Elementary Electrochemistry
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Lecture 10
Various types of Electrodes (Glass, SHE, Calomel) in Electrochemistry

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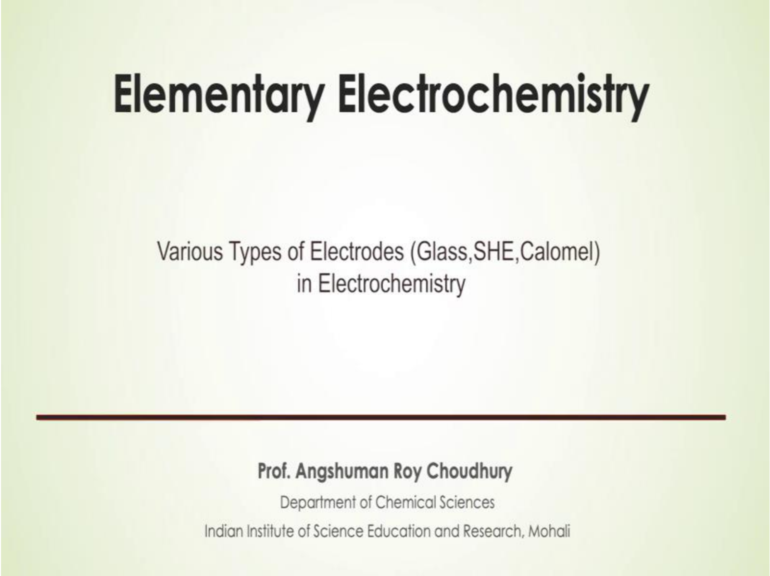

Elementary Electrochemistry

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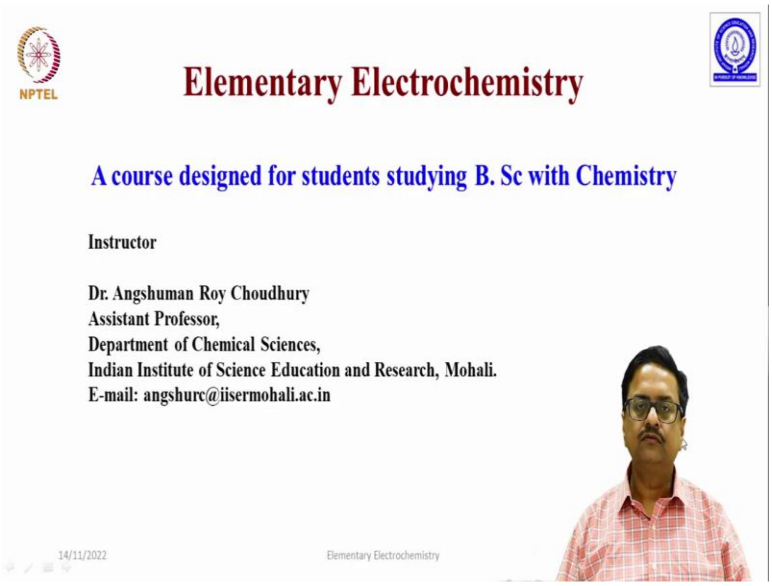

Elementary Electrochemistry

A course designed for students studying B. Sc with Chemistry

Instructor

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Welcome back to the course entitled Elementary Electrochemistry. In the previous lectures, we have discussed about the EMF and its relationship with equilibrium constant. And we have discussed about the Nernst equation how it is formed and how one can use it.

