## Introduction to Chemical Thermodynamics and Kinetics Dr. Arijit Kumar De Department of Chemistry Indian Institute of Science and Education Research, Mohali

## Lecture – 26 Electrochemistry

So, in the last class we discussed about chemical equilibrium, we discussed how the Gibbs free energy change can be used or can be estimated to understand or to predict the directionality of a reaction; whether the forward reaction is spontaneous or the reverse reaction is spontaneous.

And we also talked about the conditions at when the system or the reactant and product mixtures are at equilibrium. And we talked about the reaction quotient and equilibrium constant, we also discussed how the external conditions like pressure and temperature; if they are varied how the equilibrium constant changes or how the reaction changes or overall.

So, in today's class lecture we will discuss on based on the previous discussion of chemical equilibrium which we already had will discuss the electrochemistry or the equilibrium electrochemistry. Now to begin with as you know that electrochemistry discusses about some electrochemical reactions which are Redox reaction in nature.

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 $N^{n+} + ne^{-} \xrightarrow{\checkmark} N$ II revu KCI/ coup  $C_{\mu}^{2+}(a_{s}) + Z_{m}(b) \rightarrow C_{\mu}(s) + Z_{h}^{2-}$ electrodes Emetalic conductors

Redox in the sense that some species will be reduced says n plus and we get electron. So, that will be reduced to something that can be; n can be a metal, n can be a gas n can be anything and at the same time some other species will get oxidized. But we usually denote this reduction or oxidation with respect to always usually we write it in terms of the reduction; the standard reduction and then we will show that instead of writing the equation as this.

One of the reaction will be spontaneous; so, suppose if this is a this is some reaction say we call it as reaction I and this is some reaction which is reaction II; then if we say that there is a spontaneous direction where this is happening in the forward direction, but this is happening in the reverse direction, then the overall reaction will be something like m m plus N n plus going into. So, we will take the difference between these two reaction; so, it will be N and then we will have the metal M is getting reduced and n is getting oxidized.

Of course we do not have the electron balance here. So, we have to balance it here. So, what we can do is that we can divide the top reaction by M and the bottom second reaction by N. So, that the number of electrons exchanged they just are equal. So, we could write it as 1 over m 1 over m also here and 1 over n here 1 over in here; so, now, you see that the electrons will also be balanced. So, this is nothing, but reaction II minus reaction I. If the reverse reaction reverse is spontaneous which means the forward reaction is actually going into the reverse direction, but the second reaction is in the forward direction then the entire thing will change.

So, what is the meaning of that is that every reaction every oxidation reduction reaction what we are writing here as reaction I and reaction II when a oxidation or reduction is happening simultaneously another species is also getting reduced or oxidized. So, that is the entire concept; so, in that sense in that context we always talk about Redox couple in the sense that whenever you have an oxidizing species which is getting reduced by itself, you also have a reducing spaces which is getting oxidized by itself. So, these two reduction and oxidation happen together that so, you always say that there is a Redox couple that exists.

Now, we will start our discussion first based on this half reaction which we call as; half reaction in the sense that this is a total reaction where we did the 2 minus 1. And but we

will first study what is the half reaction what is the thermodynamics of half reaction and then we will just do addition or subtraction in the sense that whichever direction is the spontaneous, we will just keep that in mind and that spontaneity we can always discover from the sign of Gibbs free energy change associated with the overall reaction. If that is negative then the way we have written the reaction that is spontaneous if that is positive the way we have written it is not spontaneous the reverse way is spontaneous.

Now, to begin with let us just discuss what is an electrochemical cell? Now as you know that an electrochemical cell already you studied it in your high school consists of at least two electrodes. So, these are electrodes and electrodes are nothing, but metallic conductors, and these electrodes are in contact with some solution which is an electrolyte solution and that electrolyte we this is this solution is nothing, but an ionic conductor. So, there are ions which can move freely and which carry the charges. Now we can take an example the famous example of the Daniell cell suppose this metal is zinc here and this metal is copper here and zinc is in touch with zinc sulphate.

