Elementary Electrochemistry
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Lecture 9
EMF of a Cell and Equilibrium Constant of a Reaction: The Nernst Equation

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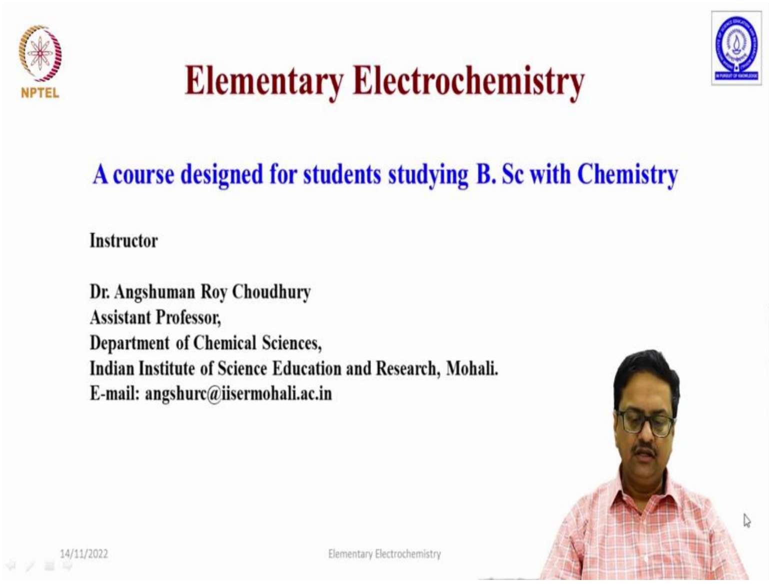

Welcome back to the course entitled Elementary Electrochemistry. In the previous lecture, we have discussed about how one can relate the emf of cell with the Gibbs free energy of that particular cell. And from that we tried to calculate the heat of reaction or heat of formation of a particular substance during the reaction taking place at the electrochemical cell.

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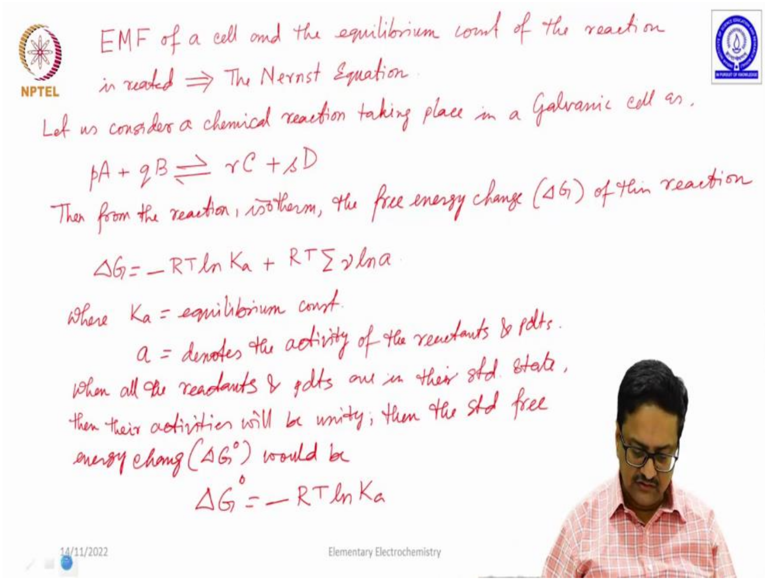

So, today we are going to learn about the relationship between the EMF and the equilibrium constant of a given reaction. So, we will discuss how the electromotive force or EMF of a cell and the equilibrium constant of the reaction is related. This relation is called the Nernst equation. So, to start with let us consider a chemical reaction taking place in a galvanic cell pA plus qB is equilibrium with rC plus sD. So, A, B, C and D are the reactants and products while where p, q, r and s are the stoichiometric coefficient required to balance the chemical reaction.

So, then from the reaction isotherm the free energy change that is the delta G of this reaction can be written as delta G equal to minus RT ln Ka plus RT some over nu ln a. Where Ka is the equilibrium constant of the reaction and a denotes the activity of the reactants and products. Now, when all the reactants and products are in their standard state then their activities will be unity then the standard free energy change which is written as delta G0 would be delta G0 equal to minus RT kn Ka.

