Elementary Electrochemistry
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Lecture 8
EMF of a Cell and Free Energy Change of a Reaction

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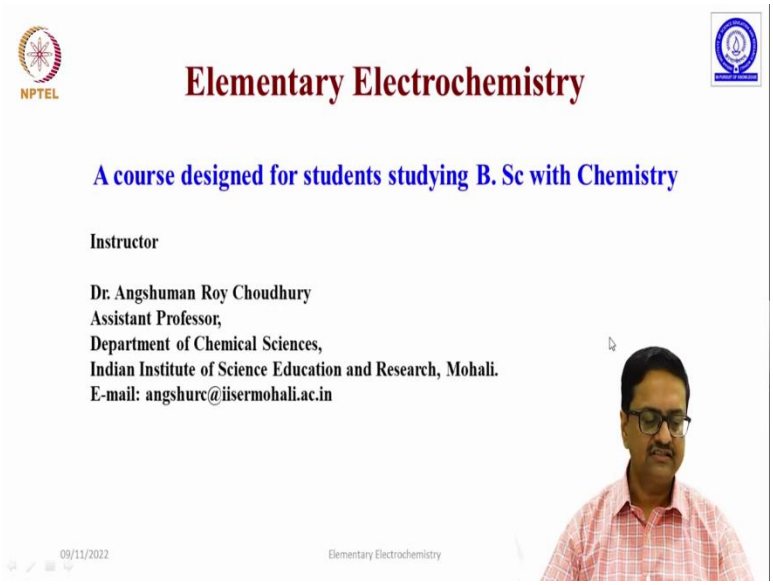

Welcome back to the course entitled Elementary Electrochemistry. In the previous lecture, we have discussed about how to determine the EMF of an unknown cell using a standard cell and then we have discussed about the construction of Weston cell.

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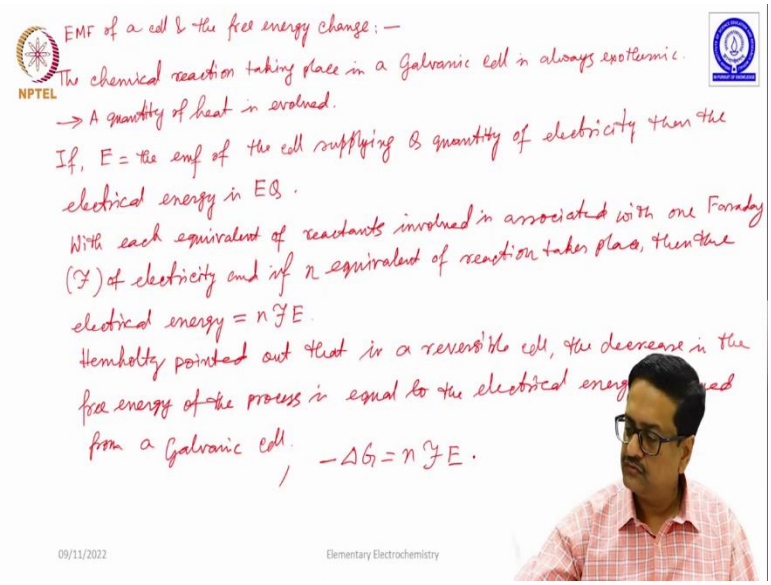

So, in this lecture I am going to talk about the EMF of a cell and the free energy change. The chemical reaction taking place in a galvanic cell is always exothermic. That is, a quantity of heat is evolved. If E is the EMF of the cell supplying Q quantity of electricity then the electrical energy released is E into Q, that is EQ.

Now, with each equivalent of reactants involved is associated with one Faraday that is written as f of electricity and if n equivalent of reaction takes place then the electrical energy is equal to n f E. Helmholtz pointed out that in a reversible cell the decrease in the free energy of the process is equal to the electrical energy obtained from a galvanic cell. That is minus of delta G is equal to n f E.

