Bio – Microelectromechanical Systems

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Module No. # 01

Lecture No. # 11

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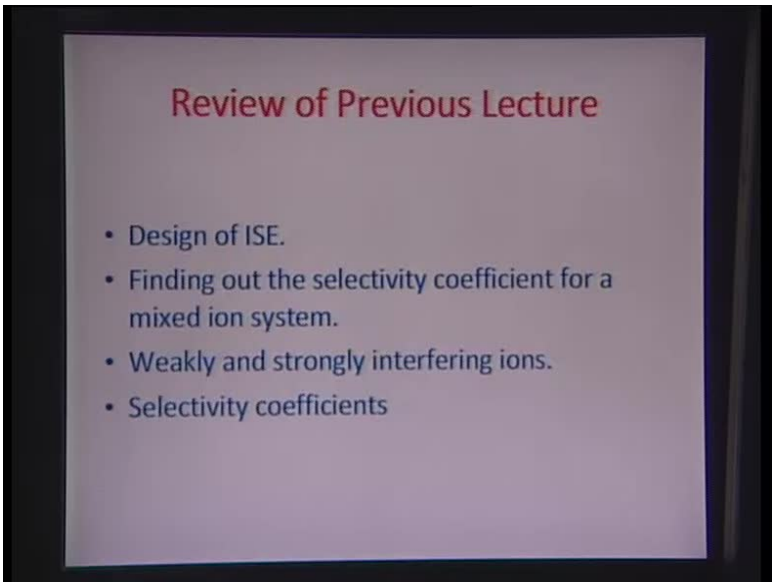

Hello and welcome back to this 11th literature on Bio - Microelectromechanical Systems. We will just like to do a brief review of what we covered last time. We talked in details about designing of the ion selective electrodes. We also tried to find out the Debye Huckle equations and how it can be used for solvated ion transport. Basically, we looked at the interaction of and a primary ion of interest in an environment of the counter ion cloud. We try to derive something called the activity coefficient, which is also important for determining the participation really of ion of interest electrolyte over the several other competing ions.

We try also to define the Nicholas ideas as on many equations where the selectivity of a particular ion of interest over the other interfering ions. Their contributions to the measured EMF were studied in details for both the weekly and strongly interfering ions. We are going to compare how this EMF variation would take place and we try to solve

several numerical examples to look at the different practical aspects of design of such electrodes.

Today we will be starting a new topic on why these sensing protocols are really needed and how this can be used to detect some of the analytes of interest, you know as we go by. We will finally converge into something which is a very important in the area of Bio-MEMs, which are surface driven flows in all these micro assays. Typically, as I have discussed often on in my previous lectures, Bio-MEMs devices do use a lot of micro fluidics. Essentially, micro fluidics also is defined as the flow of fluids in the microscopic length scale. These flows can sometimes be totally driven by charged surfaces and the flows can be: Electro kinetic flows; Electro osmaotic flows; Electro fluidic flows; and so on so forth.

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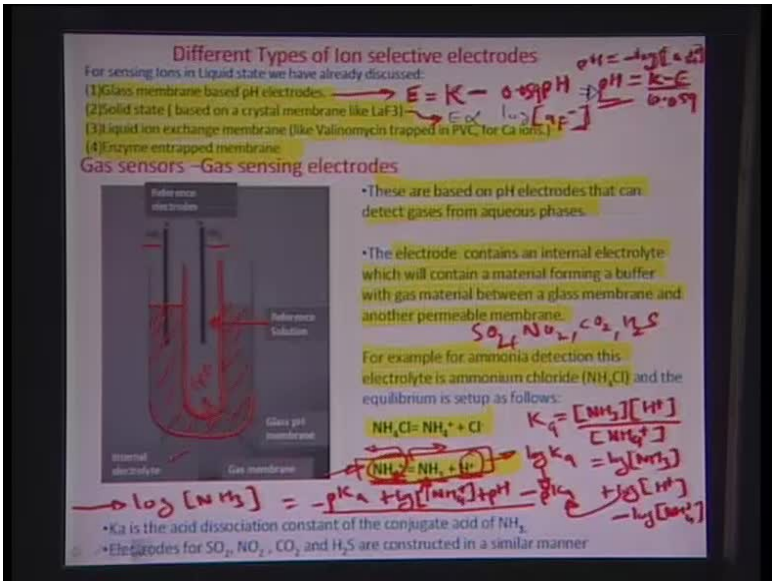

So, I will make a detailed analysis of such flows and then finally apply them to make novel mechanical devices like micro pumps, micro valves, micro mixers, and etcetera. So, this would from a small part of the curriculum on this Bio - Microelectromechanical Systems. So let us try to understand why these electrodes are used or design selective electrodes are used often on for sensing various analytes of interest. Most of these metabolites of interest are essentially found within the human body. A very important goal is to try to design something which can take up various gases which are generated

and try to identify some analyte of interest or metabolite of interest in the human blood on the basis of this measured gases.

So, let us look at what we have covered so far in as regards, the very important component of ion selective electrode that is the membrane. So, we have looked into a 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 resin attained from the extract of a tree, was an organic resin and also it is found in a cell walls and they are used as molecules which furnish the transportation of Calcium and Potassium ions.

Then, we also talked about enzyme entrapped membranes. Particularly, if you remember about the Glucose oxidize case, we described in details how an enzyme entrapped membranes can be able to pick up analyte of interest just to let you know a few mathematical details about how pH of electrodes are calibrated. Essentially, if you look at the Nernst's equation for certain electrode, the EMF measured by the pH electrode would really be equal to the intercept - the Luncheon intercept, which is k minus of the luncheon slope 0.059. Mind in this case we are talking about Hydrogen plus 1, so you have n equal to 1 here times p of H.

P of H as we know it 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 be identified as k minus E by 0.059. So, that is how you can find out the pH in the case of glass membrane pH electrodes. For the crystal membrane electrodes like let us say Lanthanum Fluoride which detects Fluorine ions or Fluoride ions, F minus, the EMF in this case, potentiometrically will be proportional to the logarithm of the activity of Fluorine ions and in a similar kind of situation, activity can be equated to the concentration or we can assume gamma to be equal to 1 in that particular case.

So, let us talk about Gas sensors - Gas sensing electrodes at the outset to know what is the basic schematic which is involved in such electrodes? This would be a kind of,

followed with a detailed 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 a glass pH membrane and this is the pH electrode. So, this - right here in this region is the glass pH membrane. You also have a gas membrane here especially, for this dissolving the gases which would be measured or which are intended to be measured in terms of a pH change. We have a reference solution here inside this particular concentric tube so this essentially is a concentric tube. So, you are separating this tube, filling it up with the reference solution or reference electrolyte and this portion here is permeable to only Hydrogen ions. So, this is the typically - if you may recall the Silicates of Chalcogenides or group 6 metals, which are able to select specifically Hydrogen ions over the other interfering ions.

