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Lecture - 31 Dissolved Oxygen Sensors – I

Welcome to the lesson 31 of industrial instrumentation. In this lesson and the subsequent lesson; that means lesson 31 and 32 we will discuss basically the dissolved oxygen sensors. Dissolved oxygen sensors was not that important I mean some time bad, but due to the evolutions of the biotechnology in a very big way. So, this is to be considered very thoroughly. And also it has a tremendous application, because the newer the biodetectors are coming up in the markets. And lots of new product are coming like I mean medicines then antibody which is a basically I mean the growth of cells.

So, and in this particular I mean situations we must consider the dissolved oxygen sensors. That is one of the only sensors, which can measure the dissolved oxygen concentrations and the partial pressure of the oxygen in a liquid medium? And this will give you a lot of other informations which is not exactly measurable which usually we have to estimate. So, that is a reason this is also this I mean this dissolved oxygen sensors we brought under the industrial instrumentations.

And it has also I mean I should say that it is also used as a I mean measurements of the dissolved oxygen's in a environments likes the in the water treatment plans. And the water discharged where it is in the, because there is some safety level of the water. I mean dissolved oxygen concentration, which is essential for the living animals like fish and others and all those things that is why that is the reason we have taken this. Now, let us look at the contents of this lesson 31 dissolved oxygen sensors.

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The contents are in this particular lessons we will basically we will see this is a probe. Actually the signal conditioning circuits all those things will be discussed later on. So, basically like a ph probe we will discuss that is of oxygen probes. We have anode and cathode we will see all this in details we will discuss at various construction. What is the theory behind this? What is the, I mean chemical equations inside this, all these things will be discussed typical constructions dimensions all those things will be discussed.

Polarographic electrode; there are 2 types electrodes we will find one is a polarographic electrodes another is galvanic electrode one need power supply other do not need. So, we will consider the one which has which usually not I mean does not need any power supply or a bias that is called the galvanic electrode. Then basically we will consider theory of operation the detailed constructions of these electrodes will be discussed in the subsequent lessons; that means in the lesson 32.

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At the end of the lesson the viewer will know the working principles of the dissolved oxygen sensor. Electrodes of the dissolved oxygen probe; what are the different electrodes? 1 layer and 3 layer model we will find that there are 2 types of model available. One is called 1 layer model of the dissolved oxygen sensor another is a 3 layer model of the dissolved oxygen sensors. Then we will discuss the reaction at anode and at cathode of the electrodes. So, there are chemical reactions which actually occur in the both anode and cathode these also will be discussed in details.

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Introductions, let us see the dissolved oxygen sensors or electrodes have been widely used both in research and industry. In the academics also we are using this probe to measure the dissolved oxygen concentration and also industries also where they are producing some biotechnical product, biotechnological product like medicines. And all those things like your antibody then antibiotics all those things you will need this type of sensor. Now, compared with the chemical analysis, now other way you can measure the dissolved oxygen concentrations or partial pressure is a chemical analysis. That means, you take out a sample and you take the make the chemical analysis.

There is lot of limitations of that type of I mean chemical analysis, because what will happen? That you have to make offline you would not get it is not very easy to get electrical output. So, if you want to control the dissolved oxygen concentrations inside the liquids you cannot do it. So, in that case this I mean the membrane based electrode which is called the, or membrane covered electrode offer the several advantages. That is the reason you can compare with the chemical analysis the measurements of dissolved oxygen's in water by membrane covered electrode offers several advantages.

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They are as follows what are those? Simplicity the design is very simple less interference by other solutes in the water it does not matter with liquids. Because if you have chemical analysis if you want to measure the partial pressure of oxygen or the dissolved oxygen concentration. So, they in turn if we have some I mean other solutes that will also react with your sample. So, that will create problem and you would not get the exact value. In-situ measurement with lower time constant, you known in-situ measurement is basically new terms in the instrumentation that is basically means on the site measurements. In their wire reactors you will find that there are various parameters which usually we measure we cannot measure. But those also when you write I mean straight equations you will find that those parameters are to be incorporated. One of those is like concentrations I mean dissolved oxygen I mean concentration is 1.

Then we have a concentration of the product, concentration of the subtract all those things will be unmeasurable. It is you cannot measure those quantity only you can online measurement is not possible you have to take out and there is there are few in-situ sensors have been reported, but it is not much of use. So, only parameters which you can measure are the dissolved oxygens concentrations by the electrical output. So, it is an insitu measurement that is on the site you can immediately measure you do not have to make a chemical analysis of your sample. Continuous measurement is possible whenever you can make the continuous, because it is the electrical output.

So, the continuous measurement also I mean will be there also accordingly if the continuous measurement you have then. Obviously, you can do you can make the control also. So, that you can precisely control the dissolve oxygen I mean in a particular medium or liquid. Real time control that is I just I have said the real time control of dissolved oxygen concentration in bioreactors or waste water treatment plant is next this I was talking what you see there are many places the water are discharged. Now, if you discharge those water as it is in a I mean environment that will create, because the plants and animals marine animals. They need some sort of oxygen in a in a when they survive want to survive in a particular liquid.