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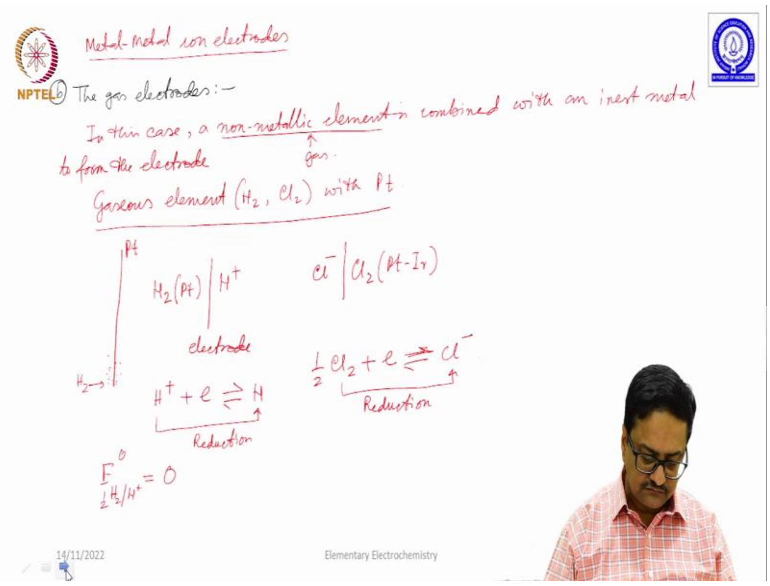

Metal-metal ion electrodes

(b) The gas electrodes:–

In this case, a non-metallic element is combined with an inert metal to form the electrode

$\uparrow$ gas.

Gaseous element (H_2, Cl_2) with Pt

$H_2(Pt) \mid H^+$

electrode

$Cl^- \mid Cl_2(Pt\text{-}Ir)$

$\underbrace{H^+ + e \rightleftharpoons H}_{\text{Reduction}}$

$\underbrace{\frac{1}{2}Cl_2 + e \rightleftharpoons Cl^-}_{\text{Reduction}}$

$E^0_{\frac{1}{2}H_2/H^+} = 0$

And then it was the end of the last lecture, we started discussing about different types of half cells and in that, we first discussed about the metal-metal ion electrodes and we give some examples of metal-metal electrodes towards the end of the previous lectures. So, now, I would like to discuss the second type of electrodes, the gas electrodes. So, you can easily understand that from the name of this electrode, one of the component of this electrode is a gas.

So, in this case a non-metallic element is combined with an inert metal to form the electrode and this non-metallic element is in general a gas, this combination of a gaseous non-metal or gaseous I would say a gaseous element like hydrogen, chlorine etcetra. with a non-metal metal like platinum forms a particular electrode which we call as the gas electrode.

So, when you have a platinum electrode and hydrogen gas is bubbled around the electrode that electrode is written as H 2 Platinum is the electrode is in equilibrium with H plus. So, this is the electrode or a chloride ion is in contact with chlorine gas with a platinum iridium alloy used as an electrode.

So, in this case the reaction is H plus taking up one electron is giving you hydrogen. Similarly, half Cl 2 is taking up one electron giving you Cl minus. So, this is the cell reaction in reduction directions, just to remind you once again the cell EMF or the half cell potential of this hydrogen platinum electrode, E0 half H 2 to H plus is taken as 0 the standard and based on this, the value of half cell potential of this reaction all other cells are determined their corresponding EMF is determined based on the value for this cell taken as 0.

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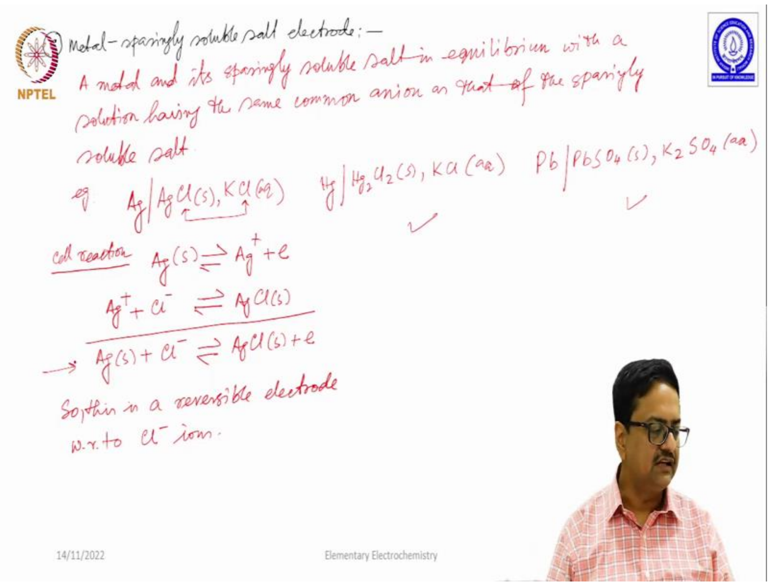

