Concepts of Chemistry for Engineering
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Lecture 55
Electrochemical Equilibrium, Nernst Equation

Hello, welcome to the next part of our discussion on Thermodynamics. So, so far, we have discussed mostly the concept and fundamentals of thermodynamics, where we have gone through the basic properties of a thermodynamic system, the work, energy and heat, how they are all connected together with respect to the first law of thermodynamics, then we have defined two important terms enthalpy and entropy.

And we have described the second law of thermodynamics and third law of thermodynamics with respect to entropic. Then we have derived the two important energy functions, the Helmholtz free energy and Gibbs free energy and to find out with respect to them, how we can define a spontaneous reaction. Now, we will go further and look how this thermodynamic parameters and understanding can be used for different chemical and physical processes, this will be the application portion of thermodynamics. So, let us begin.

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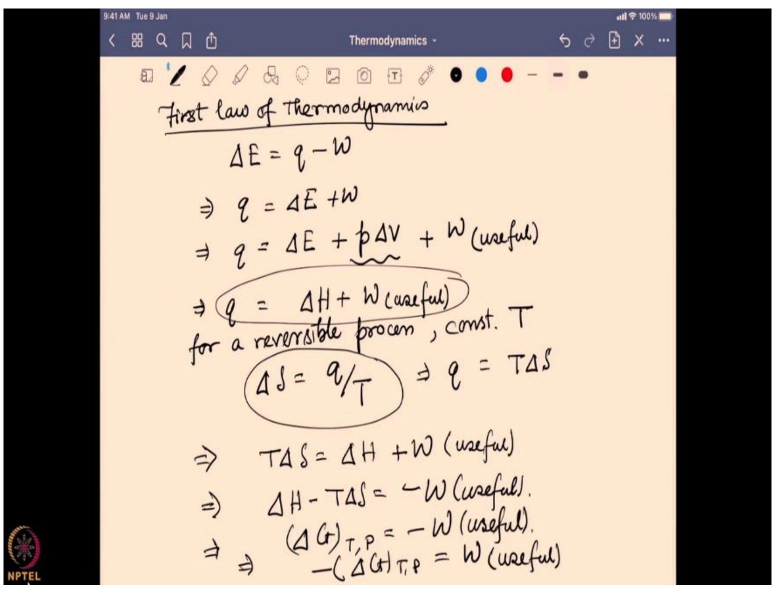

So, from the first law of thermodynamics, we have defined ΔE is = q-w, again q is positive when the heat is coming to the system and W is negative when system is doing a work and then we can write q is $\Delta E+w$, and now we are going to expand a little bit further and expanding what kind of work I am talking about.

If I am talking about $p\Delta V$, the expansion work plus W the useful work, that means without the mechanical or expansion work, as we just know, $\Delta E+ p\Delta V$ is nothing but ΔH for enthalpy change becomes this particular equation $q = \Delta H +$ useful work. Now, for a reversible process occurring at a constant temperature we know ΔS is equal to q/T or we can say q is nothing but $T \Delta S$.

So, now, if I use this particular equation and these two equations and exchange the values of q's, we can easily write $T\Delta S$ is equal to $\Delta H + w$ useful or you can write $\Delta H - T\Delta S$ is equal to useful, we are just multiplying with minus 1 on both sides. So, over there we can say this is nothing but ΔG at a constant temperature and pressure is nothing but - w useful, or taking the negative side on this side, $-\Delta G_{T,P}$ it is going to give me the idea about how much useful work I can do for a particular system.

So, it is another elongated discussion of what is that useful work and how it is connected with the Gibbs free energy that we are continuing from the discussion of the last segment. Now, with that thing in our mind, this is very critical, because now different kinds of system we can consider to find out what is the useful amount of work.

