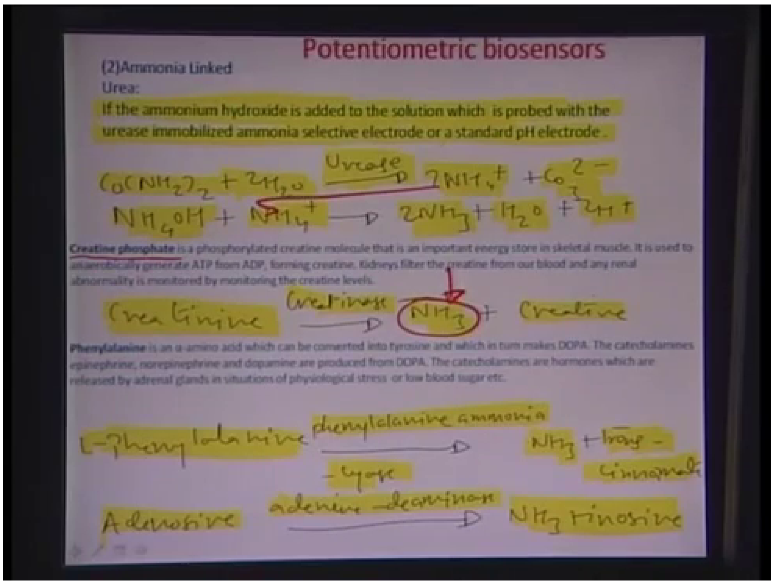

Potentiometric biosensors

(2)Ammonia Linked

Urea:

If the ammonium hydroxide is added to the solution which is probed with the urease immobilized ammonia selective electrode or a standard pH electrode .

$$CO(NH_2)_2 + 2H_2O \xrightarrow{Urease} 2NH_4^+ + CO_3^{2-}$$

$$NH_4OH + NH_4^+ \longrightarrow 2NH_3 + H_2O + 2H^+$$

Creatine phosphate is a phosphorylated creatine molecule that is an important energy store in skeletal muscle. It is used to anaerobically generate ATP from ADP, forming creatine. Kidneys filter the creatine from our blood and any renal abnormality is monitored by monitoring the creatine levels.

$$\text{Creatinine} \xrightarrow{\text{Creatinase}} NH_3 + \text{Creatine}$$

Phenylalanine is an α-amino acid which can be converted into tyrosine and which in turn makes DOPA. The catecholamines epinephrine, norepinephrine and dopamine are produced from DOPA. The catecholamines are hormones which are released by adrenal glands in situations of physiological stress or low blood sugar etc.

$$\text{L-Phenylalanine} \xrightarrow[\text{-lyase}]{\text{phenylalanine ammonia}} NH_3 + \text{trans-cinnamate}$$

$$\text{Adenosine} \xrightarrow{\text{adenine deaminase}} NH_3 + \text{inosine}$$

So, there are some other example here there are I would like to discuss there can be ammonia length bio sensors where you effectively also are able to find out how the ammonia varies, again through a pH measurement as we saw last time using NH4 plus and Cl minus that is a ammonia fluoride electrolyte and equilibrating the ammonia has respect to that. And being able to tell the concentration of ammonia based on the concentration are change in concentration of the hydrogen ion.

So, here again similar kind of set up is used that instead of a fluoride used the corresponding hydroxide. So, if the ammonium hydroxide is added to the solution, which is probed with the urease immobilized and urease if you recall is the enzyme, which is able to catalyzed urea into NH4 plus Cl minus as we just it in the last slide earlier, this urease immobilized ammonia selective electrode or a standard pH electrode they able to very, very define the amount of a ammonia with the ammonium hydroxide solution instead of fluoride, where using hydroxide here.

Let us look at the reaction here $CONH_2$ whole twice and in the presences of a water and the presence of a urease enzyme to formulate 2 NH4 plus and $CO_3$2 minus and NH4 plus for the actually equilibrates with the ammonium hydroxide solution here NH4OH to formulate 2 NH_3 and this is ammonia plus H_2O plus 2H plus. So, in this stage or in the later stage, where the ammonia can be and equilibrated with the NH4Cl of some other electrolyte we could measure the pH and be able to tell what is the ammonia concentration and corresponding what is what where the urea concentration as borrow here from the last step.