There is a particular concentration that is the reason you find that if that concentration goes down the fish and other animals will die. Now, once you discharge that waste water. So, in an environment; that means, in a swamp or something like that. So, upon you must treat that you must know that what are the dissolved oxygen concentrations or partial pressure of oxygen's in that particular liquid. In that case also we need some insitu measurement. So, that we can take care and make some artificial I mean increase of dissolved oxygen's in that particular liquid of that waste water plant. And bioreactor as I told you it is an, I mean vital parameter which is only measurable part not only that it is only measurable parameters in the bioreactors.

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Bioreactors actually I should define as it is basically it is basically a medium or reactors where the biological cells are grown. That is the reason we are calling instead of calling simple reactors you know out of chemical reactors we are calling bioreactors. Because cells are grown it does not matter mater whether it is animal cell or simple yeast these are all bioreactors. Now, dissolved oxygen sensors have been developed for different areas to meet the requirements of the specific applications. There are various applications and accordingly the people need different types of dissolved oxygen concentration measurement. The examples are the steam sterilizable DO 2 probe suitable for bioreactors. Now, you know the bioreactors if I take an example of the bioreactor it looks like this if I take a white page it looks like this.

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I have a reactor here this is a star tank reactors I have a starrer. It consists of blades 3 or 4 5 blades. So, it will rotate to look like this there are several blades. Now, this is called impeller of the bioreactor, this is a tank in which we have medium. So, tank will look like this 1. So, tank is liquid is there and it is continuously rotating either in clockwise or anticlockwise directions. If it is there, so what we find that there will be some eddies will be formed which will look like this. Like this 1 some swirl will be formed this is eddies, this is tank and this is swirl. Now, it is continuously rotating and if you increase the rotation. So, what will happen? This is called CSTR, CSTR is the continuous start tank reactor. This is called the continuous start tank reactors we can see here this is called the continuous start tank.

Reactors are various type you can have a bubble column reactors you can have a CSTR it is a continuous start tank reactors. Now, the basic principle is nothing like if you increase the blades blade speed by, because this impeller is rotated by a motor. If you increase the motor speed what will happen? That you see the oxygens is very difficult one thing you must know that it is very difficult to dissolve oxygens in a liquid. Now, only place is where the oxygens will be will be dissolved is through this through this top surface. To the top surface and top surface whenever these oxygens are getting in contact it dissolves and it is this top surface is getting saturated with oxygen.

So, this top surface is to be refreshed; that means, this lower surface of the water will go to the top like this 1. So, that it will get more and more oxygen. Now, if we if we

increase the speed of this impeller what will happen in this CSTR continuous star tank reactor? There is a frequency of this water, which is coming from the top from bottom to above the refreshing I mean of this water top surface will be faster and faster. If it faster then what will happen? That more and more oxygen will be dissolved if you lower the speed. So, the dissolved oxygen concentration also will be also, will decrease. This is a basic principles of the bioreactor, because of cell which will go inside the reactor depends on the oxygen concentrations.

It is does not end here, because these dissolved oxygen concentration is a very vital parameters in any bioreactor. Because that you know that the cell growth by if I look at the cell growth that whenever if I continuously measure this dissolved oxygen concentration. So, you will find that initial stage what will happen that? Initial stage there will be good consumptions of the dissolved oxygen. So, the cell concentration that; that means, the dissolved oxygen concentration will fall slowly fall, because it is more and more cell is getting. Now, after some time we will find that the this concentrations is getting saturated that, That means, at during that time the cells are no more no more consuming any oxygen from the liquids.

So, the health of the cell; that means, the growth of the cell can be predicted also from the dissolved oxygen sensor the output of it might be the current or voltage. Now, after some time we will find that the concentrations are getting increased; that means, during that time thus it is cell is totally saturated. There are no more cell will be grown that is the time we should take out the cell from this biological cells from the reactors. So, I can see that the dissolved oxygen plays a key role not only to maintain the growth of the cell. But also to tell that whether the entire reaction has total I mean is complete also the time when you should take out the cell from the reactor itself. So, these will this is very important and this is the only parameter as I told you I mean in the bioreactors which is measurable.

Now, this I mean if you refresh these things I mean continuously what will happen? This I mean it will be getting newer and newer surface on also you can do one thing. That means, if there is if there is oscillation of this liquid columns we will find at the dissolved oxygen also will oscillation of the liquid columns. We will find that; that means, suppose if you have a liquid here in the two columns, we will find if you may by force if you can make the oscillations. So, that the liquid the dissolved oxygen will be also getting the oxygen's will be dissolved in the liquid through the falling stream

through this one. There is another way there are also bubble column reactor then bubble column reactor, what will happen you know if I take a new page.