So, zinc solution of zinc sulphate and the copper is in touch with a solution of copper sulphate; suppose both are eco solution. And then also we say that these two solutions are in contact with each other. So, this can be something like a porous material which will allow the ions to flow across the this porous membrane or porous wall, Now think about it like when you have something like this and if we connect it then we know that electricity will flow and the cause of the electricity of course, is the cause of flowing electrons through this through this circuit.

Now, in order to make this circuit complete you see that here we have a porous wall because the ions also should flow. Now the problem is if you have a porous wall then also there is a potential that develops which is known as junction potential or more commonly as liquid junction potential. Because it is created just like the junction of the two liquids here the two liquids are nothing, but zinc sulfate and copper sulphate in water say aqua solution now because these two add for two different solution and ionic solutions.

We also develop a potential there. So, we usually want to eliminate that the reason is we want to only concentrate on the potential difference which are created at the electrodes. So, we will only consider the potential difference between this zinc electrode and the

copper electrode. If there is any additional source of potential difference which is coming from the liquid junction potential that we usually want to eliminate and for that what we do; is that we suppose these are the two electrodes, we actually connect it; so, instead of connecting it through a porous membrane we connect it through a something known as a salt bridge.

So, the salt bridge is nothing, but concentrated solution of some salt say potassium chloride in most of the cases in some gel matrix and usually this matrix is agarose gel. So, kel agarose is constitute a salt bridge. So, agarose is nothing, but just like starch it is a polysaccharide and that forms a gel like appearance and then the; we mix the kel solution and considered kel solution inside it. So, that the ions can flow through the salt bridge; so, that actually eliminates almost the liquid junction potential and in brings it down to 0. So, under that condition we can write the overall driving force or the overall potential or of the cell which is driving this electrochemical reaction which is basically coupling the two reactions.

Now, the two reactions here are two Redox reaction just like we stated in the very beginning is zinc is getting reduced to zinc ion is getting reduced to zinc metal. So, more specifically you can write it as it is in eco solution, but it is the zinc metal which is solid. And similarly copper was an aqua solution is getting reduced to copper which is solid. And then we will see that how we will define the right to minus left; in this case we will see that we have to take this 2 minus 1 and then the reaction will be spontaneous. So, that we will calculate I mean or we can calculate if we know the half cell potential, we can actually predict that which direction the overall reaction will go.

In this case although it is not clear now the overall reaction will be copper 2 plus which is in aqueous plus zinc is going to copper solid this is zinc solid plus zinc 2 plus. So, what is happening here the in a overall or the net reaction is this zinc from the zinc metal zinc 2 plus is coming into solution.

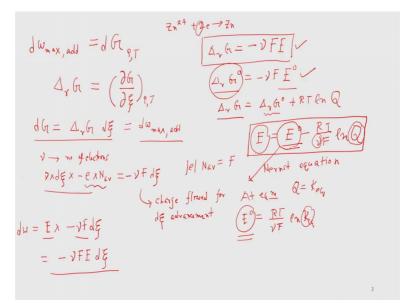
And the copper 2 plus ion are actually getting deposited into as copper metal. So, here we see that oxidation is happening for zinc; so, this is called anode already you know this thing anode means actually where that electrode where oxidation happens and that copper we see that reduction is happening; so, we call it as a cathode.

So, always the convention is that you write in such a way that you write cathode minus anode or the reduction minus oxidation. And then there will be an electron flow in this direction from zinc electrode to the copper electrode which means electricity of the current in the if we think in terms of the positive charge that will flow from copper to zinc.

Now the question is how to describe the thermodynamics of this half cell reactions and then do some addition and subtraction and then get the overall thermodynamics of the overall cell. Now in order to understand that we again we are supposing that we are doing everything in the constant pressure and temperature.

So, a natural choice is to calculate the associated changes in the Gibbs free energy.

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Now if you ask this question that we already discussed the maximum work we can get which are actually additional work that is nothing, but the Gibbs free energy or the changes in Gibbs free energy, we can write it in the differential form that the W maximum is nothing, but equal to dG now. So, this is done remember at constant pressure and temperature. So, all we have to do is to calculate dG.

Now already in the previous lecture we said that we defined the reaction free energy or reaction Gibbs free energy and there we defined it as the partial derivative of Gibbs free

energy with respect to the advancement of the chemical reaction for pressure and temperature were kept constant.