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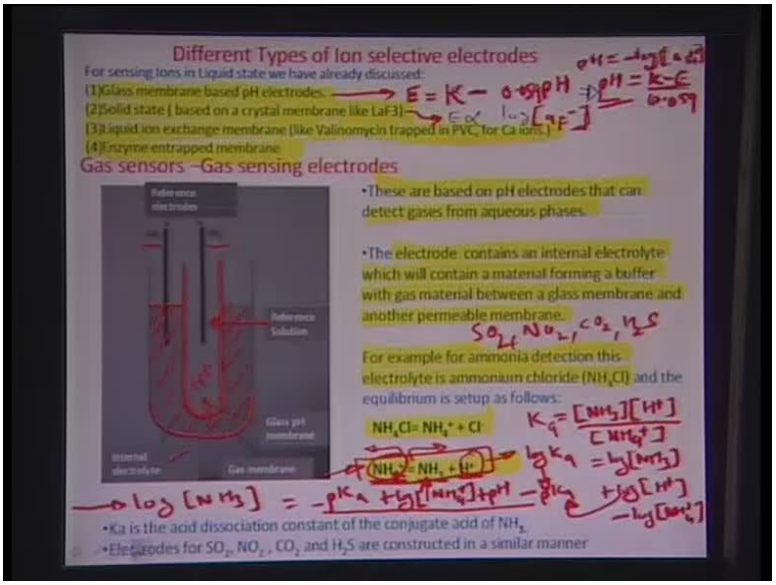

So, here also we have another reference solution in this particular zone. So you have a solution inside the glass membrane for the hydrogen ions and you have a solution outside it. We have two electrodes here Re1 and Re2, which are both reference electrodes and they would be able to sense any transfer 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 analyte of interest is being reflected here below in the following area of the slide. So essentially, these are based on pH measurement. They can detect gases from across

phases. The electrode contains an internal electrolyte which will contain material forming a buffer with the gas material between the glass membrane and the permeable or 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 being taken up from. In this particular electrode let us suppose we are trying to detect Ammonia NH 3, the system is trying to detect Ammonia gas so, electrolyte in that case would be Ammonium Chloride NH 4 Cl. The way it equilibrates with Ammonia is given in these set of equations here - so, NH 4 Cl while you put it in a solvent or typically aqueous based solvent would immediately get converted into NH 4 plus and Cl minus.

Then if we assume that there is an equilibrium relationship between NH 4 plus that is formed or the NH 4 plus concentration that is there within this electrolyte Ammonia, NH 3 and Hydrogen ions, NH plus in this following manner: NH 4 plus is in equilibrium with NH 3 and plus H plus.

So, what would happen if there is an increase or decrease in the concentration of NH 3? There would be a shift in the equilibrium either way and if this shift can be detected in terms of the pH of the medium, the negative log of Hydrogen ions in the medium are done without measurements. So, we can find out what is the concentration of NH 3 based on studying the equilibrium properties here in this particular reaction how it shifts both ways with respect to the production of H plus.

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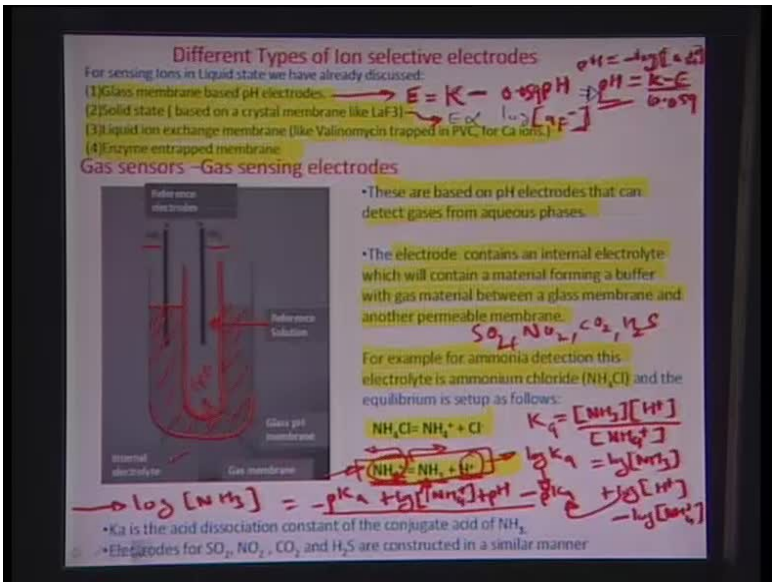

So, essentially we can also write all this down in terms of an equation, which would be able to directly read the concentration of NH 3. How? So, let us look at or let us frame that equation so you have a case here where the equilibrium constant Ka of this particular reaction. This particular reaction can be written down in the manner Ka equals the concentration of the products which is NH 3 times H plus raise to their coefficient - spatiometric coefficient, which are one in this case divided by an NH 4 plus, the ionic phase in the liquid electrolyte or the Ammonium Chloride solution. So, essentially if you take logs on both sides you have log of Ka here equals log of NH 3 concentration, plus log of Hydrogen plus, minus log of NH 4 plus and therefore, log of NH 3 here really would be defined as this - here is minus pKa; if you may recall that is the way the pKa would be defined. So this minus pKa - so you have minus pKa, plus log of NH 4 plus which is actually the concentration of NH 4 plus. You have plus pH; pH again is negative log of Hydrogen ion concentration. This is transfer to the left side and has a negative quotient and this becomes minus pKa, plus log of NH 4 plus, plus pH. So you have a direct readout of NH 3 concentration - logarithm of NH3 concentration, if you can measure these different parameters: the equilibrium constant, the NH 4 plus concentration and the pH. So, K of course is also known as the ascend dissociation constant. If you may just recall little bit of fundamental Chemistry, this is essentially a least acid; it has capability of getting protonated. So, NH 4 plus gets protonated or it protonates and then it generates Hydrogen ion and it converts into NH 3.

So, the electrodes for the other gases, that this Sulphur dioxide, Nitrogen dioxide and these are essentially sometimes polluting gases of the atmosphere, also Carbon dioxide, or Hydrogen Sulphide, and so and so forth are measured by identical techniques using one or the other equilibrium process, just as you saw in the case of Ammonia here on their constructor pretty much in a similar manner.

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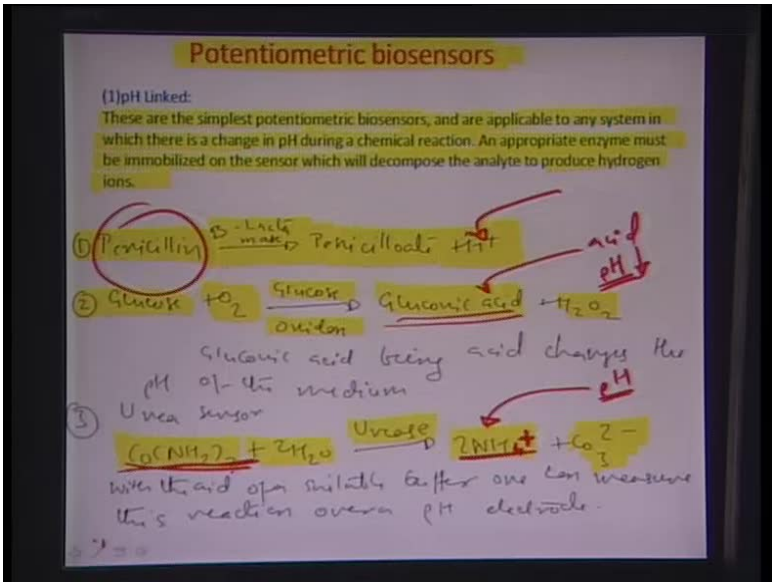

So, let us look at what these gas sensing electrodes could do? So, essentially one thing that they could be used as a very appropriately is, actually as a potentiometric biosensor. So, essentially if you recall, potentiometric is again a form of Electro Chemistry where the voltage of the EMF is proportional to the concentration of the particular solution or the concentration of the analyte of interest at of course 0 current. So, you are essentially limiting the current to 0 and trying to measure how the EMF of a system would vary with the change in concentration of the analyte.

So, potentiometric biosensors are very useful because pH sensor is essentially a potentiometric biosensor. So, as in most of the cases you see, there is always either in adhesion of a Hydrogen plus ion or consumption of the Hydrogen plus ion and there is a shift in equilibrium because of that reason almost always you know the pH linked method can be used for measurement of certain analytes.