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The oxygens are passed through a pipe and it is going out rightly this 1 through in the liquid. So, here what will happen? Again you will find that the oxygens are getting dissolved through this bubble column? If there is a various constant I mean various method of desiccating I mean getting oxygen dissolved. But you have to measure that is either through to get a continuous measurement either you have to make through a galvanic sensor or through a polarographic sensor.

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Indian Institute of Technology, Kharagpur Dissolved oxygen (DO2) sensors have been developed for different areas to meet requirements of the specific applications. Examples are ⇒ Steam sterilizable DO₂ probe suitable for bioreactor. Oxygen micro-electrodes for DO₂ measurement in human tissue. Fast responding sensor for respiratory gas analysis. Measurement of trace of oxygen in boiler feed water 6.54 6/49

So, that is called as to now, this reactor is you know you have to know basically it will be sterilized. So, this DO 2 probe there are some DO 2 probe which is suitable for making sterilizable; that means, this probe is to be sterilized how will you sterilize? You will I mean at the, you have to be when you heat the entire reactor along with the along with the probe DO 2 probe at 120 degree centigrade which by superheated steam you have to do. That means from the boiler you have to pass that team. So, that the oxygen will be is a sterilized.

Oxygen micro electrode for DO 2 measurements in human tissues then a fast responding sensor for respiratory gas analysis, because in many cases the patients need to feed the oxygen. So, that during that time; that means, you must know that, because pure oxygen is very difficult there is some problem form of impurity is always there. So, how much is impurity also you can know from the dissolved oxygen. Measurement of trace of oxygen in boiler feed water because boiler feed water is also necessary in a thermal power plant the feed water is how much oxygen is there. So, that also can be online measurement is possible through this DO 2 probe.

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Three broad areas I should say where the measurement of DO 2 concentration is essential are biochemical engineering then microbiology biochemical engineering. Obviously, includes the bioreactor microbiology and environmental engineering; that means, waste water treatment plant and all those things. So, there also we need to

measure the dissolved oxygen concentration. So, the partial pressure of the oxygen in the waste water which is getting discharged to the environment.

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Now, principle of operation there we have polarographic electrode as I told you first will discuss the polarographic electrode then will discuss the galvanic electrode principle is basically same one need bias other do not need. When an electrode of noble metal such as platinum or gold is made 0.6 to 0.8 volt negative with respect to the reference electrode made of calomel or silver chloride in a neutral potassium chloride solution. The dissolved oxygen is reduced at the surface of the cathode. This is a basic principles of the a dissolved oxygen sensor it does not matter I mean whether it is polarographic or galvanic.

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This phenomenon can be observed from a current voltage diagrams called a polarogram of the electrode. This is called the polarogram we will see the polarogram very soon. As shown in figure 1 a, the current increases initially with an increase in negative bias. Then it reaches a region where the current becomes essentially constant. It will be very clear from the next slide. In this saturation region or the plateau region of the polarogram the reaction of the oxygen at the cathode is so fast that the rate of oxygen reaction is limited by the diffusion of the oxygen to the cathode surface.

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This is our Polarographic electrode you see this is a polarogram sorry polarogram you see here. This is you see this is a negative bias we are giving as we increase a negative bias you will find that the output relative current output will increase. So, at that some position we will find there is saturation. And after there is a sudden increase that is a different thing we will find there is saturation or a plateau region. So, a percentage of oxygen, so the partial pressure of oxygen it is increased as you can see.

So, the, it is 1.5 as you increase the bias you are getting the saturation then it increases. It is a with the concentrations of the oxygen is 7 percent and if you increase the bias initially it will make a linear then it will be at saturated like this 1. Now, in the subsequent usage this is a calibration curve. So, I have plotted here the bias voltage here bias voltage is 0.7 volt I have plotted the percentage oxygens on the x axis and I am getting a relative current. So, it is almost linear curve as you can see this is called the calibration curve.

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When the negative bias voltage is further increased, that the current output of the electrode increases rapidly due to the other reactions let us go back.

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You see as shown in figure the current increases initially with an increase in the negative bias is not it as you increase the negative bias increase the negative bias current increases then it reaches a region where the current becomes essentially constant. In this saturation region the plateau region of the polarogram the reaction of oxygen at the cathode is, so fast that the rate of reaction is limited by the diffusion of oxygen to the cathode surcfae. That is a reason I am getting a plateau region or a saturation region.

This you see as you increase in the bias it slowly increases then it is, so fast that is why I am getting a saturation region here same as you increase a bias for a particular concentration negative bias it increase. Then it is gets to a plateau region after that is a slight there is a drastic increase of the current. When the negative bias voltage is further increased the current output of the electrode increases rapidly due to other reaction mainly the reduction of the water to the hydrogen. So, that is a different thing we are not concerned with that region.