So, you can easily figure out that dG is nothing, but the reaction free energy multiplied by d xi and that is the maximum work. So, that is the maximum work and not maximum work in the sense that it is the additional maximum work. Now think about a situation that we can also we could also calculate the maximum available work in terms of just say how much electron or how many electrons are flowing. So, that is very easy to calculate now suppose that we are considering some reaction where nu is the number of electrons in the stochiometry like for example, the zinc 2 zinc 2 plus zinc to plus 2 zinc, we added 2 electrons and same was for copper.

So, in this case number of electrons will be nu will be 2; now if I have a nu number of electrons. So, the advancement already we discussed suppose we have a desire amount of advancement. So, the number of electrons that actually got lost or gained is nothing, but nu times d xi and since each electron carries charge of minus e. So, that will be the total change in charge due to advancement of the reaction by d xi amount; for 1 mole of this reaction it will be just multiplied by the Avogadro number.

So, this quantity electronic charge multiplied by Avogadro number already you studied this that these is nothing, but constant which we call as 1 Faraday. And then we can just write it that the total number of electrons that has flown for 1 mole of the substance per for an advancement which is equivalent to d xi will be nothing, but nu into F into d xi with a negative sign.

Now, this is basically the charge float for we are writing it for d xi advancement or when the advancement is d xi in terms of say 1 molar we are saying always. Now you can also because we all these are reactions which you are writing in you were writing it in terms of 1 mole amount of the of public spaces.

Now you can think that if I have one electronic charge flowing through a circuit through a potential drop which is say e; then the work done will be just charge multiplied by this potential drop. And if we call this potential drop as e then the work done will be nothing, but this dW will be nothing, but e times the whatever charge was carried out say if we call it as some Q ah; it is not necessary because it will create confusion because Q we desert for heat.

So, we can just write it like the charge the work done will be the potential drop multiplied by the amount of charge which is flown. So, this is nothing, but minus nu into F into E into d xi. now you see the work done expression here and compare it with the work done expression here.

So, by comparing these two equations we can easily write that the reaction Gibbs free energy is nothing, but minus nu F into E, where e is the potential drop that we can actually measure. Now the question is; so, for any half reaction for example, you can actually define a standard state just like we defined the standard state when we discussed the free energies. This standard state corresponds to for gaseous state it is one bar of at I mean pressure for if it is in liquid pure liquid or pure solid form we will see that how the standard state can be defined.

But let us say that we are running this reaction at the standard condition and the corresponding potential we are calling as say standard potential which we write as E 0. So, just like here we write at delta z 0 we are also writing it as E 0. Now the question is how this how you define this E 0? But before that you know that we just like in chemical equilibrium we had delta r G was nothing, but if you remember it was delta r G 0 plus we had RT ln Q.

And this is nothing, but equivalent to RT ln K minus RT ln K. So, and Q is the reaction quotient; so, we can just add all these values here and you can just use minus n minus nu F E for delta z and minus nu F E 0 for delta G r and then you can easily figure out if you just divide both side by minus nu F.

So, what we get is on my left hand side I have E because I am dividing by minus nu F on my right hand side I will get E 0 minus RT by nu F ln Q. So, this equation is known as Nernst equation. So, it is a Nernst equation for electrochemistry and what you see here I can actually connect the potential drop which is known as electro motive force will come to that.

Electromotive force right now we are discussing for the hop cell and then that is equal to the standard electro motive force which corresponds to which is directly connected to the standard Gibbs free energy change and minus RT by F which are always constant and nu which is nothing, but that change in the number of electrons in this stochiometry which in this case is two in the example of zinc 2 plus going to zinc. And then ln Q and Q

already you know is the reaction quotient basically it is the activities of the reactants taken to their exponent divided by the activities of the products or the yeah.

So, you have to take basically the multiplied version activities of all the product versus reactant and, but these activities are to also taken into their raised to their power of according to their the quotient. Now what do you see here that we have something defined as E 0; now you can easily figure out what is E 0 at equilibrium you can easily argue that Q is nothing, but K. So, all these equations you can easily figure out that this at equilibrium the left should be 0. And then we have E 0 is nothing, but RT by nu F ln k. So, K is nothing, but we can actually get either E 0 in terms of. So, this equation suggests that it will be RT by nu F ln K.