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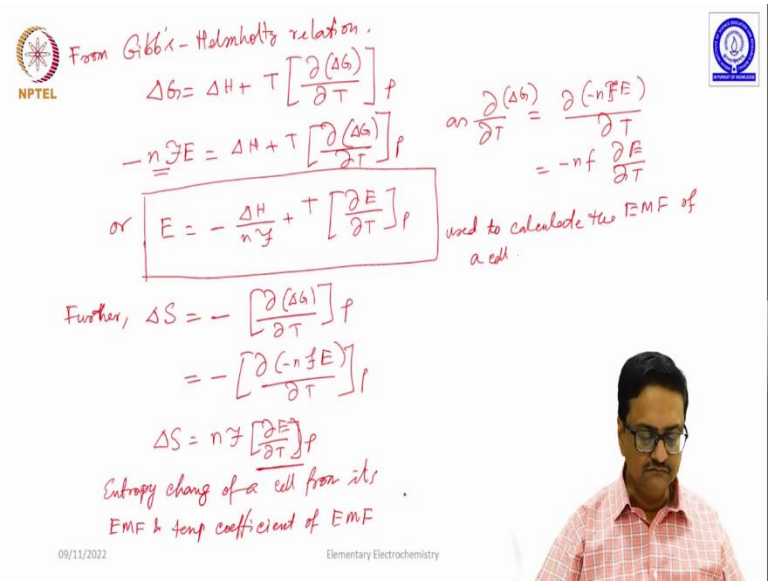

So, now, from our knowledge of basic thermodynamics we know from Gibb's-Helmholtz relation delta G is equal to delta H plus t del delta G del T at constant pressure P. So, now, we replace this delta G by n f E that is minus n f E which is equal to delta H plus T as it is del delta G del t P. Or simply one can write E equal to minus delta H by n f plus T del E del T P as del del T delta G is nothing but del minus n f E by delta t or minus n f del E del T.

So, now, that n f which was here when it comes down gets cancelled and you get this equation. The minus sign also gets removed, so you get the expression like this. So, this equation also can be used to calculate the EMF of a cell. Further, we know that delta S is equal to minus of del delta G del T P. And then you can replace delta S equal to minus del del G del T P. So, you can again replace delta G by minus n f. So, you can write del minus n f E by del T P.

Or delta S equal to n f del E del T at constant pressure P. So, here we are getting the entropy change of a cell from its EMF and temperature coefficient of EMF because this is the temperature dependence of the EMF. So, if you know EMF and its temperature variation, then you can easily calculate delta S for a given cell.

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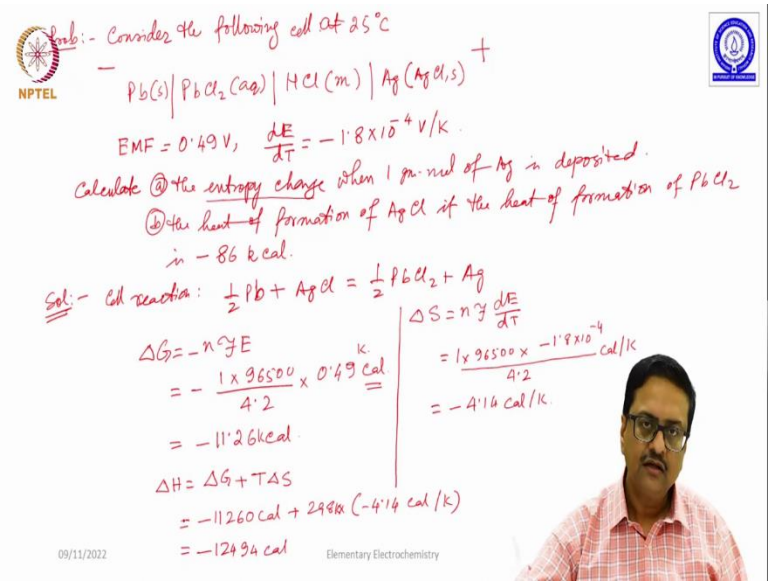

So, let us discuss one simple problem here. Consider the following cell at 25 degrees centigrade Pb solid used as electrode PbCl2 in aqueous medium is with HCl sub molarity aqueous HCl and Ag AgCl solid as the electrode. So, of course, when some electrode the cell is written like that the left side is negative and right side is positive. And it is given that EMF is 0.49 volts and dE dT is equal to minus 1.8 into 10 to the power minus 4 volts per Kelvin.