So, that is all you can measured urea dependently also by just using ammonia use measurement method although effectively everything based on pH measurement there is some other analytes of interest with in the human body one, which again tells a very good information of gives very information about the URINAL system is creatmine . So, creatmine is essentially stored is a phosphate form and it is first slide form of the criteria molecule it is an important energy store skeletal essentially it converts anaerobically the A T P well remain admission try fast it into die phosphate form and results in formation of a creating molecule.

So, therefore, as specifically in micelles when you work out and the muscle is start of osculation sometimes you know the human body such the blood essentially in the human body is great transport of oxygen. So, as you run the heart beat increase and why it show because oxygen has to be delivered at a huge amount of or a huge rate to the various issues within the human body as you work it out sometimes that heart of a patient not being normal patient may mole function we to, which there may be a requirement of oxygen.

So, in that case how the body manages again is a very effective way in a very effective way. So, what it does it again converts in the stored A T P at to assign five fast way in to the A d p die phosphate form and this is at the fast of create and essentially this is that done; that means, in the absence of oxygen. So, even though that reaching the particular muscle issue is a lesser in amount still it is able to harness energy generates it is energy, but creatmine produce within the body creates a problem.

Because, it has to be filter and the kidney are effectively the filtration mechanism for all the body as we have known and the blood essentially it is a purifier for metabolite like black, which go through and handful products are created of the human body urea is one of them the urea is one of them another is **creatmine** . So, create in if you know generated are if it goes unfiltered is also indicative of that the and all functions. So, we can very well find out the urinal health by looking at creatmine levels in human body.

So, creatmine essentially again its molecules which is responsible for generating these Hormone's called there are about goes two twelve endocrine clans human body. And I am sorry about eighth are nine looking in the clans within the whole human body and the clans are the essentially on the cause of secretion of these uniquely you know function organic molecules called Harmon's. So, essentially what the Harmon's do is the up regulated down regulates certain psychological process is within the body.

They are these attunal in there is these clans within the human body, which able to generate particular names stressful situation situations are extreme psychological stress are may be low blood sugar giving this stress causing the stress there is huge generation of these means is the essentially a function of the dopa molecule the presence or absents of molecule, so these are very interrelated. So, it all start with the cycle from this basic alpha ammonia I said it is important to measure the content in the in a human body for understanding whether the endocrine land is able to generate or the original land is able to generate sufficient amount to body kind of going in terms of in stress psychological stress which situations.

So, how do you do that there are ways a means of finding out some of the buyer like a bin a friend nor a bin friend dopa man all these mightiest are essentially produced form molecule toba within the body they are they are the amount of the alpha amino acid phenylalanine. So, phenylalanine actually composed again by this molecule call phenylalanine ammonia lyase as cen be seen here to convert of get to converted into NH_3 and this trans cinematic. So, this is again other organic species or from phenylalanine.

So, again measurement of ammonia would be able to certain how much amount of phenylalanine is there then the metabolite of interest of the other blood of that patient of interest other kind of measurement that we often do is this adenine measurement have another enzyme here called adenine demonize which converts into NH3 and I am assume and essentially these are all measured by ammonia electrodes.

So, I have just trying to give though few of these slides some flayer of what actually goes into the bio diagnostics the typical diagnostics area as regards human patients all this sensors are very, very important from the point of view of few measuring the different physiological conditions of the human body.