So, we can actually calculate K from E 0. So, if you can measure the E 0 we can actually measure the equilibrium constant of this reaction also. So, the meaning of this is do not get confused that E 0 is something new; E 0 is deeply connected to the delta z 0 which means actually the system when the system has at in equilibrium, the quotients are actually comparable to the equilibrium constant at that condition; we can write you can express the E 0 in terms of the equilibrium constant or I means, we can actually say it in putting put the words in the other way that the equilibrium constant can now be determined from if we can measure the E 0 of the standard Gibbs it is a reaction potential at the electro motive force at in the standard condition which is equivalent to 1 bar.

Now the question is suppose we have we already gave you an example of that there are two reactions that zinc 2 plus is going to zinc and copper 2-plus is going to copper. And we will take the right minus left; now which will dictate the right differences left direction. (Refer Slide Time: 23:49)

Now if you remember that we already discussed that the when we discuss the direction of the spontaneity of a reaction that the Gibbs free energy will always try to get minimized. So, if we just plot it the Gibbs free energy with respect to the advancement; we said that for a particular forward reaction.

So, we will see that the slope here is negative which means actually the Gibbs free energy for if we call it as a on the forward direction. So, we see that the slope which means these dG or del G del xi whichever way we write it which is equivalent to the reaction Gibbs free energy delta r G that is 0. And in this case it is positive we already discussed it and at this situation delta r G is 0.

Now, this means that if the forward reaction for or is spontaneous then we will have the reactant minus product that will be negative. Then we will have delta the reaction Gibbs free energy, we will have a negative slope which means the reaction is proceeding in the forward direction; however, if this situation happens that the reaction Gibbs free energy is positive which means react a product minus reactant is positive which means the reaction will now go into the opposite direction.

So, that already we discussed, but now we can also discuss it in terms of the electro motive force or the potential drop which we wrote as minus N F E or nu F E. So, nu is a constant here F is also constant; mu is constant for a particular reaction of course.

Now, we can see that the sign of will always get reversed for if we had plotted it in terms of E. Because we you can see here that the E or which is related to this slope actually is positive here and E is negative here and that is the meaning of which direction or is this direction of the spontaneity. And when the equilibrium is at each attained the e will be of course, equal to 0.

So, what it means is that instead of writing the reaction or this spontaneity or the directionality of the reaction in terms of the Gibbs free energy, we could also look at the directionality in terms of the E or the electro motive force, but this is again for a half cell reaction we are still discussing. Now suppose we have the same example we can write say we have zinc 2 plus I am writing it once again; I am going to zinc and we write it very specifically and then we have copper 2 plus in aqueous solution getting reduced to copper.

Now, each of the reaction has an E or electro motive force that can be written as E 0 minus RT by nu F times your reaction quotients. Now for this particular reaction the question is how you will calculate the E 0 or the E of the cell. Now in order to do that we have to first make a notation how will you represent this entire reaction?

So, as we said that in this reaction there we always say that one reaction is going in this direction which is this reaction, but the other reaction is going into the reverse direction which we discussed, but we just took it as it is for granted; in the sense that we do not know yet that whether the this if we write it this reaction as a forward reaction and this first reaction is the reverse reaction whether that will be spontaneous or the other way will be spontaneous.

For that we have to check what as; what is associated delta G of this total reaction. Now suppose we assume that fine the this reaction; which is the copper 2 going into copper that is a positive that is the forward reaction, then we will that cathode reaction we will always write on the right and side and with a vertical bar and this vertical bar dictates or denotes; that it is basically an electrode in equilibrium with its some ion.

And similarly we will write the zinc on the other hand side and for the which is known as the left electrode. So, this is basically the right electrode and cell electrolyte combination. So, we always write it as right cell and this one which we write as zinc is going to zinc 2 plus as the left cell and overall the potential will be always potential of the cell will be always we can write it as E right minus E left something like that.

Now, the question is what happens ah; so, these vertical verses I said that it is basically showing the electrode and electrolyte interface. But what about between two electrodes electrolyte; so, we already said that there could be a porous material which actually creates a liquid junction potential; in this case if it is a liquid junction potential we just denote it by vertical dots.