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Now, if a fixed voltage in the saturation region of the polarogram is applied to the cathode. Then the current output of the electrode can be plotted for different dissolved oxygen concentration that is figure 1 shows such a calibration curve. What is it saying that? The fixed voltage in the saturation region of the polarogram is applied to the cathode fixed voltage. I have given in the previous curve you see we have given a fixed voltage of 0.7 volt right cathode.

Then the current output of the electrode can be plotted for the current dissolved for the different dissolved oxygen concentration. Current outputs are plotted on the x axis dissolved oxygen. Now, percentage partial pressure of the oxygen in the figure b shows that which is called the calibration curve of a polarographic electrode for dissolved oxygen measurement. It has to be noted that the current is proportional not to the actual concentration, but the partial pressure it does not matter say the partial pressure is the high the concentration also will be high.

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But due to the activity or equivalent partial pressure of the dissolved oxygen which is often referred to the oxygen tension. A fixed voltage between 0.6 to 8 volt is usually applied as the bias voltage or polarization voltage when using silver chloride as the reference electrode.

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When the cathode comma anode and the electrolytes are separated from the measuring medium with a plastic membrane which is permeable to gas, but not to the most of the ions and when most of the mass transfer resistance is confined in the membrane the electrode system can measure the oxygen tensions in the various liquids. So, what is the main, what is the key a plastic membrane which is permeable to gas, but not to the most of the ions.

So, the gas will be permeable through this medium and through this membrane and when most of the mass transfer resistance is confined in the membrane the electrode system can measure oxygen tensions in various liquids. This is the basic operating principle of the membrane covered polarographic DO 2 sensor. This is the basic requirement or basic operating principles of the membrane covered polarographic DO 2 sensor in both the cases we will find we may use the membrane we will be clear after some time.

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A polarographic electrode is shown in figure 2 for polarographic electrodes the reaction are as follows. I will show the figure 2 after sometime reaction at cathode O 2 plus 2 H 2 O electron gun plus 2 electron is equal to hydrogen peroxide plus hydroxide H 2 O 2 plus 2 electrons it is 2 hydroxide reaction at anode AgCl it will be AgCl plus e 1 Cl is negative discharge. So, that it will release 1 Cl and will get AgCl with 1 electron.

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Overall reaction 4 Ag plus O 2 plus 2 H 2 O plus 4 chlorine equal to 4 AgCl plus 4 hydroxide iron. The reaction produces alkalinity in the medium of quite; obviously, you can see 4 OH. So, it will make it alkaline and a small amount of hydrogen peroxide is also produced that we have seen in the previous.

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Now, this is our Polarographic electrode you can see this electrode it is basically a cylindrical in nature. You see I have an ammeter which is basically a micro ammeters we have a, we have a cathode there is a membrane this is a membrane you can see this is our membrane. You can see that this is our this is a membrane permeable membrane the gas

can be permeable most of the irons will be blocked here, because this entire thing please note will be dipped in the reactor itself or in the waste water. This is a tank or the reactor tank or in the waste water this entire thing is be dipped entire assembly. So, this whole assembly this is our probe this is our total probe. You see electrolyte is here we have put anode here insulation is here there is a membrane and there is a cathode.

This is the diagram and we have given a bias we have seen that if we increase bias; obviously, that I mean output will increase with the concentration. Now, for a fixed bias what will happen if I; obviously, I will for different increased concentrations. I will get the higher relative current outputs, which will be utilized for the measurement or for the control of the I mean dissolved oxygen partial pressures in the liquid. Now, if I draw the actual diagram it will looks like, because you see this electrode as I told you it should be combined in the tank and this entire electrode. This entire electrode actually will find that it will be in the form of it will be in the form it is a very handy things and it will be in basically cylindrical in-situ let us look at the diagram.

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Let me take a white page it will look like this one see it will look like this you see that a cylindrical in shape this entire thing. So, it will come down here sorry it will now, we can take a new page and see it will come down here and we have a probe here and go down there is an anode cathode this is cathode. So, entire thing like this one, so there is another one it looks like this one the membrane is here membrane is here. We need as better supports and all these things that is I am not discussing because it cannot hang in a

air as you know you need a support and this will work as a your anode and this will work as a cathode of your systems. And we have a glass cylinder the entire thing we put on a glass cylinder it looks like this. It is coming like this I mean a glass cylinder like this one it will look like this.

There are various dimensions I mean typically in electrical surface we made it like this one and we put Teflon here now, it is Teflon is very extensively used which is 100 micron thicknesses. This is this diameter is 2 centimeter sorry this diameter is 2 centimeter and this diameter is 1.4 centimeter 4 centimeter like this 1. And this is quite small this diameter is 0.75 centimeter. These all the dimensions it will go to anode and this will also, will get a signal here. I am not showing the bias, because the galvanic also has a same type of forms and this can be made this can be made or anode can be made of lead this lead and cathode can be made of silver. These are polarographic electrodes insulation we have membrane here where I can use Teflon here.

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This is a galvanic electrode. So, this is we have shown that is an ammeter there is no bias electrolyte is here anode insulation membrane and cathode.