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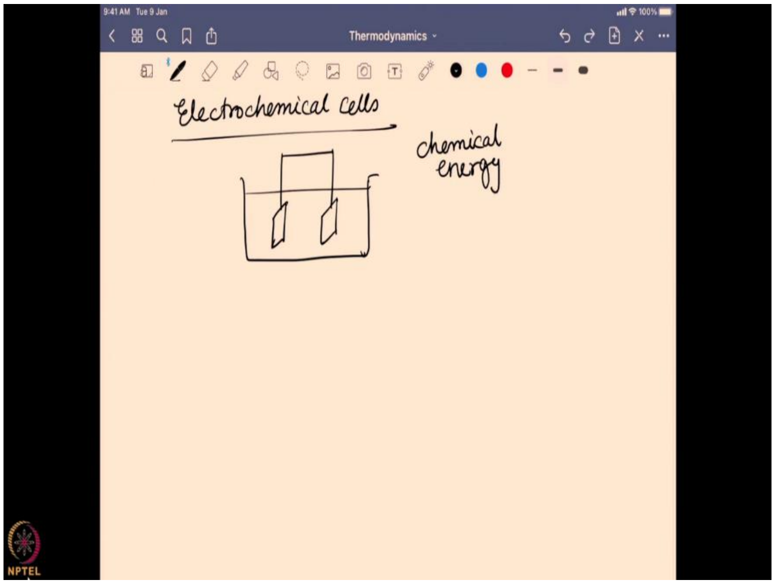

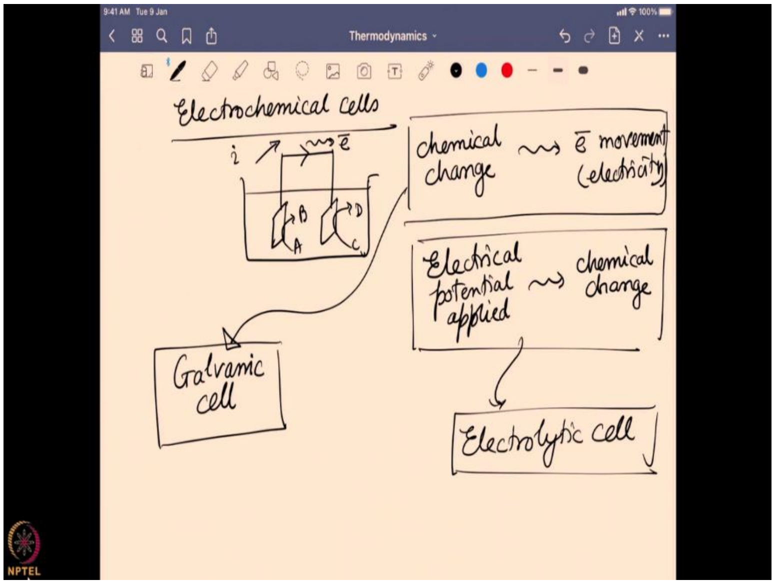

So, for the first system of this one, we are going to consider is that electrochemical cells. Now, what is an electro chemical cell, electrochemical cell is a particular vessel where we have two electrodes present there which are connected to each other and over here either a chemical energy or a chemical transformation I should say chemical change can trigger an electron movement in the form of electricity or vice versa an electrical potential applied on the system creates a chemical change or a chemical transformation.

So, either that chemical change creating the electricity or the electricity is actually doing the chemical change either way it is possible, and depending on which side of the thing we are doing, so, there is a chemical reaction happening and it is actually creating a movement in electron which can be given as electricity.

Now, if the first system is happening a chemical change is happening first and that is creating the electricity movement that is known as a galvanic cell and if the second thing is happening, where the electricity is actually bringing the chemical change, it is known as electrolytic cell. So, these are the two different variations of electro chemical cells we talk about, and it all depends on the directionality of the system like it is a chemical change bringing the electricity or the electricity is bringing the chemical change, and depending on that we can differentiate them with galvanic cell an electrolytic cell.