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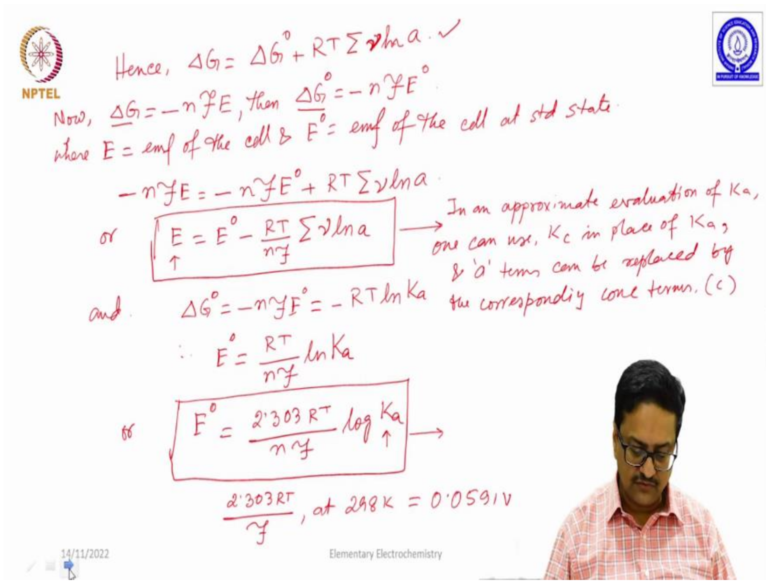

So, then the equation for delta G can be written as delta G0 plus RT sum over nu ln a. Now, in the previous class we have seen that delta G is equal to minus n f E then delta G0 could be equal to minus n f E0 where E equal to emf of the cell and E0 is the emf of the cells at standard state. So, then if we replace these values for delta G and delta G0 in this equation, so one can write that minus n f E equal to n F E0 plus RT sum over nu ln a.

Or E equal to E0 minus RT by n f some over nu ln a. And delta G0 which is equal to minus n f E0 is also equal to minus RT ln Ka which we saw in the previous slide. Therefore, one can write E0 equal to RT by n f ln Ka. Or simply E0, one can evaluate this you can convert this ln to log and write it as 2.303 RT by n f log Ka. We have two equations that we have got here.

So, one equation is for the standard EMF that is E0 of a cell in terms of the equilibrium constant and the other one is the emf of the cell in terms of the activities of the reactants when they are not in their standard state. So, in an approximately evaluation of Ka one can use the Kc in place of Ka, that is the equilibrium constant in terms of concentration and activity terms can be replaced by the corresponding concentration terms that is small c. So, now, if you try to evaluate this 2.303 RT by f at 298 Kelvin this turns out to be 0.0591 watts. Taking Faraday number as 96500, R at its standard unit and temperature in Kelvin one can evaluate the value of this constant as 0.0591 watts.

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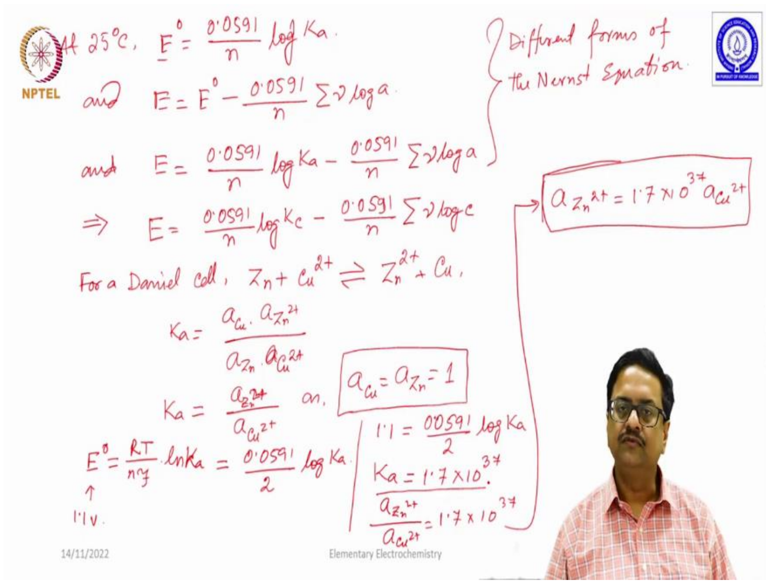

So, then one can write at 25 degrees centigrade E0 of a cell is nothing but 0.0591 psi n log Ka and E equal to E0 minus 0.0591 by n some over mu log a. And also, one can write E equal to we replace E0 by that expression 0.0591 by n log Ka minus 0.0591 by n some over nu log a. All of these are different forms of the Nernst equation. So, then one can approximately write in terms of concentration E equal to 0.0591 by n log Kc minus 0.0511 by n sum over nu log c.