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Galvanic electrode the galvanic electrode is shown in figure 3. The galvanic electrode is different from the polarographic type in that it does not require external voltage source for the reduction of oxygen at the cathode that is the basic difference.

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When a basic metal or base metal such as zinc lead or cadmium is used as the anode and a noble metal such as silver and gold is used. And the cathode the voltage generated by the electrode pair is sufficient for a spontaneous reduction of oxygen at the cathode surface. In IIT Kharagpur actually in our Bioprocess Instrumentation Laboratory, we have developed a DO 2 senses, which is giving quite good response where we are using lead as an anode and silver as a cathode.

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The electrode reaction of the silver-lead galvanic probe is as follows. Reaction at cathode an O 2 plus 2 H 2 O plus 4 e 4 electrons equal to 4 hydroxyl ions. Reaction at anode Pb to it is I mean positively charged then and 2 electros, so look like this. Overall reactions will be O 2 plus 2 Pb plus 2 H 2 O equal to 2 Pb O H 2.

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As shown above the oxygen is reduced via 4 electron reaction this reaction is called 4 electron reaction. And unlike the Polarographic probe these electrolyte does not

participate in reaction, but the anode is gradually oxidized, that is one problem with this unlike the polarographic probe the electrolyte does not participate in the reaction, but the anode is gradually oxidized. Therefore, the life of the probe depends on the exposed surface area of the anode.

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Whether the polarization voltage is applied internally in the case of galvanic or externally which is applied in the polarographic the operating principle of the electrode remains the same. Operating principle same whether you applying a galvanic I mean I mean polarographic in the case we are giving it externally in the case of galvanic it generates internally. There are some gases, which reduce in the presence of 0.6 to 1 volt in the test medium. Examples are halogens which is chlorine bromine and iodine and oxides of the nitrogen it will lead to erroneous output in the measurement systems. So, you have to be very careful if you have the presence of this type of gas in the liquid where we are interested to measure the dissolved oxygen.

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Theory of operation the basic principle of measurement for the membrane covered D O 2 probes can be summarized as follows. If the oxygen diffusion is controlled by the membrane covering the cathode, the current output of the probe is proportional to the oxygen activity or the partial pressure in the liquid medium basic principle is same.

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The following assumptions enable a mathematical analysis of the pressure profile of oxygen in the liquid and the current output of the dissolved oxygen sensor. What are those assumptions? Let us look at the cathode is well polished and the membrane is tightly fit over the cathode surface. So, that the thickness of electrolyte layer between the

membrane and the cathode is negligible. So, that we are assuming there is no there is absolutely no layer of the electrolyte in between the cathode and the membrane usually which is deformed membrane. The liquid around the probes will start, so it is mostly in the in the case of I mean whether you are measuring I mean it is it is a well start liquid. Whether you are using in the bioreactors or the waste water I mean it is a well start; well start and agitated. So, that the partial pressure of oxygen and the membrane surface is same as that of the bulk liquid, because we will need these assumptions otherwise very difficult to calculate the establish the basic the current equations.

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So, the oxygen at the membrane surface is the same as that of the bulk liquid. At present we consider that the oxygen diffusions occur only in one direction that is perpendicular to the cathode surface. We are assuming in the one direction only that is perpendicular to the cathode surface. It is, so called 1 layer model, but it can be modified to include the effects of other layers as will be discussed later. (Refer Slide Time: 35:09)



Now, suppose the electrode is immersed in a well-agitated liquid and at time zero the oxygen partial pressures in the liquid is changed from the 0 to Po. According to Fick's second law the unsteady state diffusion in the membrane is described as delta p del p by del t. That means partial derivative of p with respective to t equal to D m D subscript m del square p by del x square double derivative of partial derivative of p with respect to x this is equation number 1.

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Where Dm is the oxygen diffusivity in the membrane and the Teflon membrane x is the distance of cathode surface it will be clear from the figure 4. What is actually fourth the

initial and the boundary conditions are p equal to 0 at t equal to 0, initially there is no partial pressure P equal to 0 at x equal to 0 at the cathode surface. There is no p equal to p naught at x equal to Tm, T is a thickness of membrane, please note T is thickness of membrane. So, we start at the 0 and we end it T equal to Tm x equal to Tm.

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So, this is a 1 layer model. So, we have a as we have shown that is we are considering the perpendicular the cathode surface this is our cathode surface. So, we are considering at X equal to Tm P note this a thickness of the membrane, because you remember that the reactors are looks like this, I mean sorry the membrane I mean a membrane here is not it.

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So, we have the cathode here, so perpendicular to cathode surface. So, as we are going like this 1 this directions that is the this is x equal to 0 and this is x equal to this x equal 0 and this x equal to Tm; that means, thickness of the membrane. So, we are considering that this needs to be inserted in a tank or liquid medium X equal to Tm. So, X we are from the cathode surface we are getting this is our thickness of our membrane this is again we are coming to the liquid this is a 1 layer model of the electrode. So, we have a 2 layer model or 3 layer models also we have electrolytes. So, we are assuming there is absolutely almost there is no electrolytes in between this cathode and the membrane surface that is actually we are making the assumptions.