(3) Metal-sparingly soluble salt electrode:—

A metal and its sparingly soluble salt in equilibrium with a solution having the same common anion as ~~that of~~ the sparingly soluble salt

eg $Ag | AgCl(s), KCl(aq)$ $Hg | Hg_2Cl_2(s), KCl(aq)$ ✓ $Pb | PbSO_4(s), K_2SO_4(aq)$ ✓

cell reaction $Ag(s) \rightleftharpoons Ag^+ + e$

$Ag^+ + Cl^- \rightleftharpoons AgCl(s)$

$\longrightarrow Ag(s) + Cl^- \rightleftharpoons AgCl(s) + e$

So, this is a reversible electrode w.r.to Cl^- ion.

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The next type of single electrode is metal and sparingly soluble salt electrode. So, in this case we take a metal and its sparingly soluble salt in equilibrium with a solution having the same common anion, having the same common anion, as that of the sparingly soluble solids. So, some examples are like this silver is the metal the corresponding sparingly soluble salt is AgCl, which is inert a solid and you take a solution of KCL in water where the anion is found. Similarly, one can use Mercury, Hg 2, Cl 2, solid with KCl aqueous. Pb with Pb SO 4 solid with K 2 SO 4 aqueous.

So, just I am writing one of the cell reactions, so, for this half cell reaction, you will have a set of two reactions Ag solid comes in equilibrium with Ag plus, plus electron and then this Ag plus reacts with a Cl minus from the solution and forms AgCl solid. So, the overall half cell reaction is Ag solid that is the metal taking up Cl minus from solution which comes from KCL is in equilibrium with Ag Cl solid plus electrode.

So, this is a reversible electrode with respect to chloride ions so, for your practice you try to write down the Half cell reactions for the other two cells which I have indicated here. So, those will help you understand how to write the half cell reactions and drawing them and write the complete half cell reaction.

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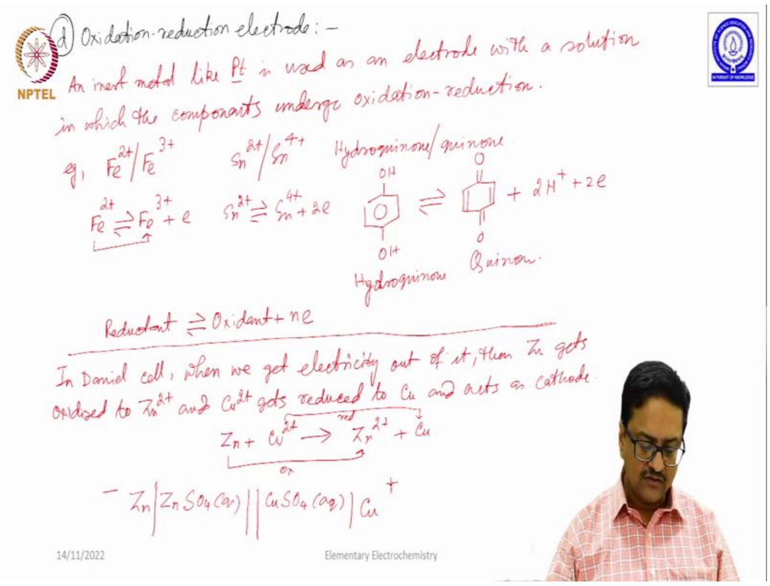

d) Oxidation-reduction electrode: –

An inert metal like Pt is used as an electrode with a solution in which the components undergo oxidation-reduction.