So, let us look at some of the analytes which are important from the bio-perspective. So, before doing that we can define them as the simplest potentiometric electrodes applicable

to any system in which there is a change in pH during a chemical reaction. So, an appropriate enzyme has to be immobilized sometimes onto the sensor which is also known as recognition limited. If you look at the sensor model which we did earlier which will decompose the analyte of interest to produce Hydrogen ion and an increase in the Hydrogen ion, would mean reduction in pH. Therefore, you can accordingly 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 it is administered in most of the times in patients and sometimes for a variety of different infections. There is a huge problem related to infection, sometimes there are allergic behaviors of the particular patient to Penicillin. Therefore, it is supposed to be some kind of a bedside care which we have to provide to kind of detect.

Suppose there is an allergic response like this to a patient, the first case which especially postsurgical patients - the first case the doctor would have is, it might be due to an antibiotic like Penicillin. Therefore, pertinent to kind of decipher, the penicillin concentration of the patient is blood sample and then related that to the allergic behavior of the allergic response the patient suffers from. The way you do it is very simple you design again a pH based electrode and use an enzyme, here the Beta Lactamase. So, penicillin as you see here in the first equation here or the first chemical reaction here in the presence of this catalyst Beta Lactamase converts into Penicillinase, which is again certain kind of reduced form of Penicillin and it actually liberates Hydrogen ion here.

So, the Penicillinase that is produced is essentially one charge less or one valency less than the Penicillin. So, it produces the Hydrogen ion getting reduced by the Beta lactamase and then this Hydrogen ion can be easily measured by means of pH electrode, which would give you a basis of the concentration of the Penicillin in the patient's blood sample, one of them being Glucose. Particularly people suffering Hyper, Hypoglycemia would need a through investigation probably on real time basis, sometimes of the blood glucose level. It is more so needed because sometimes there has to be that there is a requirement of adhesion in insulin and system if you can decipher either rise or a fall in the blood sugar level would accordingly release a certain dosage or stop the dosage from being released of the insulin particularly in patients who suffer from these hyper, hypoglycemia syndrome.

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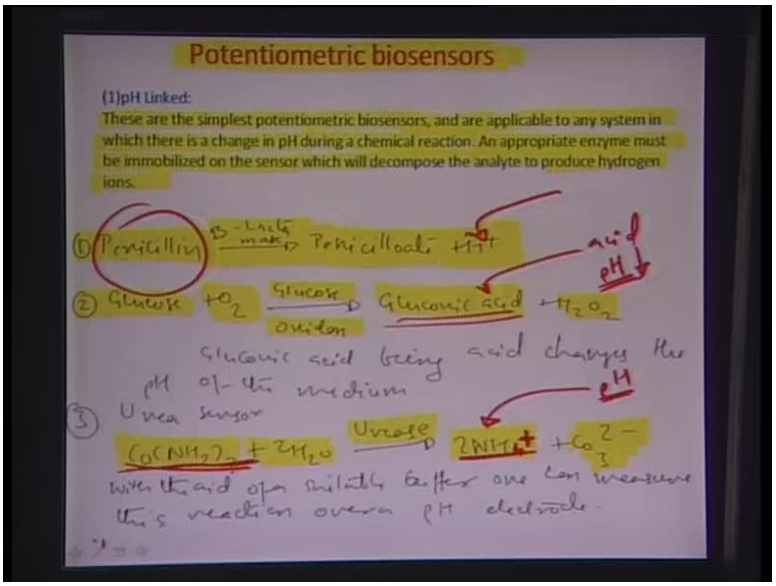

So, the way you detect the glucose is very simple. Again you try to oxidize Glucose by another enzyme called Glucose oxidase; this is equation number 2. Here we talks about how Glucose has been broken down. So, Glucose essentially in the presence of Oxygen and in the presence of this catalyst Glucose oxidase, it is an enzyme would convert into Gluconic acid and H 2 O 2.

A Gluconic acid being an acid would essentially change the pH of the medium. So, this is an acid and so it would be result in a decrease in the pH of the medium because of an increase in the Hydrogen ion concentration. Therefore, we can safely assume that if the - Glucose concentration can be deciphered by looking at the pH based on the formulation of Gluconic acid.

Similarly, another very important metabolite of interest is blood urea. Blood urea is essentially indicative of renal problems and the patient. Particularly, you know patient with kidney problems, renal problems, problems on the renal systems, they have this tendency of the blood urea level to be uncontrollably high sometimes. Therefore, it is important to try to find out what is the abnormality by looking at the urea concentration in the blood sample of the patient. Therefore, the one good way of looking at urea could be by again using a pH based electrode.

If you look at this particular equation here, it talks all about urea which is CoNH 2 whole twice, which actually kind of hydrolyses in the presence of water and this enzyme here

urease which converts into NH 4 plus. This is the acid which is generated - least acid which is generated in Co 3 minus 2. Therefore, an increase in NH 4 plus concentration would indicate again an increase in the reduction in the pH because it is essentially acidic, it is lease acid.

It has an additional hydrogen ion here it can actually go very well with the kind of electrode that we have been discovering or discussing earlier in the earlier slide by using the Ammonium Chloride solution of the electrolyte. Therefore with the aid of a suitable buffer solution one can measure this reaction like buffer solution like NH 4 Cl. As we saw in the last slide over a pH electrode, the pH measurement here would be indicative 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 for bio sensing, particularly of metabolites of Biological importance lead to the human body.

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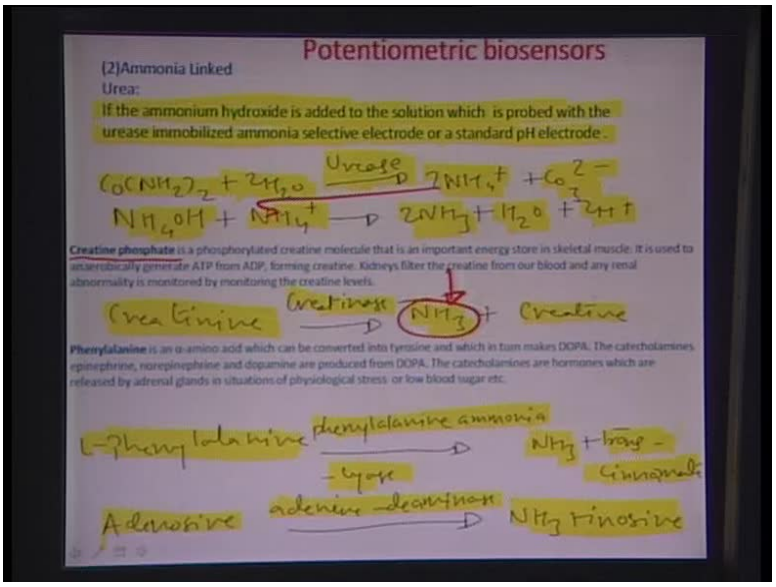

So, there are some other examples here that I would like to discuss. There can be Ammonia linked biosensors, where you effectively also unable to find out how the Ammonia varies. Again it is to a pH measurement as we saw last time using NH 4 plus and Cl minus - that is Ammonium Chloride electrolyte and equilibrating the Ammonia gas with respect to that and being able to tell the concentration of Ammonia based on the concentration or the change in concentration of the Hydrogen ion.