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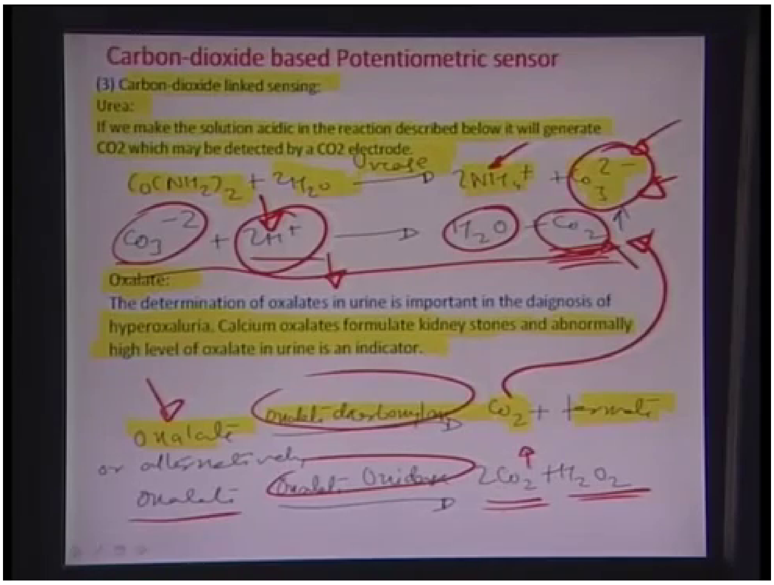

Carbon-dioxide based Potentiometric sensor

(3) Carbon-dioxide linked sensing:

Urea:

If we make the solution acidic in the reaction described below it will generate CO2 which may be detected by a CO2 electrode.

$CO(NH_2)_2 + 2H_2O \xrightarrow{Urease} 2NH_4^+ + CO_3^{2-}$

$CO_3^{-2} + 2H^+ \longrightarrow H_2O + CO_2$

Oxalate:

The determination of oxalates in urine is important in the daignosis of hyperoxaluria. Calcium oxalates formulate kidney stones and abnormally high level of oxalate in urine is an indicator.

$\text{Oxalate} \xrightarrow{\text{oxalate decarboxylase}} CO_2 + \text{formate}$

or alternatively

$\text{Oxalate} \xrightarrow{\text{Oxalate Oxidase}} 2CO_2 + H_2O_2$

So, following this we can look into some carbon dioxide link sensing mechanism. So, we have already recover ph as you did in the first slide followed by ammonia based where this different time lines of interest what recorded using ammonia and then, you know trying to essentially look at it through the pH electrode. But, then equilibrating that the some kind of a sort solution of ammonia.

Now, looking into carbon dioxide the processes pretty much similar as before you know you can you can make it using reading for NH4 plus or you can make it using some kind of a equilibrium between carbonic acid and this CO_2 or 3 minus 2, which is generate as a result of you know different chemical steps. So, we can again detect urea blood urea by using carbon dioxide sensors.

So, if you may make solution acidic in reaction described below in generates here two and this may be detected by due to electrode. So, let say urea CO NH2 equal twice utilize in the presence of urea as we note convert into 2NH4 plus CO_3 minus 2, so if I take this component of this reaction and instead of the NH4 plus of. So, if I take 0 3 minus 2component of this reaction and then, converted by mixing it with the some kind of a acidic solution where you have an access hydrogen ion you get converted into a NH_2 and CO_2.

So, produces carbon dioxide by the cost of reduction in the hydrogen ion concentration there is a change in ph then you could detect how much of amount of Co2 is produced by looking at how much amount of reduction in the hydrogen plus ion concentration would typically take place. So, that is how you can using carbon dioxide based sensor we able to tell urea. So, one hand in the earlier slide you saw that we measured using NH4 plus and the ammonia bio sensor and this case we are using the Co_3 minus 2 carbon dioxide base electrode to measure the same level of urea on the on the block example.

So, different times you know you really meet to use different sensors based on the availability or availability of many you know species or conditions within the human body particularly in case of implantable sensors very common problem, but not all places of the body would have tall analyte of interest. So, there are some places which are scarves about certain analytes in there is some other space they may be abandon of other kind of electrode line.

So, you design your electrodes design a mechanisms based on what is available what portion of the body another important aspect is oxalate measurement we are all were of this critical problem related to kidney stones that is essentially also medically known as hyperoxaluria. So, essentially more amount of oxalates the in the patient's blood again suggesting in normality would mean the accumulation such oxalates and through that there may be problems related to stones are in the calcium deposits in certain areas of the kidney or may be parts of the gall bladder it is of importance to detect the oxalate level that the in the blood just to monitor whether patient is encrypted with this problem of stones.