eg, Fe^{2+}/Fe^{3+} Sn^{2+}/Sn^{4+} Hydroquinone/quinone

$Fe^{2+} \rightleftharpoons Fe^{3+} + e$ $Sn^{2+} \rightleftharpoons Sn^{4+} + 2e$

Hydroquinone ⇌ Quinone $+ 2H^+ + 2e$

$\text{Reductant} \rightleftharpoons \text{Oxidant} + ne$

In Daniel cell, when we get electricity out of it, then Zn gets oxidised to Zn^{2+} and Cu^{2+} gets reduced to Cu and acts as cathode.

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

red

ox

$$- \; Zn \,|\, ZnSO_4(aq) \,||\, CuSO_4(aq) \,|\, Cu \; +$$

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The next type of Half cell is the oxidation reduction electrode, here you may ask one question that why suddenly this electrode is called just the oxidation reduction electrode. Where, well all the previous reactions involved oxidation and reduction, see if you have noted or if you have noticed the cell reactions whatever we have written in the previous cases of metal, metal ion electrode, metal sparingly soluble some electrode, gas electrode everywhere we have talked about the oxidation and reduction process involving the particular element in its elemental state that is oxidation state 0.

The hydrogen electrode chloride, chlorine electrode and then metal-metal ion electrode everywhere the one of the elements is taken out it is oxidation state 0. So, in this case, we have a slight difference here, an inert metal like platinum is used as an electrode with a solution in which the components undergo oxidation or reduction.

So, here we should have a solution in which we should have some elements in its lower and higher oxidation state and during the half cell reaction one the lower oxidation state can go to higher oxidation state, higher oxidation state can come to the lower oxidation state and if such reaction happens with the platinum electrode, we then call it as oxidation reduction electrode. Remember here the elements which are undergoing oxidation and reduction are not used as in its elemental state in these cells. So, such examples are like this. Fe 2 plus, Fe 3 plus electrode, S n 2 plus, S n 4 plus electrode (())(13:14) or hydroquinone, quinone.

So, in this case the Iron 2 plus is in equilibrium with Iron 3 plus, plus electron. Similarly, S n 2 plus is in equilibrium with S n 4 plus, plus 2 electrons and as you know hydroquinone is an organic compound with OH group 1 and 4 position of (())(14:02) the phenyl benzene is in equilibrium with this ketone or di-ketone which is called the quinone and it releases 2H plus, plus 2 electrons.

So, in general, one can write it as reductant is in equilibrium with oxidant plus n number of electrons that is the difference in their charge. So, now if you remember at Daniel's cell where we had zinc and copper as electrodes, those represent a cell where one uses the metal metal-ion as electrode. So, in Daniel cell, when we get electricity out of it then Z n gets oxidized to Z n 2 plus that is metal-metal ion electrode and copper 2 plus gets reduced to metallic copper and acts as cathode. So, this cell reaction is written as Z n plus Cu 2 plus giving you Z n 2 plus, plus Cu.

So, here this is oxidation, this is reduction so, if you try to write this cell in one line, once you write the negative electrode that is the anode on the left-hand side, which is Z n in equilibrium with Z n SO 4 aqueous, and it is kept in isolation, but through a connection which I will explain what does that mean in a future lecture. Copper sulfate aqueous, in connection with metallic copper which serves as the cathode the positive electrode. So, what one can do using these electrodes is the following.