So, here again a similar kind of setup is used that instead of Chloride you use the corresponding Hydroxide. So, if the Ammonium Hydroxide is added to the solution which is being probed with the urease immobilized and urease if you recall is the enzyme which is able to catalyze urea into NH 4 plus Co 3, 2 minus, as we just said in the last slide earlier. This urea is immobilized, Ammonia selective electrode or a standard pH electrode would be able to very well define the amount of Ammonia in equilibrium with the Ammonium Hydroxide solutions; instead of Chloride we are using Hydroxide here.

Let us look at the reaction here CoNH 2 whole twice hydrolyses in the presence of water and the presence of urease enzyme to formulate 2NH 4 plus and Co 3, 2 minus. The NH 4 plus further actually equilibrates with the Ammonia Hydroxide solution here, NH 4OH to formulate 2NH 3. This is Ammonia plus H 2O plus 2H plus. So, in this stage or in the later stage where the Ammonia can be kind of equilibrated with NH 4 Cl or some other electrolyte we could measure the pH and be able to tell what does the Ammonia concentration and correspondingly what were the urea concentration, as borrowed here from the last step.

So, that is all you can measure urea independently also by just using Ammonium measurement method. Although effectively everything is based on pH measurement there are some other analytes of interest within the human body one which again tells very good information or gives very good information about the renal system is Creatinine.

So, Creatinine is essentially stored in a Phosphate form and this Phosphorylated form of the Creatinine molecule and it is an important energy store skeletal muscles essentially it converts anaerobically the ATP that is Adenosine tri Phosphate into di Phosphate form and this results in the formation of a Creatinine moiety. Therefore, especially in the muscle cells when you work out and the muscle is starved of Oxygen sometimes you know the human body’s sucks the blood essentially in the human body is a great transport of Oxygen.

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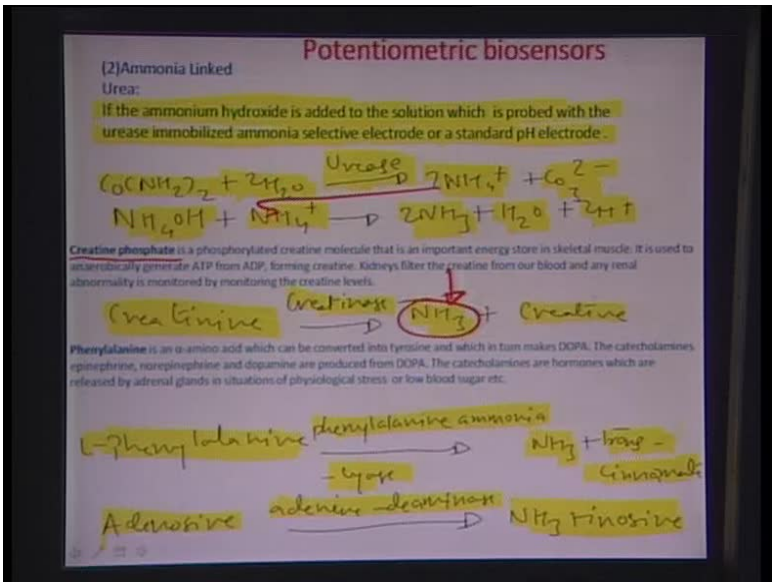

So, as run the heartbeat increases and why is that so because Oxygen has to be delivered at a huge amount or a huge rate into the various tissues within the human body. As you work it out sometimes the heart of a patient not being normal – abnormal, patient may malfunction due to which there may be a requirement of Oxygen. So, in that case how the body manages again in a very effective way, in a very effective way? So what it does is, it again converts the stored ATP the Adenosine triphosphate into the ADP or the Adenosine diphosphate form and this is the cost of creatinine and essentially this is done anaerobically - that means in the absence of Oxygen. Even though Oxygen reaching the particular muscle tissue is lesser in amount, still it is able to harness its energy or generates its energy, but creatinine produced within the body creates a problem, because it has to be filtered. The kidneys are effectively the filtration mechanism for the body as we all know and it at the blood – essentially, it is a purifier for metabolites like blood which flow through. Harmful products are secreted out of the human body: urea is one of them; blood urea is one of them; another is creatinine.

So, creatinine if you know generated or if it goes unfiltered is also indicative of that the kidneys are malfunctioning. So, we can very well find out renal health by looking at the creatinine levels within the human blood. So, creatinine again if you look at, is essentially with a mechanism of an enzyme called creatiness would decompose into to NH3, the ammonia and creatine.

So, essentially because there is an NH 3 component in this particular reaction would be able certain how much this equilibrium would shift to and what side? As the NH 3 is produced less or more, the NH 3 can be produced or measured of course by using a Ammonia based electrode as we have talked about before. So, the creatine level if it goes high it automatically means that it is at the cost of more creatinine and that means more Ammonia is generated. So, that is a way of finding out how the renal health is functioning of a particular body.

Another interesting example is to measure the Phenylalanine. It is an alpha Amino acid which can be converted into tyrosine which in turn makes a molecule dopa. So, dopa essentially is again its molecule which is responsible for generating these hormones called Catecholamines. There are about close to 12 endocrine glands with in the human body and I am sorry about 8 or 9 endocrine glands within the whole human body. These glands are essentially on the cause of secretion of these uniquely functioning organic molecules called hormones.

So, essentially what the hormones do is? They up regulate and down regulate certain Physiological processes within the body and there are these adrenalin. There is this adrenal glands within the human body which are able to generate this Catecholamines particularly in stressful situations. So in situations of extreme physiological stress or may be just low blood sugar giving the stress or causing the stress. There is a huge generation of these catecholamines.

So, this catecholamine is essentially a function of the dopa molecule or the presence or absence of a dopa molecule. So, these are all very interrelated. So, it all starts with this cycle from this basic alpha amino acid phenylalanine. Therefore, it is important to measure in phenylalanine content in a human body for understanding whether the endocrine gland is able to generate or the adrenal gland is able to generate sufficient amount of catecholamines which keeps the body kind of going in terms of in stressful physiologically stressful situations.

So, how do you do that? There are ways and means of finding out some of the Catecholamines by our like a epinephrine, norepinephrine, dopamine in all these different moieties are essentially produced from molecule dopa within the body. They are that the brute cause of all - that is the amount of the alpha amino acid phenylalanine.

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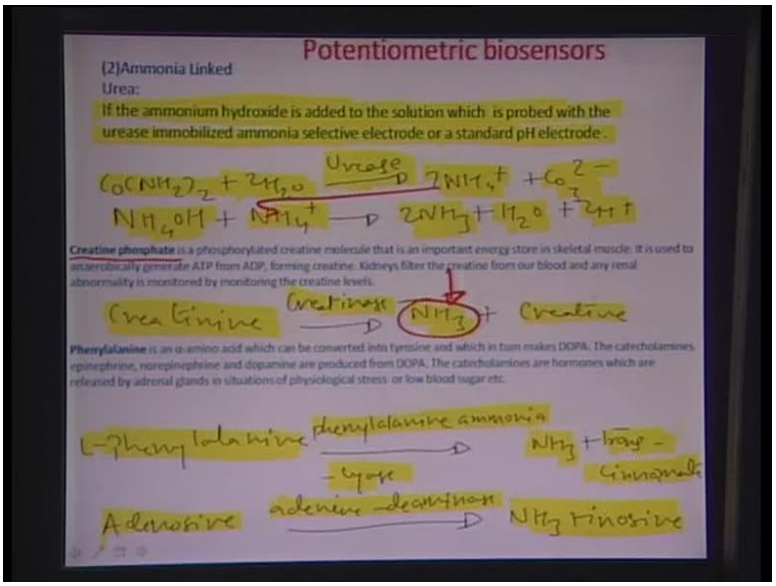

So, Phenylalanine is actually composed again by this molecule called Phenylalanine ammonia-lyase as can be seen here to convert or to get converted into NH 3 and this Transcinnamate. So, this is again another organic species from Phenylalanine. So, again measurement of Ammonia would be able to a certain how much amount of ion is there in the metabolite of interest of the other blood of the patient of interest.