So, that dot is denotes liquid junction potential. So, if they are connected by a salt bridge where the liquid junction potential is removed; then we write the total electrode as two vertical bars when the liquid junction potential is removed and we denote the entire cell as this. So, this is for liquid junction potential remote which is equivalent to saying that it is connected via a salt bridge.

So, this is a representation of the entire cell in this case this cell is very famously known as the Daniell cell already you studied this in your high school electrochemistry. Now the question is fine we can write the E cell as E right minus E left, but E right if we half electrode also has E 0 of right minus RT by nu F ln Q of right minus the corresponding terms for left.

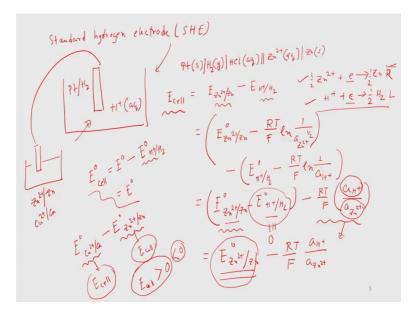
So, now, the question is will have something like E 0 right minus E 0 left something like that, but how will you define this E 0? We already said that it is with respect to our standard condition, but always as you can see here we measure an electrode potential in a cell in the sense that always what you can measure is a difference of the two electrode potential.

So, when I say that E 0 write minus E 0 left for that we have to take a condition where actually we make it as say 1 bar pressure, but then also we have to measure it with respect to some other electrode. Because otherwise we cannot measure it there is nothing called E 0 right absolute scale.

Now everything here is a relative thing; so, what I am trying to say here is that think about this half cell reaction to calculate the E 0 we will go to a standard condition which is 1 bar of atmosphere. But then we have to measure it in a cell, but which cell we will take so, that the cell potential will take as nothing, but the potential of this guy itself. So,

for that what we do is that we always take a reference and this reference usually is the known as standard hydrogen electrode.

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Standard hydrogen electrode S H E where there is a platinum metal on which hydrogen is absorbed hydrogen gas. And then there are also protons in aqueous solution, usually you take it as a 1 molar H C L and that half cell we call as the standard hydrogen electrode.

So, all everything will measure or with respect to this standard hydrogen electrode only. So, let us give an example suppose we have a particular cell say for example, it is a platinum. So, since it is measured with respect to this cell; so, this cell is regarded as the left cell or the left hand side cell. So, we are writing it as platinum solid and then hydrogen it is in gas because it is adsorbed species on the gas and then we have H C L which is aqueous we could also write H plus aqueous. And then we connect this to some reference things suppose we are writing it as say the zinc electrode for example.

So, here the zinc will always consider as the right whichever we want to measure whichever electrode do you want to measure the electro motive force that has to be always written as right because we will take right minus left and whatever we get we will take it to be 0 we are we are coming to that what that 0 means.

Now, if we write the electro motive force for this cell now that we can write as before it will be E of this cell which is zinc 2 plus going into zinc minus E of the left cell which is H plus going into H 2; Every time you see the notation that I am using the only the reduction form.

Now, what are the reactions here? The reactions are something like you can write it in many different ways say zinc 2 plus is taking 1 electron going to say zinc. So, then it used to be half and also this has to be half and the other reaction is half of hydrogen sorry it will be just h plus electron is going to half H 2. So, that is the other half and then we take this is my right electrode right now and this is my left half cell.

So, right minus left we have to calculate now if we do that then there will be some E 0, but the difference between E 0 of zinc 2 plus zinc minus E H plus H 2 the difference in the E 0s then we will have RT by nu F and that nu we have deliberately written in such a way that it is already 1. So, write RT by F; now it will be if you remember that what was this? So, this was nothing, but a if we can write it in terms of say delta G 0. So, delta G was delta G 0 plus RT ln Q.

And since we converted into it into E; so, E and delta G has a negative sign in their relationship. So, that became E minus E; E 0 minus RT by nu F and that nu is 1 here and then we have basically all the reaction quotient for this reaction minus this reaction; this reaction minus this reaction. Now in the logarithmic way we can always write it as the reactant minus product let us actually write it in detail first and then it will be more clear.