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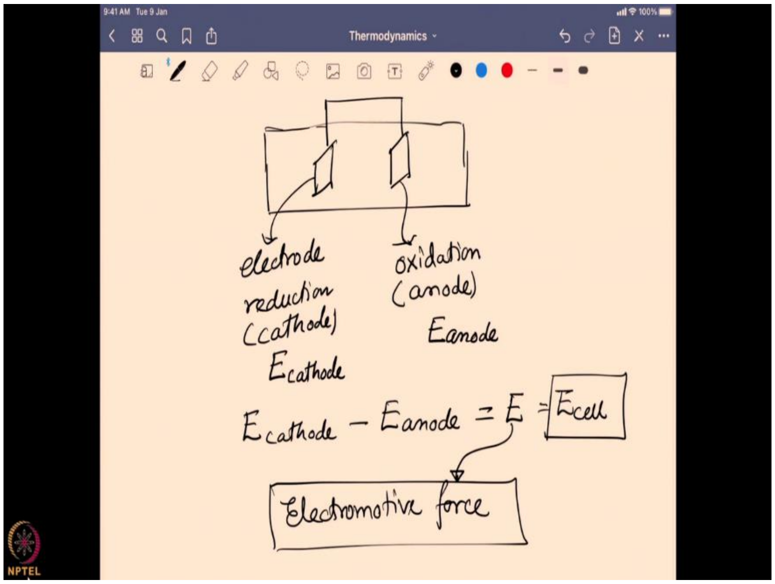

Now, I am drawing the electro chemical cell one more time, now what kind of reaction is happening in these two particular electrodes present in the electrochemical cell. So, in one of the electrodes happens the reduction and that is known as the cathode, and the other one happens the opposite reaction the oxidation which actually completes the overall cycle, this is known as anode.

And these two reactions happen at a particular energy and that energy we can measure with respect to the potential or the voltage we have applied, and say this is happening as $E_{cathode}$ or reduction and this is happening as Eanode or oxidation, and the difference between this cathode and the anodic potential gives me the overall E or sometime as it written E_{cell} the overall capacity of this electrochemical cell in galvanic stage or electrolytic stage to do the maximum amount of work.

So, this is the overall amount of work we can do which is given by this value of E which is known as the electro motive force. So, this is the potential which actually is the driving force behind these chemical reactions to be happening. So, this is actually a measure of the overall chemical reaction is possible in this particular cell. Now, how to connect that with ΔG that Gibbs free energy value.

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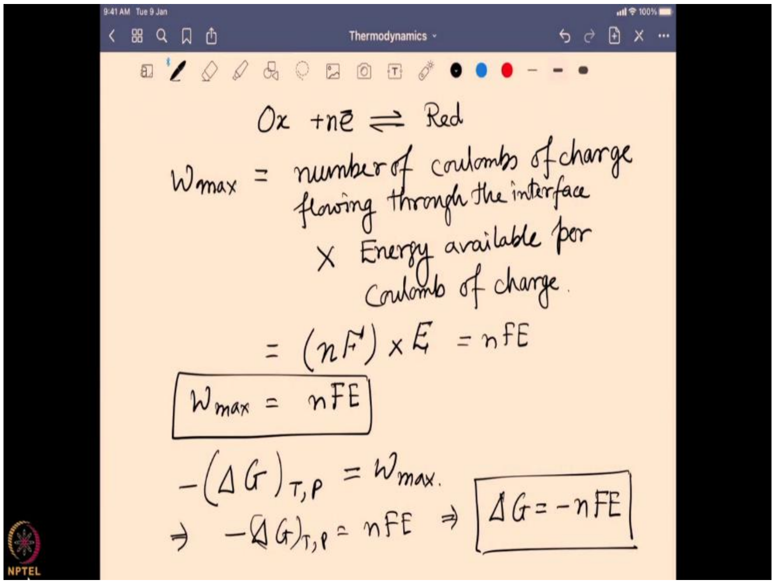

So, now, if we look into a chemical reaction which is happening say we are taking an oxidant molecule, we are giving him n electrons and then the system is producing the reduced equivalent. Now, over here what is the maximum work possible for this redox reaction in electrochemical cells?