Another kind of measurement that we often do is, this adenosine measurement. You have another enzyme here called adenine deaminase which converts into NH3 and inosine. Essentially, these are all measured by Ammonia electrodes. So, I have just trying to give through a few of these slides, some flair of what actually goes into the bio diagnostics. So, the clinical diagnostics area as regards human patients all the senses are very important from the point of view of you know measuring the different physiological conditions of the human body.

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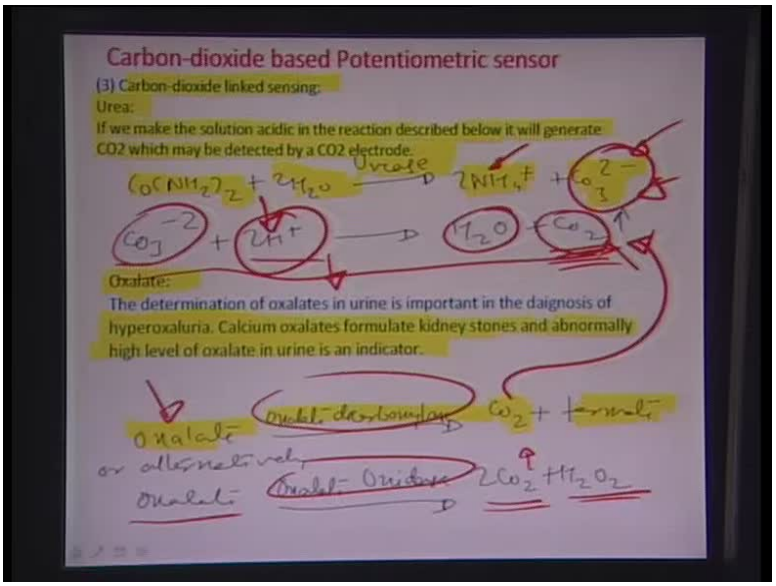

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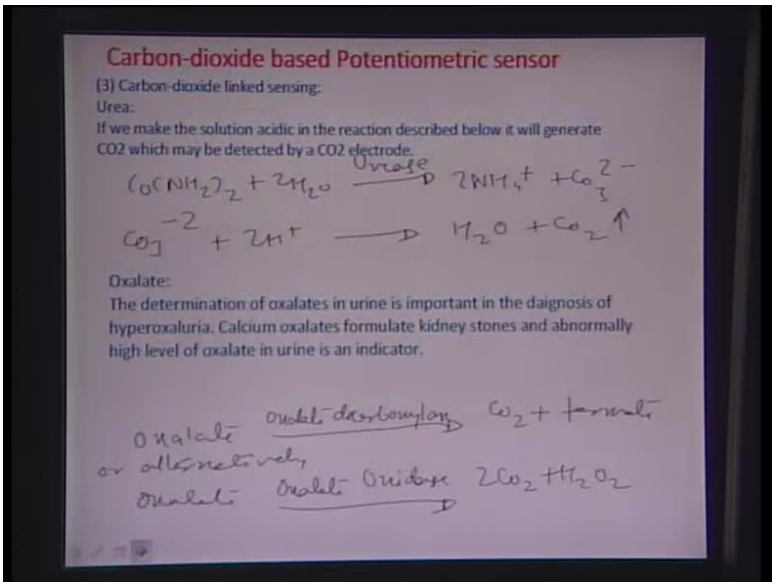

So, following this we can look into some Carbon dioxide linked sensing mechanisms. So, we have already covered pH as you did in the first slide, followed by Ammonia base, where there is different analytes of interest were recorded using Ammonia. Then you trying to essentially look at it through the pH electrode, but then equilibrating that with the some kind of salt solution of Ammonia and now we will be looking into Carbon dioxide. The process is pretty much similar as before you know you can make it using reading for NH 4 plus or you can make it using some kind of equilibrium between

Carbonic acid and this Co 2 or Co 3 minus 2 which is generated as a result of you know in a different Chemical steps.

So, we can again detect blood urea by using Carbon dioxide sensors. So, if we make a solution acidic in a reaction described below, it will generate Co 2 and this may be detected by Co 2 electrode. So, let us say urea CoNH 2 whole twice analyses in the presence of urease as we know it converts into 2NH 4 plus Co 3 minus 2. So, if I take this competent of this reaction instead of the NH 4 plus, so if I take Co 3 minus 2 component of this reaction and then converted by mixing it with some kind of a acidic solution where we have an excess Hydrogen ion, you get converted into H 2O and Co 2. So, it produces Carbon dioxide at the cost of reduction in the Hydrogen ion concentration. So, there is a change in pH and you could detect how much amount of Co 2 is produced, by looking at how much amount of reduction in the Hydrogen plus ion concentration would typically take place.

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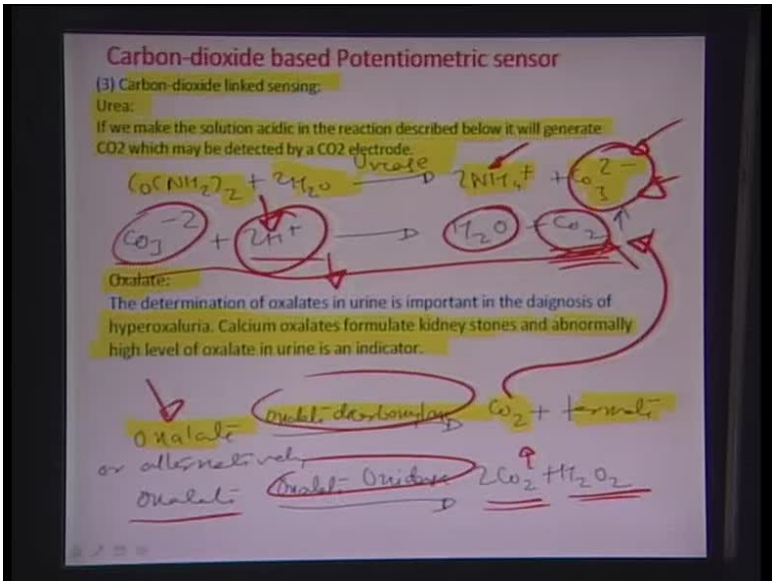

So that is how you can - using a Carbon dioxide based sensor able to tell urea. So, on one hand in the earlier slide you saw that we measured using the NH 4 plus, an ammonia bioscience sensor and in this case we are using this Co 3 minus 2 and a Carbon dioxide based electrode to measure the same level of urea in the blood sample.

So, at different times you know, you really need to use a different sensors based on the availability or unavailability of many you know species or conditions within the human

body. Particularly, in case of implantable sensors this is a very common problem that not all places of the body would have all analytes of interest. So, there are some places which are starved of a certain analytes and there is some other space where there may be abundance of another kind of electrolyte. So, you design electrodes or design your in sensor mechanisms based on what is available and what portion of the body.

Another important aspect is oxalate measurements. We all are aware of this critical problems related to kidney stones. So, that is this essentially also medically known as hyperoxaluria. So, essentially more amount of oxalates in the patient's blood again suggesting renal abnormality would mean the accumulation of such oxalates. Through that there may be problems related to a stones or you know this Calcium deposits in certain areas of the kidney or may be parts of the gallbladder. It is of importance to detect the oxalate level in the human blood just to monitor whether patient is inflicted with this problem of stones.