So, calcium oxalate formulate kidney stones as we are all way of this and this essentially means is normally high level of oxalate in urine how we can detect that say again through a carbon dioxide base sensor. So, this is a enzyme called or oxalate decarboxylase, which can break down oxalate into Co_2 and format and you can measure this we using electrode like the buff as you saw here.

Essentially that, if you put this an equilibrium with this particular reaction you might be able to formulate an idea of, how much oxalate was there in the patients plate alternatively you could also convert oxalate using another enzyme called oxalate oxidates this case the enzyme was different it is decarboxylase this is oxalates and you get converted into Co_2, H_2, O_2 again you could measure it using Co_2 sensor by finding out the co level is gone up. So, principle we have more or less covered the different kind of gas sensor that are reduced for different bio applications or like to.

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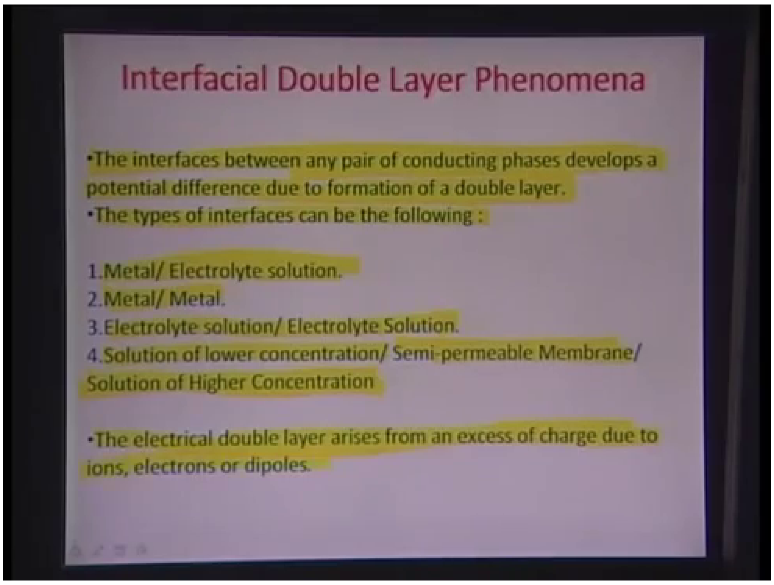

Interfacial Double Layer Phenomena

- The interfaces between any pair of conducting phases develops a potential difference due to formation of a double layer.
- The types of interfaces can be the following :

1. Metal/ Electrolyte solution.
2. Metal/ Metal.
3. Electrolyte solution/ Electrolyte Solution.
4. Solution of lower concentration/ Semi-permeable Membrane/ Solution of Higher Concentration

- The electrical double layer arises from an excess of charge due to ions, electrons or dipoles.

Now, go ahead with another very interesting and important phenomena of what we call the double layer phenomena as I told you before that in micro scale flows very important problem is surface charge less the charges on a particular channel surface micro channel surface would actually feel relate to developing density gradient of the opposite counter charge it is solution and this could be basis of movement of fluids would small capillaries.

So, let us look at this problem little more closely and try to make an analytical model for this particular problem. So, let say the interface between, so let us first we find out what happens to the interface between pair of conducting phases phase can be a solid electrode could be liquids it could be you know a liquid in the solid could be solid in a solid. So, at the interface between any pair of conducting phases we are always develops a potential difference due to the formation of this double layer we have enough on talking about what the double layer is in our earlier electro chemistry lessons.

So, the various types of interfaces can be following it can be metro electrolyte interface it could be metal and metal could be an electrolyte solution with another electrolyte solution or it could also be solution of a lower concentration separated by a semi permeable membrane with respect to the solution of a higher concentration if you may remember you know for the electro chemistry lectures we have talked about this kind of a electrode they are two different oxidant concentration.

There is a boundary between these two and the this can be an alternate means of designing and ion selective electrode. So, the electric double layer really if you look at the it arises from an excess of charge due to ions electrons are dipoles and this is more Kind of diagrammatically a visually represented by this particular figure here.