So, it says calculate, a, the entropy change when 1 gram mole of Ag is deposited and, b the heat of formation of AgCl if the heat of formation of PbCl2 is minus 86 kilocalories. So, how to solve this problem? First, we need to write down the cell reaction, half lead plus AgCl equal to half PbCl2 plus Ag. One can also write Pb plus 2 AgCl giving you PbCl2 plus 2Ag and so on. So, now, we know delta G is equal to minus n f E.

So, when you replace these values what you get is minus 1 into 96500 divided by 4.2 into 0.49 Calorie, why, we are dividing this by 4.2 is 4.2 joule per calorie. So, we want the result in calorie. So, we converted it into calorie by dividing it with 4.2. So, the value turns out to be minus 11.26 calorie. And then when you try to calculate delta S which is equal to n f dE DT you can simply replace the values as 1 into 96500 coulomb into dE dT is given as minus 1.8 into 10 to the power minus 4 and again divided by 4.2 and the unit should be calorie per Kelvin that is minus 4.14 calorie per Kelvin.

So, what we have got? The entropy change. So, now we need delta H which is nothing but from thermodynamic knowledge, knowledge of thermodynamics delta G plus T delta S. So, now, we have delta G is equal to, I think this is not calorie this is kilo calorie because this is like this is kilo calorie. So, this delta G is minus 11260 Calorie plus T is 298 into minus 4.14 calorie per Kelvin. You will see these 298 is Kelvin so that per Kelvin and Kelvin gets cancelled, so at the end you get minus 12494 calorie is your delta H.

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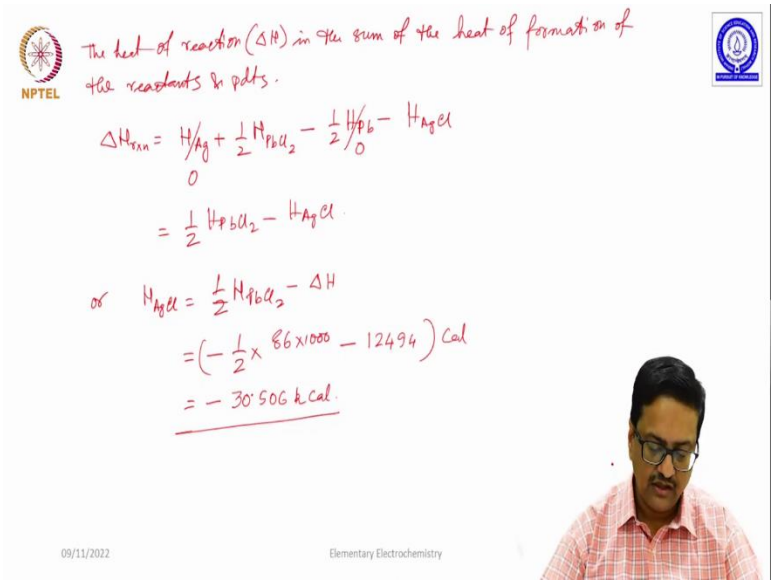

So, now the heat of reaction that is the delta H that we have found is the sum of the heat of formation of the reactants and products. So, one can write delta H reaction is equal to heat of formation of Ag plus half the heat of formation of PbCl2 minus half the formation of lead minus the heat of formation of AgCl. So, now, at standard state the heat of formations of pure elements is taken to be 0. So, it is nothing but half of H PbCl2 minus H of AgCl.

So, H of AgCl is nothing but half of H PbCl2 minus delta H of reaction. So, now what was the heat of formation of lead chloride it is given as 86 kilocalories, so that is this value is 86 kilocalories always delta heat of formation is negative. So, we take it as minus half into 86,000 minus the delta H that we found in the previous page is 12494 calorie. So, the heat of formation of AgCl is nothing but 30.506 kilo calorie.

So, this is how one can estimate the heat of formation of a reactant that is involved in a chemical reaction in an electrochemical or electrolytic cell. So, there will be several problems similar to this in your textbook. So, you should go back and try to solve similar problems using the method I have shown and you may have to utilize some other similar related concepts of thermodynamics, which is taught in different course to solve such problems. So, we will continue from here in the next class. Thank you.