So, Calcium oxalates formulate kidney stones, as we are all aware of this and this essentially means abnormally high level of oxalates in the urine. How we can detect that is, again through a Carbon dioxide based sensor. So, there is an enzyme called Oxalate decarboxylase which can break down oxalate into Co 2 and formate and you can measure the Co 2 using an electrode like the above as you saw here. Essentially that if you put this in equilibrium with this particular reaction you might be able to formulate an idea of how much oxalate was. Where the patients blood alternatively you could also convert Oxalate using another enzyme called Oxalate-oxidase. In this case enzyme was different decarboxylase. This is oxidase and you get converted into Co 2 and H 2 O 2 again you could measure it using a Co 2 sensor by finding out whether the Co 2 level has gone up.

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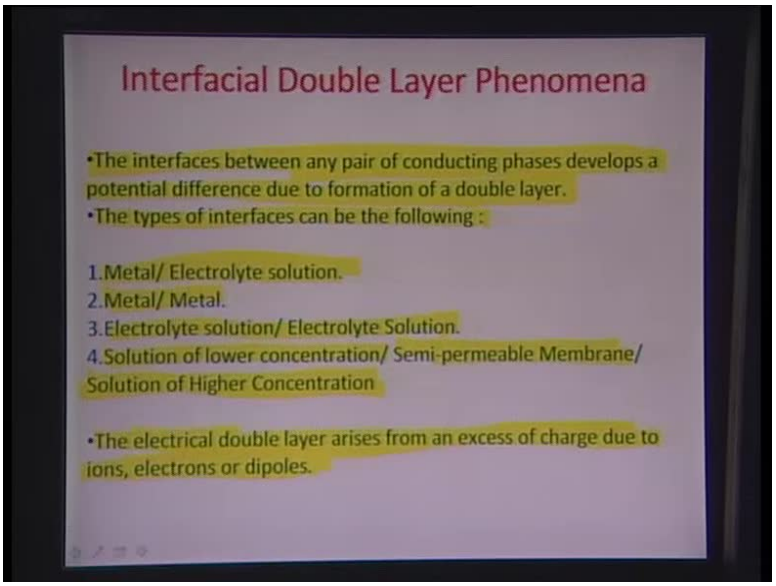

So, principle we have more or less covered different kind of gas sensors that are used for different bio applications. We would like to now go head with another very interesting and important phenomenon of what we call the double layer phenomena. As I told you before that in micro scale flows a very important problem is surface charges. The charges on a particular channel surface - micro channel surface would actually relate to developing density gradient of the opposite countercharge of the solution. This could be a basis of movement of two edges within small capillaries.

So, let us look at this problem a little more closely and try to make an analytical model for this particular problem. So let us say the interface between – so, let us first trying to find out what happens to the interface between a pair of conducting phases. A phase can be a solid electrode, could be to liquids. It could be you know liquid in a solid or it could be a solid in a solid. So at the interface between any pair of conducting phases there always develops a potential difference due to the formation of this double layer.

We have been often 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 metal electrolyte interface; it could be a metal on a metal; could be an electrolyte solution was another electrolyte solution; or it could also be a solution of a lower concentration separated by a semipermeable membrane with respect to the solution of a higher concentration. You may remember in one of our Electro Chemistry lectures we have

talked about this kind of electrode, where there are two different Oxygen concentrations and there is a boundary between these two and this can be an alternate means of designing an ion selective electrode.

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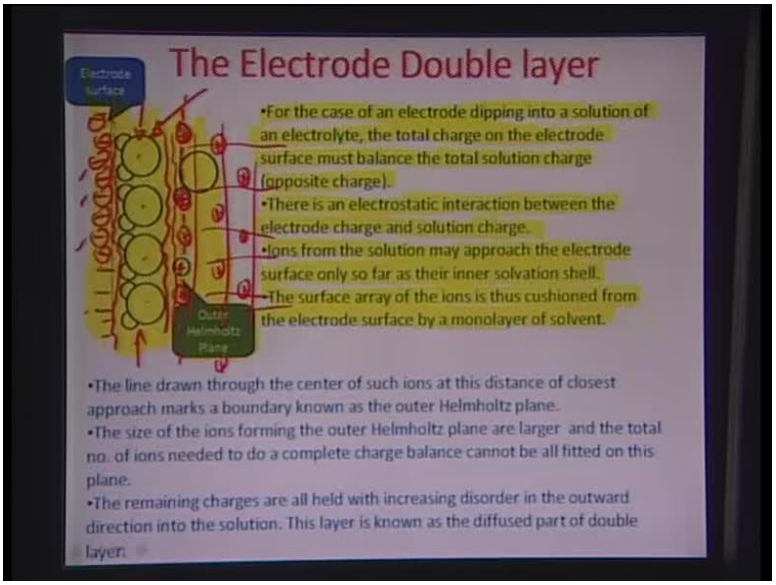

So, the electric double layer really if you look at it arises from an excess of charge due to ions, electrons, or dipoles. This is more kind of diagrammatically visually represented by this particular figure here. Essentially, this is representing an electrode and its behavior with respect to a solution which is adjacent to it.

Let us suppose that this electrode surface has a tendency of getting a negative charge. If you remember Zinc leaves the metal surface into the solution and gets into Zinc ion thus leaving the electrons on the surface of this particular electrode. Therefore, there is a negative charge on this particular surface and there is a positive ion or there is a bunch of positive ions which have left the surface into the solution which are formulating this particular layer. So essentially, when this ion separate out they have this small layer of water as you know that this interface between a solid and a liquid is an interface between a solid electrode and a liquid. So, the liquid always aqueous in nature almost always aqueous in nature. So, there is a tendency of this layer of water or water molecules to 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 electro double layer and this have represented here is essentially the formulation - you know the formulation of the double layer. Essentially, here the interesting thing to be seen is that a number of electrons being small as is always almost responsible for creating a certain charge density on the surface of this electrode has a post to the number of positive ions which are in the solution. So, the electrons here in the surface are densely located and they would create dense amount of charge because of the smaller sizes. The electrons are always smaller in size than the corresponding metallic ion solution.

So, one of the - you know the outcomes of this kind of a size difference between the negative and the positive charge centers would essentially result in a thin amount of charges because of their size restrictions or its bigger size. 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 than the negative charges correspondingly in due to the electrons on the surface of the electrode. The first layer really which is presented here, which is just about separated by this layer of water molecules, the 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 these layers with kind of still are able to hold positive charges and the density reduces with distance again. The neutralization would occur somewhere in the bulk of the solution. Therefore, there would be layers of charges in the solution with decreasing intensity or decreasing density of this charge till and until and the whole negative charge on this electrode is neutralized because of the positive charges in the solution.

So, this brings us very interesting characteristics. It essentially tells us that you know whenever there is a surface in close proximity to a solution like this, there would always be a distribution of charge of the opposite kind as the surface more into the bulk of the solution. That is number 1 and number 2 is that if we have this distribution of the opposite charges to that of the surface on the bulk, then we can as well use these to flow the whole fluid, particularly when the length scales that we are talking about is close to the length scales this bulk charge layer.