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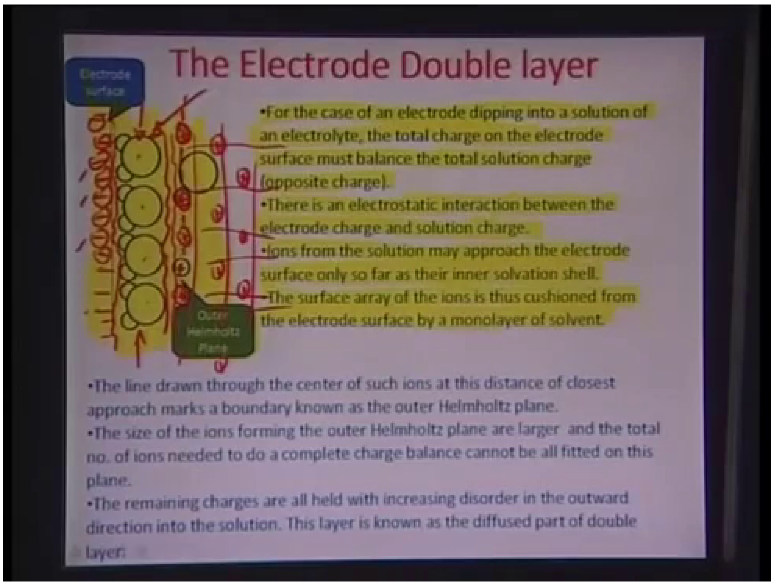

The Electrode Double layer

- For the case of an electrode dipping into a solution of an electrolyte, the total charge on the electrode surface must balance the total solution charge (opposite charge).
- There is an electrostatic interaction between the electrode charge and solution charge.
- Ions from the solution may approach the electrode surface only so far as their inner solvation shell.
- The surface array of the ions is thus cushioned from the electrode surface by a monolayer of solvent.
- The line drawn through the center of such ions at this distance of closest approach marks a boundary known as the outer Helmholtz plane.
- The size of the ions forming the outer Helmholtz plane are larger and the total no. of ions needed to do a complete charge balance cannot be all fitted on this plane.
- The remaining charges are all held with increasing disorder in the outward direction into the solution. This layer is known as the diffused part of double layer.

So, essentially this is representing an electrode. And it is behavior with respect to the solution, which is adjacent to a let suppose that this electrode surface has tendency of getting a negative charge if you remember zinc leaves the metal surface into the solution and gets into zinc ion, because leaving the electrons on the surface of this particular electrode. So, therefore, there is a negative charge on this particular surface and there is a positive ion with this punch of positive ions, which have left this surface into the solution which have formulating this particular layer.

So, essentially when this ion separates out they have this small layer of water as you know that this interface between solid and liquid is a interface between the between solid electrode in a liquid. So, the liquid always is aquatic nature almost always aquatic nature there is tendency of this layer of a water molecules you come in between as a dielectric between the positive charge and negative charge here. And, so it gets separated with this thin dielectric layer of water.

So, we were talking about this electrode double layer and this as represented here is essentially the formulation we know the formulation of double layer is essentially. So, the interesting to be seen is that the number of electrons being small has a is always almost responsible for creating a certain charge density on this surface of this electrode as suppose to the number of positive ions which are in the solution. So, the electrons here in the surface or densely located and they would create dense amount of charge because of this smaller sizes the electrons are always smaller in size then corresponding metallic ion and solution.

So, one of the of you know the outcomes of this kind of a size difference between the negative and the positive charge centers would essentially the result in a thin amount of charges, because of the size restrictions are bigger size and really the first layer here separated by this layer of water molecules will not be able to totally neutralize the negative charge on this electrode surface. So, let me just come again with this idea that you have these positive layers here positive charges here, which are bigger in sizes.

Then, the negative charges correspondingly in the to the electrons on the surface of the electrode and the first layer really the first layer, which is represented here which is just about separated by this layer of a water molecules electric would not be able to neutralize the total amount of negative charges here because of the greater sizes. So, what would be an outcome the outcome would be that this layers with kind of still be able to hold positive charges and the density dense with distance again and the neutralization would occurs somewhere in the bulge of the solution somewhere in the bulge of the solution.