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Where Tm is the membrane thickness and the first boundary condition, which is equation 3 assumes very fast reaction at the cathode surface. And the solution of the equation 1 with boundary conditions will be given by P by p naught x by Tm summation n equal to 1 to infinite 2 by n pi into multiply by 1. I mean 1 to the minus n sin of n pi x by Tm exponential minus n s of n square pi square Dm t by Tm square.

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The current output of the electrode is propositional to the oxygen flux at the cathode surface. Now, NFAP m will be equal to a multiplied by a partial derivative of p with respect to x at x equal to 0; that means, at the cathode surface.

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Where N F A and Pm are the number of electrons per mole of the oxygen reduced and Faraday's constant it is the F. F is the Faraday's constant is the surface area of the cathode which is very easy to calculate. Because this is pi r square or pi D square by 4 and the oxygen permeability Pm is the oxygen permeability of the membrane respectively. N is the number of electrons per mole of oxygen reduced F is the Faraday's constant A is a surface area of the electrode cathode and Pm is the oxygen permeability of the membrane respectively. The permeability Pm is related to the diffusivity of the oxygen by the following expression what is the expression? Pm equal to Dm into Sm what is the Sm? Let us look at...

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Where Sm is the oxygen solubility of the membrane and from equation 5 and 6 the current output, it current output, because actually that is only measurement that is a reason we are going for the membrane based electrode. I mean powered electrode otherwise we can make the we need this current output for continuous measurement or continuous control of the partial pressure of oxygen or dissolved oxygen concentration either in the bioreactors or in the waste water treatment plant. As function of time will be expressed as follows this is equal to you see the current output I t equal to N F A Pm by Tm multiplied by Po 1 plus 2 summation n equal to 1 to infinity minus 1 to the power n exponential minus n square pi square Dm t of a Tm square. This is equation number 8.

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The pressure profile and the current under steady state conditions can be obtained nothing, but what will happen this steady state condition this time will go this time will be 0, because a steady state conditions. Because it is a negative exponential power then what will happen? If the as the time grows, so this will be larger and larger, because it is 1 of this. So, this will become this. So, it will be 0 at the time goes. So, only this portions will remain that is the steady state current output. And the pressure profile and the current under steady state conditions can be obtained from the equation 5 and 8 let us look at what is 8 and 5?

So, we are combining 5 and 8. So, we are getting that p by p naught equal to x by Tm. And I as steady state current you see that I t is the total current or transient current I should say not total current transient current equal to N F A Pm by Tm into P naught equation number 10. At steady state the pressure profile in the membrane is linear and electrode current is proportional to the oxygen partial pressure of the bulk liquids. So, equation 10 forms the basis for DO 2 probe measurements. What is equation 10? This is equation 10. So, this is this is for all DO 2 measurements or DO 2 probe.

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Another important consideration in the time response or the time constants of the probe, how we can make the time constant lower and lower? Because you see it if the time constant is large though the bioprocess usually I mean we do not need very fast measurements a typically we can make 5 to 6 minutes most of the reaction are lying. Because you see the reactions in the bioprocess usually is quite long I mean sometimes it 30 hours I mean 40 hours.

So, you do not needs like a I mean very fast sampling I mean you do not have to make the measurement very fast. You can measure in the 6 minutes 10 minutes, but still that I mean you must consider the time constant of the response time of your DO 2 probe. These important issues are important parameters of a probe. According to equation 8 the probe response depends on the probe constant K defined as follows. That K equal to bi square into Dm by Tm square equation number 11.

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A large K, which means a thin membrane and at a high Dm divisibility large results in a low value of time constant quit. Obviously, a large K which means a thin membrane is thin and diffusivity is high for the membrane is high result in a low value of time constant. So, this will make the time constant low and the consequence of the probe response will be very fast.

However, the assumptions of the membrane controlled diffusions will be more valid in these conditions. It is very contradictory, so way we are reducing the time constant time constant also always should be lower for any instrumentation system for any sensors lower is better. Thus a compromise has no has to be made for an optimum performance of the DO 2 probe. Thus, a compromise is to be has to be made for an optimum performance of the DO 2 probe.

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Limitations of single layer electrode model in reality the assumptions one and 2 made earlier are not entirely satisfactory. So, a made some assumptions at the beginning to establish or to build the theory are not entirely satisfactory often there exists a finite thickness of electrode layer between the cathodes. We have assumed that the there is no electrolyte layer in between cathode and the membrane, but there is finite layer of electrolyte in between cathode and membrane. And the membrane because of the roughness of the cathode surface though we clean that the cathode if the cathode surface are membrane is absolutely plane. So, there is no chance of I mean liquid electrolyte coming in between, but if there is slight roughness.