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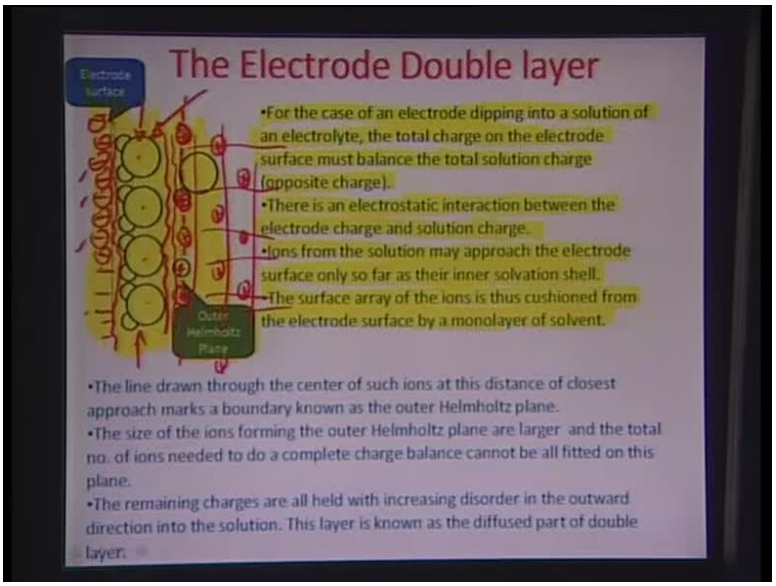

So, we essentially from the days when it was first this theory was proposed, identified the first layer of charges here which is close to the electrode as also the outer Helmholtz plane. So, the first layer of charges which is directly facing after this water layer is a crossed over from the electrode is known as the outer Helmholtz plane. So, this particular this other layer which is going into the bulk of the solution is also known as you know the bulk charge of the particularly solution.

So, the even 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 solution charge, it is also the opposite charge. Therefore, there is a tendency of a distribution of charge within the bulk for obvious reasons. So, there is an electrostatic interaction between the electro charge and the solution charge and ions from the solution approach the electrode surface only. So far as their inner solvation cells shells and the inner solvation cells is essentially single monolayer of water which is separating both the ion of interest and the ion in the solution. The negative charge on TH electrode and the surface array of the ions is thus cushioned from the electrode surface by this monolayer of dielectric, which is water. Most of the electrolyte is our actually immersed in an aqueous based solvents; so, you have water as the canning medium in most of the electrolytes.

So, the line gone through the center of such ions at this is distance of closest approach marks a boundary. We call this the outer Helmholtz plane and the other portion of the charge that cancelling charge were away from the electrode as the bulk charge on the solution and the size of the ions forming the outer Helmholtz plane the larger and the total number of ions need to do a complete charge balance and because they cannot be fitted on this one plane, they have to go in to the bulk. So, this is also known as the bulk charge or the diffuse layer or the diffuse charge in the solution.

So, the remaining charges are all held with increasing disorder in the outward direction into the bulk of the solutions. So, they are also known as the bulk charge of the solution or the diffused part of the double layer. So, it is called the diffuse layer of the diffuse charge with respect to an electrode. So in essence, this is the dynamics of the double layer which is formulated when electrode or one phase be solid or liquid comes in contact with another phase.

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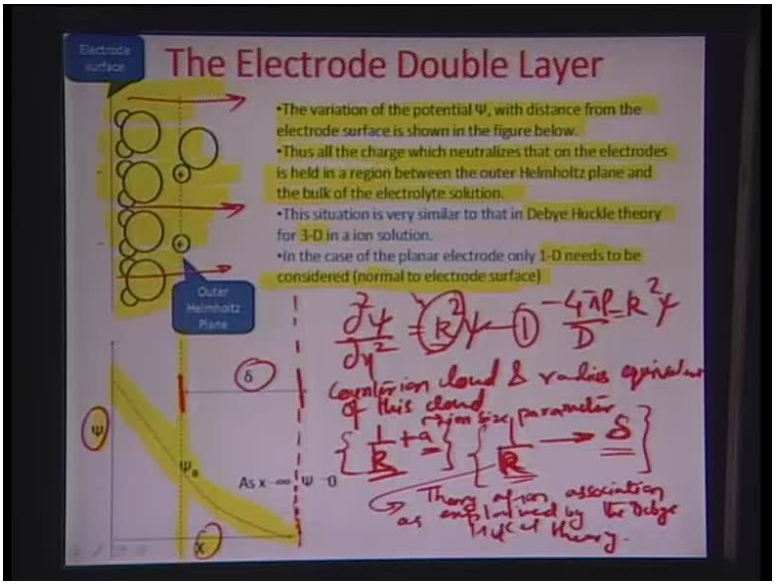

So, let us do some detailed modeling and studying of how we can use Poisson's equation to find out the behavior of potential as we move in an outwardly direction from the electrode to all the way to the solution. So, couple of interesting things are that if we plot the potential with respect to the distance, the variation of the potential let us say psi, in this case with distance from the electrode surface is linear as long as is between the inner

solvation shell or layer. Then it falls down rapidly into the bulk as it crosses the outer Helmholtz plane.

So, the charges which utilizes that on the electrode is held in region called outer Helmholtz plane. So up to outer Helmholtz plane the electric field drop as linear as if it shows that in this region really it is resistive drop, you know because the only thing which is available here is a layer of dielectric. So, it is a layer of huge resistance. So, you have a case here in this particular region where there is a drop in potential, it is a resistive drop and then in this particular portion as we 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 fluidics. So we will be calculating what the potential here is and what may be the distribution of potential as we go from this particular outer Helmholtz plane all the way up to about the point where the diffuse layer ends or the bulk charge layer ends the solution.

So, the situation is similar to that of the Debye Huckle theory as we had generated for a single point time. Of course, this case it is not a 3D case, it is more a 1D - 1 dimensional and this needs to be considered in the direction normal to that of the 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 of the potential, phi with respect to that direction X.

So let us look at into little bit of modeling. So, essentially here what you see in the one dimensional case - really there are 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 4 psi rho by the – so, is equal to k square psi, this is something I am borrowing from the earlier Debye Huckle equation that we just about solved in the last lecture - last three lectures.

Give me a minute, this is the square of K. Some interesting facts about this outer Helmholtz plane that if you remember when we talked about the counter ion cloud and the radius equivalent of this cloud, we generated a term which was equal to 1 by K plus a, a was essentially the ion size parameter. The iron size parameter and k was something that we assumed to be the equivalent of whatever the charge term was in the Poisson's equation here.

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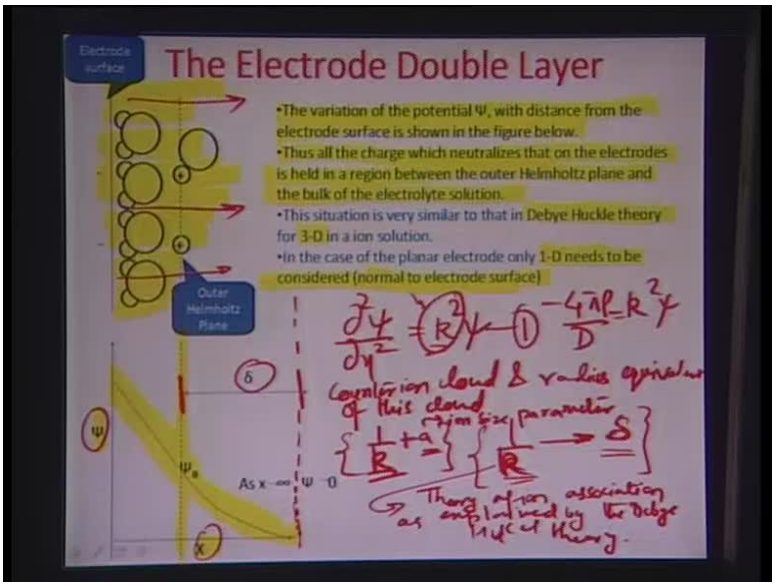

So, this is essentially the effective ion radius. In case of the electrode from 1 by k is replaced by thickness of the diffused layer delta. So, here to see really delta is away from this outer Helmholtz plane all the way when the potential drops down to 0. The diffuse layer of charge of the - bulk layer of charge ends really up to this point here when the potential 50 and so delta is essentially the distance between the outer Helmholtz plane. This particular layer with the potential ends up to be 0 or where the diffuse layer ends in the bulk of the solution.