So, first let us write it as the E cell for the half cell or the right cell. So, that will be nothing, but RT by F and ln now we have the reaction quotient and look at the reaction here what is the reaction ? So, we have here activity of zinc, but a zinc activity will be 1 because it is a pure metal and metals we always consider as a pure state; so, the activity of zinc will be 1.

So, it will be just 1 divided by the activity of zinc 2 plus raised to half here and multiplied by electron, but that is also we take as 1. So, this will be the E right minus we will have a E left that also we can write it as the similar way it will be RT by F ln.

Now, it is activity of H 2, but H 2 we have taken for this electrode as 1 bar. So, we can actually write there also as 1 because it is in pure state already and divided by activity of

H plus. So, that is the E right minus E left and then if we collect the E 0 terms together; zinc 2 plus zinc minus E 0 H plus H 2 minus; we can take the minus common RT by F.

And then we will have a H plus because that goes up divided by a zinc 2 plus. Now what you see here is very interesting or you could write it as a plus sign and a zinc 2 plus divided by a H plus. Now here we need to know again the E 0 values of H 2 and h plus, but here the definition is the E 0 values are always measured with respect to this electrode.

So, this one we take it to be 0; so, that whatever  $E \ 0$  we are measuring is actually the  $E \ 0$  of the half other half cell itself. So, if you want to measure any metal or any cells reduction potential; what you have to do is that you have to just couple it to the standard hydrogen electrode and then measure the E at standard condition which means it is  $E \ 0$  and that  $E \ 0$  which is the  $E \ 0$  of the cell.

But now the E 0 of the cell is nothing, but E 0 of that particular Redox couple or it is its particular that half reaction that particular thing which we just write it E 0; minus E 0 of this couple which is H plus H 2, but that we that is a relative thing. So, that we take as 0; so, that we the E 0 of the cell where the one part is standard hydrogen electrode is called the E 0 of the half cell itself.

So, now in order to do this thing which we just discussed in the earlier slide that how will you measure the E right minus E left, but the right is zinc and the left is sorry right was copper and left was zinc; than then what we will do is that we have to bring this zinc 2 plus zinc cell measured the E 0 with respect to the standard hydrogen electrode.

Similarly, we have to bring the copper 2 plus copper; measure the E 0 with respect to the standard hydrogen. And electrode and then we can actually take the difference which is in this case will be copper 2 plus copper minus E 0 zinc 2 plus zinc. So, these two again are was measured as e cell of the cell where one component was standard hydrogen electrode.

So, that way each one of them who are measured with respect to the standard hydrogen electrode and the standard hydrogen electrode  $E \ 0$  we took as 0. So, then we can easily figure out that is will be nothing, but  $E \ 0$ , but now you can see that for standard hydrogen electrode this also we can make to be close to 1, but this is not necessary you can always

measure it and you can also measure the activity because you can always write the activity in terms of activity coefficient times the mole fraction and you can measure this quantity.

And you can also measure the E cell and thereby you can measure the E 0 zinc 2 plus zinc. And then once you measured the E 0 then there is already table available for that where every value of the many of the Redox half reactions are tabulated. And from there you can actually take the value of that particular Redox couple or that or half cell value.

And then you can use it to construct all the other combined cell value; where you take one half cell and measure it with respect which is already measured with respect to the standard hydrogen electrode. So, that you know the E 0 and you also take another half cell and then you see that if I do the right minus left whether the E cell has positive direction.

If it is a positive direction then the way we have written is correct there are otherwise if it is a if we find that it is negative, then the right cell which we are we have considered should be the left cell and the left cell should be the right cell. So, the direction of electron flow will change, the cathode will become anode and the anode will become cathode.

So, this is the overall discussion which we had today on electrochemistry. So, we will give some problems at based on this as well as we will give you a handout first which will describe all these things which we discussed here particularly the convention which we are using for the standard state.

And electrochemistry has many interesting examples which we are not discussing here for example, it is extremely useful in biological context, it is also extremely useful in material science context where you reduce metal for example, in metallurgy also like you extract the any metal from its ore which is in its salt form.

And then electrochemistry is the only way or one of the it is it is actually the only way you can do it in a electrochemical way or in a slightly different to it, but the Redox reactions has to be carried out and you can figure out that in the problem sets will ask you to solve many interesting problems, which are related to all these practical issues. Thank you.