So, therefore, there would be layers of charges in the solution with decreasing in density or decreasing density of these charges till and until the whole negative charge on this electrode is neutralized because of the positive charges in the solution. So, this brings us a very interesting characteristics, it essentially tells us that you know whenever there is a surface in close proximity to solution like this there would always be distribution of charge the opposite kind as the surface more into the bulge of the solution that is number 1 and number 2 is that if we have this distribution of a the opposite charges to that of the surface on the bulge.

Then, we can as well as these to flow the whole fluid particularly when the length scales that you are talking about is close to the length scales of this bulge charge layer. So, we essentially from the base length was first was various proposed identified the layer the first layer of charges here which is close to the electrode as also the outer Helmholtz plane. So, the first layer of charges which is directly phasing after this water layer is a crossed over from the electrode is known as outer Helmholtz plane.

So, this particular this other layer which is a going into the bulge of the solution is also known as you know the bulge charge of the particular solution. So, in an in summarily for the case of an electrode dipping into a solution of an electrolyte the total charge on the electrode surface must be balanced by the total solutions are. So, also the opposite charge and therefore, there is a tendency of a distribution of charge within the bulge obvious reasons.

So, there is an electro static interactions between the electrode charge in the solution charge

Einstein solution approach the electrode surface for. So, for as the inner salvation shells and the inner salvation shells is essentially this single mono layer of water which is separating both the ion of interest or the ion. In the solution and the negative charge on the electrodes and the surface array of the ions is the form the electrode surface by this mono layer dialectic which is water mostly the electrolytes are actually immersed in solvents.

So, you have the water and in the medium most of the electrolytes. So, the line gone through the center of such ions and this distance of closes the plot marks boundary we call this outer Helmholtz plane and the other portion of the charge the canceling charge away from the electrode as the bulge charge in the solution and the size of the hands and forming outer Helmholtz plane larger. And the total number of ions need to do a completed charge balance and because this can be fitter on the one plane they have going to the bulge.

So, this is also known as the bulge charge or the defuse layer or the defuse charge in this solution. So, the remaining charges or all held with increasing this order in the outward direction in to the bulge of this solutions. So, there also known as the bulge charge of the solution or the defused part of the double layer is called the defuse layer defuse charge with respect to an electrode. So, in a sense this is dynamics of double layer which is formulated with an electrode or one phase these solid or liquid comes in contact within the other phase.

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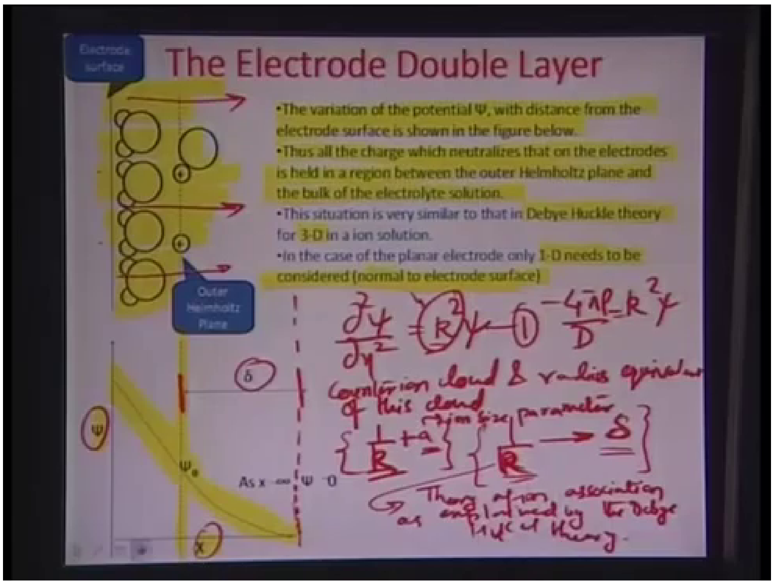