So the 1 by k here is replaced by delta this actually comes out from another theory which is beyond this scope of this course. It is of the theory ion association as predicted by the Debye Huckle theory. So I will just assume here that this 1 by K is equal to delta in case of an electrode just to make life simpler. We will not be really looking at why that is so, you can just remember this and actually you know later on may be do a reference search where you can see the theory of ion association as explained by the Debye Huckle equations.

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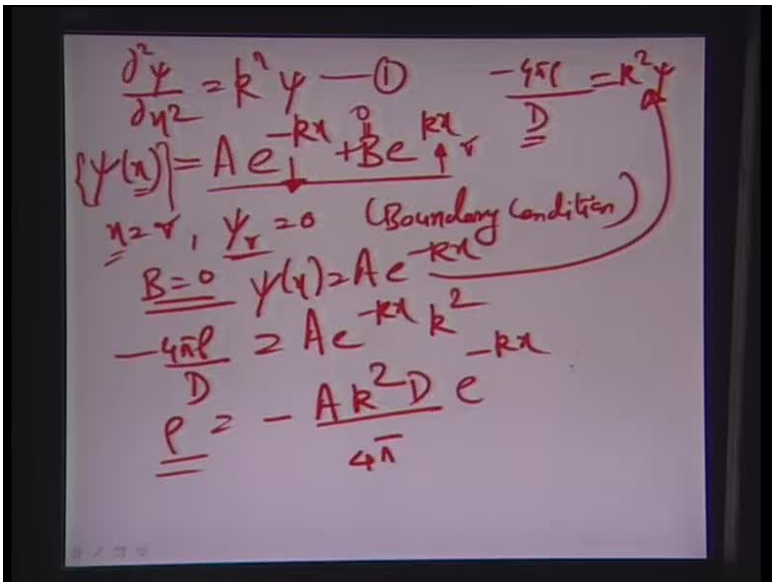

So, then let us try to solve this Poisson's equation here equation number 1 and see what the solution would look like about the form of the solution would be like really. So, essentially the d square psi by dx square is equal to square of k times of psi. The general solution for this kind of an equation can be represented as psi effects, mind you psi is a potential drop is already in one direction that is perpendicular to that of the electrode is A e to the power of minus Kx plus Be to the power of minus Kx.

So, that is what the solution is for this. I am sorry this is plus Kx - this thing is plus Kx, this is were a general solution of this equation 1 in a differential equation here would be looking like to apply the boundary conditions x equal to 0; or x equal to infinity; the psi infinity is actually 0. So applying this boundary condition this can only happen if B is 0.

So, if x is infinity this term here goes all the way up to down to 0, but this goes to infinity and therefore, the only way that psi infinity here - that the potential at infinity is 0 could be B 0 because then it would take care of this infinitely growing term this automatically 0 by virtue of e to the power minus Kx converging to 0. Therefore, psi x is really A e to the power of minus Kx.

So, we already know that the real Poisson's equation is really in terms of the charge density. So minus 4 pi rho by D; D was the dielectric constant, rho is the volume charge density and that was equal to this case course psi as we have talked totally. So if you put the psi value here in this particular equation, we get minus 4 pi rho by D equals A e to

the power minus Kx times of square of K. Therefore, the charge density also can be represented as minus A k square D, divided by 4 pi e to the power of minus Kx. So that is what the volume charge density row would be in this particular case.

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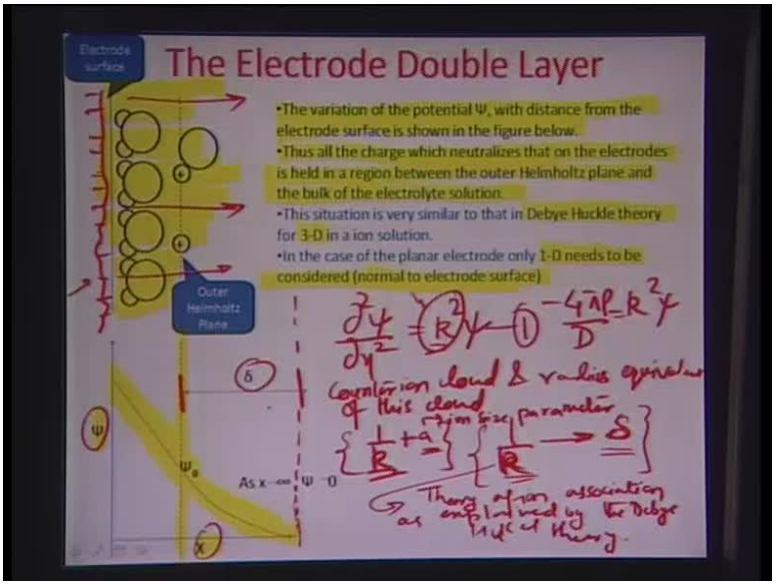

So let the charge density on surface of the electrode be sigma. We are making a presumption here that because we were talking about an electrode surface, as you look at here this area - the dynamics of the charge density on the bulk layer or the outer Helmholtz plane is really driven by the amount of charge density on the surface of the electrodes. So, it is a 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 the diffuse layer or the outer Helmholtz layer.

Only the factor that I would like to mention here is that you know the basis of this density of charge would be the dependency on the surface of a particular electrode. In case of micro channel flows, electro kinetic micro channel flows if the surface is Silicon, there would be a certain bond density and there would be this huge number of Silicon bonds on the top of the surface which would give it to a negative charge, a psi, o minus kind of you know moieties is as it exposes to certain pH of certain solution of a certain pH.

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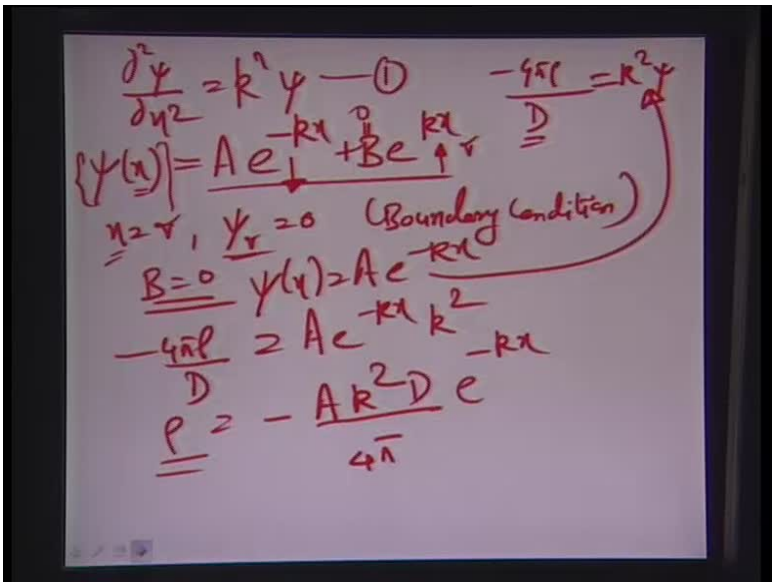

So, if this kind of a treatment is given on the surface there is a tendency of the fluid to develop a diffuse layer which is a positive charge. There would you counter ion glad which is a positive charges and therefore, the surface charge density would be a function of how many active sites are there on the surface really 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.