So, now, if we assume, if we try to think about a Daniel cell. For Daniel cell, where the cell reaction is Zn plus, Cu2 plus in equilibrium with Zn2 plus plus Cu. One can write Ka equal to activity or Cu into activity of Zn2 plus divided by activity of Zn into activity of Cu2 plus, which can be equated to activate of Zn2 plus by activity of Cu2 plus as the activity of pure metallic copper is equal to activity of pure metallic zinc which is assumed to be equal to 1.

So, using this assumption that the activity of pure elements pure substances is always 1 one can eliminate them and write this expression as Ka equal to activity of Zn2 plus divided by activity of copper 2 plus. So, now if you try to calculate the corresponding E0 value for this cell one can write E0 equal to RT by n f ln Ka or equal to 0.0591 by 2 that is the charge of the cation log Ka. And we know the E0 for Daniel cell is 1.1 volt.

So, using that 1.1 volt as its standard EMF is equal to 0.0591 by 2 log Ka. So, from this one can calculate the value of Ka equal to 1.7 into 10 to the power 37. Which essentially means that activity of Zn2 plus by activity of copper 2 plus is nothing but 1.7 into 10 to the power 37 or one can write that activity of Zn2 plus is equal to 1.7 into 10 to the power 37 activity of Cu2 plus. So, like this one can do some simple calculations based on the EMF and one can calculate the equilibrium constant and from that one can calculate the ratio of activities of the corresponding consequence.

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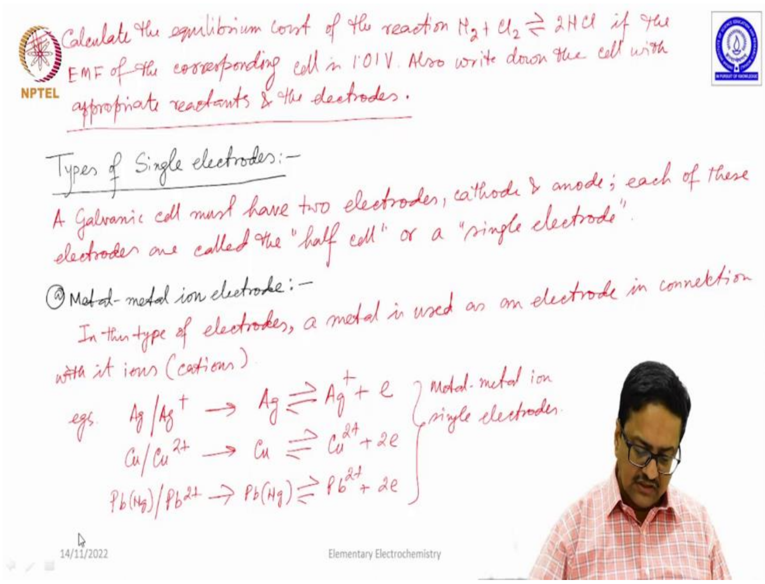

So, based on this I would like to give you one assignment or one problem for you to try. Calculate the equilibrium constant of the reactions H2 plus Cl2 in equilibrium with 2HCL if the emf of the corresponding cell is 1.01. And also, write down the cell with appropriate reactants and the electrodes. So, this is one of the problems that you should try to solve at home. This will help you in understanding the subject and basics properly.

So, now, I would like to start discussing about different types of electrodes because as you have already seen there are types of electrodes where one gas is involved like hydrogen gas somewhere you have a metal and metal ion electrode and so on. So, based on the type and nature of constituents nature of chemicals used to form an electrode, there are several different types of electrodes and these are called types of single electrodes.

As you all know that a galvanic cell must have two electrodes namely cathode and anode, each of these electrodes are called the half cells or a single electrode. And depending on the type and nature of its constituents of the chemicals that are used there are several types of such electrodes. So, let us try to understand some of those one by one. The first one is metal-metal ion electrode.

So, here what you can easily understand that this electrode consists of a particular metal in equilibrium with its cation. So, in this type of electrodes a metal is used as an electrode in connection with ions that is cations. So, when a metal rod is dipped in a solution of its cation then the combination is called the metal-metal ion electrode. Some examples are silver-silver plus electrode where the reaction is silver is in equilibrium with Ag plus plus 1 electron.

Similarly, copper-copper 2 plus where the reaction is cu metal is in equilibrium with Cu2 plus and two electrons and there can be amalgam electrodes where you have led amalgam with Pb2 plus. So, the reaction of the electrode is led amalgam is in equilibrium with Pb2 plus plus 2 electrons. So, these are examples of metal-metal ion single electrodes.

Each of these single electrodes will have their own standard electrode potential and that standard electrode potential can be easily determined from the corresponding, from the measurement using a potentiometer using standard hydrogen electrode or using cation electrode. So, like this there are other single electrodes, which we will discuss in the next class. Thank you.