The Electrode Double Layer

- The variation of the potential Ψ, with distance from the electrode surface is shown in the figure below.
- Thus all the charge which neutralizes that on the electrodes is held in a region between the outer Helmholtz plane and the bulk of the electrolyte solution.
- This situation is very similar to that in Debye Huckle theory for 3-D in a ion solution.
- In the case of the planar electrode only 1-D needs to be considered (normal to electrode surface)

$$\frac{\partial^2 \psi}{\partial x^2} = k^2 \psi$$

So, let us do some detail modeling studying how we can use the Poisson's equation to find out the behavior of potential is moved in outward direction from the electrode to all the way to the solution couple of interesting thing is or that if you plot the potential with respect to the distance the variation of the potential. Let us say psi in this case distance from the electrode surface is linear as long as is between the inner salvation shell or layer and then it falls down rapidly in through the bulge I would crosses the outer Helmholtz plane.

So, all the charges which neutralizes that on the electrode called region to Helmholtz plane up to two outer Helmholtz plane the electric filed opposite linear as if shows that in this region really it is a resistive drop because you know the only thing which is a available here is a layer dialectic, so it is a layer of resistance. So, you have a case here in this particular region where there is a drop in potential resisting drop and then in this particular portion as will be shortly calculating how this varies or what the potential here is in this particular outer Helmholtz plane this is also of great significance especially to micro fluid.

So, will be calculating more the potential here is, what may be the distribution of potential as we go from this particular outer Helmholtz plane in all the way up to about the point where the defuse layer ends the bulge charge layer ends this solution. So, the situation is similar to that Debye huckel theory as we are generated for a single point time. Of course, this case it is not a 3 d case it is more 1 d 1 dimensional and this needs to become considered in the direction normal to that electrode surface.

So, here for calculating the potential we can consider just one direction normal to that of the electrode surface and try to understand what is the variation if the potential pi with respect to the direction x, so let us look at into little bit of modeling. So, essentially here we see in the one dimensional case really the couple of interesting things one is the Poisson's equation can get converted. Now, mostly into the partial of psi with respect to x twice equals k square times of psi if you remember this essentially was also minus four pi row by d.

So, equal to k square psi this is a something I am borrowing from the earlier de by huckle equation with just about solve in the last lecture last few lectures give me a minute this is a square of k. So, some interesting facts about this outer Helmholtz plane that if you remember when we talked about the counter ion cloud and the radius of the radius equivalent of this cloud we generated a term, which is equal to 1 by k plus a was essentially the ion size parameter ion size parameter and k was something that we assumed to be the equivalent of whatever the charge term was in Poisson's equation here.

So, this is essentially the effective ion radiant, so in case of the electrode in the 1 by k is placed by thickness of the defuse layer delta. So, here it will see really delta s away from this out to Helmholtz plane on all the way when the potential drops down to 0 of the defuse layer of charge of the bulge layer of charge ends really to this point here when the potential phi 0. And, so delta is essentially the distance between the outer Helmholtz plane and this particular layer where the potential ends out to be 0 or where the defuse layer ends in the bulge in the solution.

So, 1 by k here is replaced by delta this actually comes out from another theory, which is beyond scope of this course it is the theory of ion association as predicted by the Debye huckle theory. So, I will just assume here that this one by k is equal to delta in case of an electrode plus to make life single and will not be really looking at y that is. So, this the you can just remember this you can actually you know later on maybe for a different search, where you can see the theory of ion association as explained by the Debye huckle theory equations. So, then let us try to solve this poison's equation here equation number one and see what the solution would look like what form the solution would be like really.