So, the maximum work possible over here is going to be number of coulombs of charge flowing through the interface, that means from the solution to the electrode through the circuit, that is how much coulombs of charge is actually exchanging, multiplied by the energy available per coulomb of charge. If you combine them together that is a maximum work we can do that is totally how many charge how much charge is actually converting over there, and for each amount of charge how much work can be done.

So, the number of coulombs transforming over there is equal to n is the number of electrons involved into Faraday, Faraday's unit, which is equivalent to 96485 coulomb, so that gives us the overall charge flowing multiplied by the energy available per coulomb of charge which is nothing but the E the electromotive force that we have discussed just in the initial part, which is the overall energy the difference between the anodic and cathodic section and that is the overall energy available for this particular reaction to happen for one unit of charge and it is totally doing for nF unit of charge it all multiplies together to nFE.

So, the overall maximum work doable in the system is nFE. And now, we have already described the -ΔG at constant temperature and pressure is equal to W_{max} the maximum work possible without the non-expansion work and over there the most non-expansion work possible for the electrochemical cell is nFE.

So, now we can combine them together and we can say $-\Delta G_{T,P}$ = nFE and this gives us the famous equation ΔG is equal to nothing but -nFE. So, for electro chemical cell we can easily find out what is the overall Gibbs free energy change, which is nothing but -nFE, n is the number of electrons involved in this reaction for this redox change, F is the unit Faraday which take care of the overall coulombs of charge available and E is the energy available for this particular reaction per unit of coulomb. So, this is the factor it is coming into the picture. Now, we can go a little bit further to expand it a little bit more.

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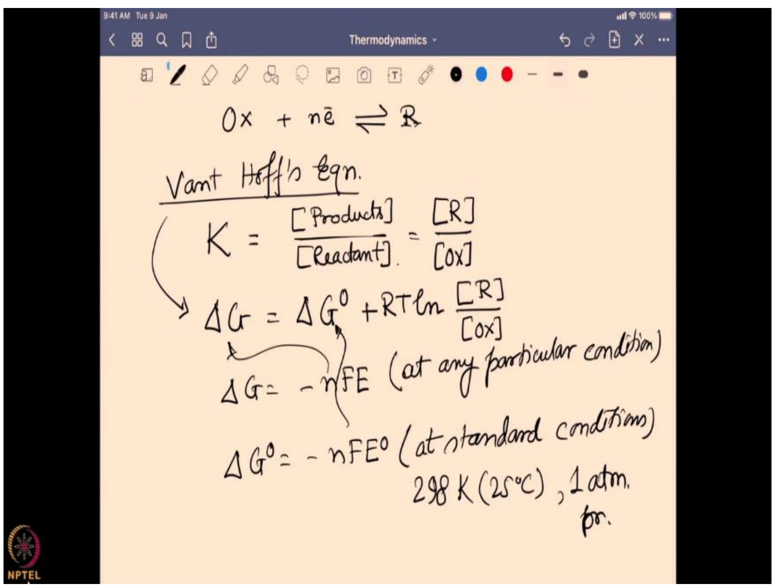

So, now say we are still looking the same reaction oxidant plus n electron is giving me the reduction product, now using Vant Hoff's equations that is out of the ambit of this particular segment, but I encourage you to go and look into the Vant Hoff's equation and how it is connected, that actually says an equilibrium constant of a system can be given by the concentration of the products and concentration of the reactant in this case it is a product is reduced and oxygen concentration from the Vant Hoff's equation I can write this one ΔG = ΔG° that means the Gibbs free energy we calculated at the standard state + RT ln $\frac{[P]}{[R]}$. So, that is what is given by the Vant Hoff's equation.