So, a layer of liquid or a layer of electrolyte will come in between membrane and the cathode. So, that is to be taken care in the in the single layer model we are not taken we have assumed that that is zero thickness of the electrolyte is zero in this that region. Also a stagnant liquid film always exists outside the membrane even at very high liquid velocity. Even though we had a very good start I mean, because in the starting you are doing you see in the reactors. Now, usually the there will be a liquid I mean because it is inside the liquids it will be shorted I mean. So, always there is a stagnant liquid film always exists outside the membrane we are consuming assuming that it is a liquid a liquid which is contact the membrane we are consuming assuming that it is a liquid film exists which is stagnant what is that look at very carefully it will look like this 1.

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So, we are way you see the probe is like this one we are way probe here membrane. So, we are way cathode here and this we are inserting insight the liquid is not it is our membrane this is our cathode this is connected like this one. First of all, we are assuming that this cathode there is a layer. That we which we have assumed that the layer of thin liquid d is I mean it was electrolyte does not present in the in the in the case of in the case of 1 layer model that is not true. If it is there is a slight roughness electrolyte will come in between. Secondly the film even though it is rotating I mean this we have a agitators either in the continuous CST; that means, continuous start time by reactors or your other type of reactors what will happen? That there is a continuous I mean moment are agitations of the liquid even though we will have a thin layer in contact with this one will be stationary or stagnant thin layer of liquid in contact with the membrane.

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A more realistic model of the electrode is shown in figure 5, which is called basically 3 layer model. All the 3 layers namely the electrolyte, the membrane and the liquid film have been considered all the 3 layers have been considered.

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You see they are we have considered this is our electrolyte in between this is our cathode this is our cathode. I can take this one this is our cathode we have a membrane after that we have a I mean a a definite thickness of the electrolyte. Then we have a this is a membrane thickness Tm; this is a membrane thickness and this is our liquid film thickness. You see it is slowly increasing. So, like this one it is increasing you see here

after that we are getting the main liquid bulk liquid. But here this is a film thickness which is in stagnant with the with the membrane itself. So, may be larged though this is very, very small in the order of excuse me in the order of micro meters. But just to explain to the students we have I mean elaborated it like this one.

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The effect of different layers on the electrode behavior can be estimated by using the one layer model. At steady state the oxygen flux J through the each layer at figure 5 becomes identical. But J equal to K naught into P naught Klm P naught minus Pm Km multiplied by Pm minus Pe which is equal to we can write Ke into Pe which is equation number 12.

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Where K 0 is the overall mass transfer coefficient and small k's represent individual mass transfer coefficient corresponding to the liquid film Klm the membrane Km and the electrolyte Ke respectively. The overall mass transfer I mean resistance one by K 0 is then expressed as the sum of the individual resistances, which can be given like this one. 1 by K 0 1 by Klm is a liquid film the master transfer of coefficient 1 by Km membrane mass transfer coefficients and 1 by Ke electrolyte right.

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Indian Institute of Technology, Kharagpur Eqn (13) can be rewritten by using the oxygen permeability and the thickness of each layer as follows $\frac{1}{K_n} = \frac{T_L}{P_1} + \frac{T_m}{P_m} + \frac{T_e}{P_a}$ (14)Where T_L, T_e, P_L, and P_e are liquid film thickness, the electrolyte thickness, the oxygen permeability of the liquid film and that of the electrolyte layer, respectively. - ----

Equation 13 can be rewritten by using the oxygen permeability and the thickness of each layer as follows. We converting layers 1 by K 0 equal to Tl by Pl Tm by Pm Te by Pe, where Tl Te Pl Tl already we have defined it is a thickness of the membrane Tl Te Pl. And Pe are the liquid film thickness this the liquid film thickness this the liquid film thickness this is the electrolyte thickness. The oxygen permeability of the liquid film liquid film only and that of the layer itself this is of the electrolyte itself this Pe is clear.

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A completely stagnant liquid film was assumed here although it is more accurate to use the convective mass transfer coefficient. This is typically more complicated other convective mass transfer coefficient and the condition for membrane controlled diffusion becomes that Tm by Pm will much, much greater than Tl by Pl plus Te by Pe equation number 15.

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This means that a relatively thick membrane with low oxygen permeability is required which contradicts the requirement for a lower time constants of the probe. That justify I mean you can be just this can be justified, because in the most of the, I mean this dissolved oxygen measurements. We do not need very fast response for I mean controls I when if you can measure only 6 minutes or every 10 minutes that will suffice. Same thing with the waste water plant treatment plants also we do not need that faster even if we measure. If we have a sensor, which can measure the dissolved oxygen I mean partial pressure of the oxygen or dissolved oxygen concentrations very frequently every second that does not make any sense. Because you need to control if you want to control that will increase the dissolved oxygen concentrations in the particular liquid. The mechanisms, which we have to follow that we increasing the starrer filed or any other oscillations or anything it will take a large time.