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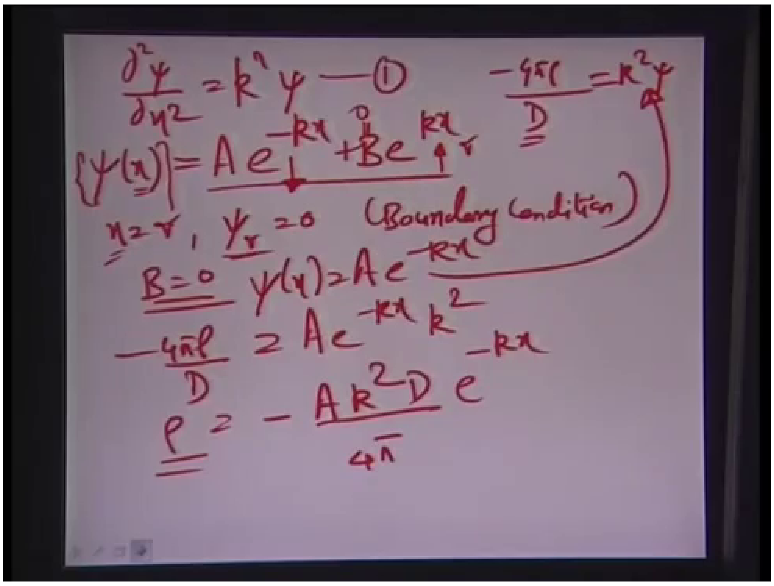

$$\frac{\partial^2\psi}{\partial x^2} = k^2\psi \text{ — ①} \qquad \frac{-4\pi\rho}{D} = k^2\psi$$

$$\{\psi(x)\} = A e^{-kx} + \overset{0}{B} e^{kx}$$

$$x = \infty, \ \psi_\infty = 0 \ \text{(Boundary Condition)}$$

$$B = 0 \quad \psi(x) = A e^{-kx}$$

$$-\frac{4\pi\rho}{D} = A e^{-kx} k^2$$

$$\rho = -\frac{A k^2 D}{4\pi} e^{-kx}$$

So, essentially d 2 psi by d x 2 equals to k square of time the general solution for this kind of a equation can be represented as psi effects mind you the psi is potential in one direction $\frac{\partial^2\psi}{\partial x^2}=k^2\psi$ this perpendicular to the electrode is a it $\psi(x)=A e^{-kx}+B e^{kx}$. So, that is what the solution for this plus k x this thing is plus k x. So, this is what a general solution of this equation one differential equation here would be looking like if you apply the boundary conditions x equal to 0 x equal to infinity the psi infinity 0, so applying this boundary condition this normally happening B= 0.

So, if x is infinity this tern here goes all the way up to down to 0 for this goes to infinity and therefore, only way that phi infinity psi infinity here the potential infinity here is 0 could be B 0, because then take care of this infinitely growing term this automatically 0 by virtue of e to the power minus k x converted into 0. So, therefore, phi e^{-kx} , so we already know that the real poison's equation is really in terms of the charge density. So, minus 4 pi row by d was the dialectic constant row is the volume charge density and that is equal to that is equal to this k square psi as we have talked neutrally.

So, if you put this I value here in this particular equation we get minus 4 pi row by d equals A e to the power of minus k x times of square of k. Therefore, the charge density also can be represented as $-\frac{A k^2 D e^{-kx}}{4\pi}$. So, that is what the volume charge density row would be in this particular case. So, let the charge density on surface of the electrode sigma we are making them to presumption here that.

Because, we are talking about out of electrodes surface as a look at here this area the dynamics of charge density in the bulge layer or the outer Helmholtz density really do not the amount of charge density on the surface of the electrode. So, it is very critical parameter and somehow we need to put this into our model. So, that based on this charge density we could predict the nature of defuse layer or the outer Helmholtz layer only factor that I would like to mention here is that you know the basis of this density of charge would be the dependency on this surface of the particular electrode.

In case of micro channel flows electro-kinetic micro channel flows in the surfaces silicon there would be bond density and there would be this is a huge number of (52.09) top of the of the surface it would get negative electric charge psi o minus kind of you know mightiest as it exposes to certain pH certain solution of a certain pH. So, if this kind of a treatment is given in the surface there is a tendency of the fluid they develop in defuse layer, which is of positive charge there would be a counter ionic cloud which is of positive charges.

Therefore, the surface charge density to be a function of how many active sites and their on a surface really, which can gets a nice, which can get converted into a psi o minus. So, we would look at this part of the solution in the next lecture.

Thank you.