Now, using this factor, I can write it out ΔG as we already know is equal to -nFE. Similarly, ΔG^o will be equal to nFE^o which is nothing but this is measured at any particular condition, whereas this superscript 0 defines that it is measured at standard states or standard condition, what is the standard conditions?

As defined again earlier 298 Kelvin or 25 degrees centigrade temperature, 1 atmospheric pressure and for solid state it is always in the standard state 1. So, all these things if we combine them together and replace these two values over here and there, what we are actually going to get is the following.

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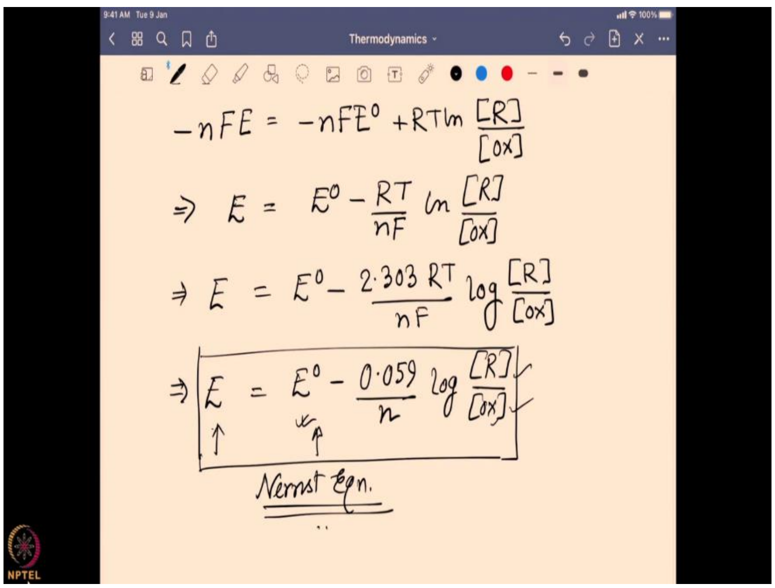

$-nFE = -nFE^0 + RT \ln \frac{[P]}{[R]}$ that is we are actually getting. Now, if we divide everything by -nF we are going to get $E = E^0 - \frac{RT}{nF} \ln \frac{[P]}{[R]}$, we go a little bit farther $E = E^0 - 2.303 \frac{RT}{nF} \log \frac{[P]}{[R]}$ and I am changing this to the log to base 10 from the natural log this factor.

And over here this value can be further simplified by putting this R is nothing but the universal gas constant, T is the absolute temperature and if we consider at 25 degrees centigrade the T is nothing but 298 Kelvin, we all bring it together to this particular value 0.059/ n where we also use F equal to 1 Faraday which is also a constant to log of [R]/[O].

So, over there you can see by using the Gibbs free energy and is expansion its connection to the potential of a system ΔG is = - nFE and using the Vant Hoff's equation we require, we arrived to this particular equation E= $E^0 - \frac{0.059}{n} \log \frac{[R]}{[O]}$ where we can define the potential of any particular condition connected to the standard potential with respect to the how much oxidant and reductant is particularly present in that particular condition.

And this equation is nothing but known as the Nernst equation. And this Nernst equation is very important because by looking into the change of the potential from the standard state, we can actually find out how much reduced and oxidized species is present, what is their equilibrium, where it is actually lies. So, from there, we can actually find out what is the concentration of different analyte and this particular function has been used not to find only particular chemicals, but also to measure even the pH of a solution where proton is one of the reactants.

So, pH meter calculation is also based on the Nernst equation. So, Nernst equation is actually an application of the thermodynamics of Gibbs free energy of Vant Hoff's equation and their interaction, and over there we arrived to this Nernst equation, which actually gives us a very clear idea how to measure the different concentration of reactants and products with respect to a change in the equilibrium potential. So, that will be the conclusion of this particular segment of the application. Thank you.