So, there is no use of measurements of very fast I mean. So, that is I mean little large a time constant will be justified if you have a proper model in that sense. So, that is most important this means that a relatively a thick membrane with a low oxygen permeability is required which contradicts the requirement. Because if you make the thick membrane low oxygen permeability; obviously, what will happen that constants of the system will increase. For a given cathode geometry the resistance of the electrolyte is almost fixed for the resistance of the electrolyte is fixed that is not a very problem right for a particular geometry of the cathode. Also since the also since the electrolyte is contained inside the membrane it does not affect the measurement.

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Indian Institute of Technology, Kharagpur
• Therefore, the condition for accurate
measurements of dissolved oxygen becomes:

$$\frac{T_m}{P_m} + \frac{T_e}{P_e} \gg \frac{T_L}{P_L} \qquad (16)$$
When the individual resistances are taken
into account, the steady state current output
can be written as,

$$I_s = NFA(P_m/T)P_0 \qquad (17)$$

Therefore the condition for accurate measurement of dissolved oxygen becomes the Tm by Pm plus T by P much, much getter than Tl by Pl which is equation number 16. When

the individual resistances are taken into account the steady state current output can be written as when the individual resistances are taken into account. Then steady state current output can be written as Is steady state current NFA Pm by T bar into P naught this equations are already we have written we have just modified according to this expressions right.

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Where T bar is defined as the T bar equal to Tm plus Pm by Pl into Tl plus Pm by Pe into Te that is equation number 18. In this case the probe constant k is modified as follows we write K equal to bi square into Dm diffusivity of the membrane often T subscript small T dash square with this equation number time 19 what is known t Tt, let that will be clear from the next expression?

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Where T subscript small T bar equal to Tm plus under the square root Dm multiplied by Tl over Dl plus under the square root Dm of Te multiplied by De equation number 20. Equations 17 and 19 and show that the steady state current decreases and the probe response time increases when there is a significant mass transfer resistance in the liquid film around the membrane which is quite obvious, right.

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Normally probes are operated such that the effect of liquid film resistance is negligible. It is achieved by using membranes of low oxygen permeability and by the well agitation of the liquid around the probe. So, there is I mean all this compromise you have to make. In fact, actually we in the IIT Kharagpur, we have developed a DO 2 sense now DO 2 sensing if you look at. So, actually it looks like this if you if we look at the complete instrumentation diagram.

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So, it will look like this I have a DO 2 probe sorry I have a DO 2 probe I am getting a current. Current output is steady state current this current is converted to the current voltage converter current to voltage converter in the near way a voltage amplifier amplifier. Now, it is easier to make then we again we can convert to the difficult current because these amplifications will make us to the proper voltage because most of the convertors. So, we have a way V to I convertor here because once it is current to its current to voltage this can be difficulty. I will get the voltage usually typically the current voltage is 0 to all the convertor available for 0 to 5 volt which respect which will give you 4 to 20 mille ampere.

So, this can be done here itself; that means, 0 to 5 volts this will give you now I am getting a current output which is 4 to 20 mille ampere which is used for the measurements as you know industry that 4 to 20 mille ampere is a standard. So, you will get like this one Moreover you see that we have used a I mean a plot what we found that we basically made we made in a this measurements you made in a bioreactors. In IIT Kharagpur in the bioprocess instrumentation lab and we found that we got a consistory good results though the result in consistent; obviously, but when you measure with the other sensors. So, the galvanic is slight absent that which is quite obvious.

So, this galvanic letters actually it worked very nice in our laboratory right. So, with this I come to the end of lesson 31 of industrial instrumentations. Basically we have considered the dissolved oxygen sensing here and basic more details of the sensor 4 different will more details of the sensing will come in the lesson number 32. Welcome to the lesson 32 of industrial instrumentation. This is a continuations of lesson 31 actually the we will consider here the dissolved oxygen sensors. We discussed dissolved basic principles of the dissolved oxygen sensors in details in the lesson 31. This particular lesson will consider the different types of electrodes its calibration type of membranes. These are the very important things for designing any D O 2 probe and type of is I mean type of materials which is used for making the for making the electrodes specially the electrolytes.

And what should be the suitable nature of the membrane also that is also very important. Because in some cases we have to sterilize the dissolved oxygen sensors when it is used in the bioreactor or you will put in the auto clamp. So, the temperature minimum temperature there will be 120 degree centigrade. So, in that type of situations we will discuss we need some sort of some sort of auto cleaving and with the or some sort of sterilizations. And these particular lessons we will discuss all those in details and we as I told you earlier that is it is a continuations of 31. Let us look at the contents of this lesson 32 dissolved oxygen sensors 2.

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Contents: construction of electrodes; all the electrodes what is there, what is anode, what is cathode, what type of materials used for making anode and cathode, what type of electrolytes we are using where the membrane lies? So, all these things we will discuss.