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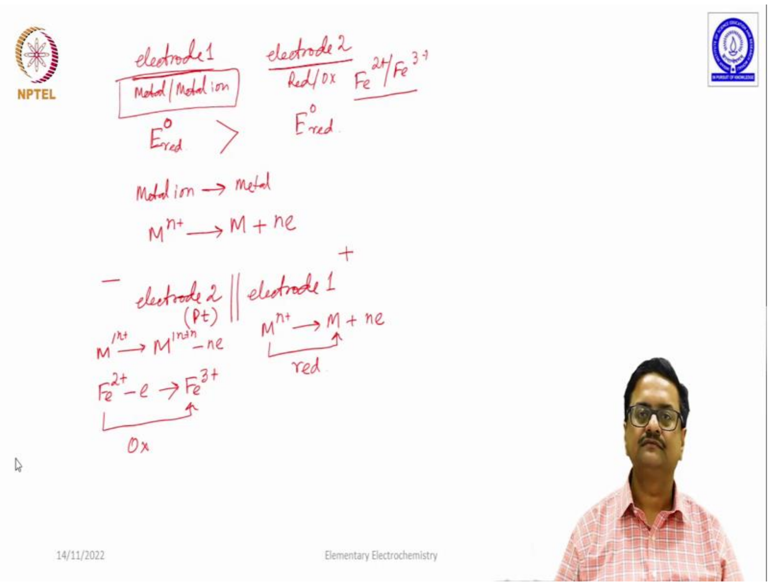

electrode 1 electrode 2

$\boxed{\text{Metal / Metal ion}}$ Red/Ox Fe^{2+}/Fe^{3+}

$E^0_{red} > E^0_{red}$

Metal ion → metal

$M^{n+} \longrightarrow M + ne$

$-$ electrode 2 || electrode 1 $+$

(Pt)

$M^{n+} \longrightarrow M^{n+n} - ne$ $M^{n+} \longrightarrow M + ne$

red

$Fe^{2+} - e \rightarrow Fe^{3+}$

Ox

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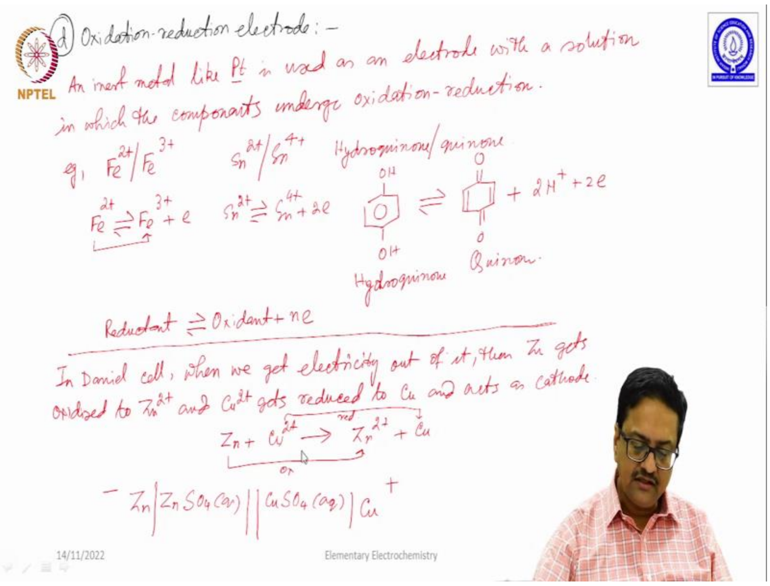

(d) Oxidation-reduction electrode:-

An inert metal like Pt is used as an electrode with a solution in which the components undergo oxidation-reduction.

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$Fe^{2+} \rightleftharpoons Fe^{3+} + e$ $Sn^{2+} \rightleftharpoons Sn^{4+} + 2e$ $\rightleftharpoons$ $+ 2H^+ + 2e$

Hydroquinone Quinone.

Reductant $\rightleftharpoons$ Oxidant + ne

In Daniel cell, when we get electricity out of it, then Zn gets oxidised to Zn^{2+} and Cu^{2+} gets reduced to Cu and acts as cathode.

$$Zn + Cu^{2+} \xrightarrow[\text{ox}]{\text{red}} Zn^{2+} + Cu$$

$$^{-}\ Zn | ZnSO_4(aq) || CuSO_4(aq) | Cu\ ^{+}$$

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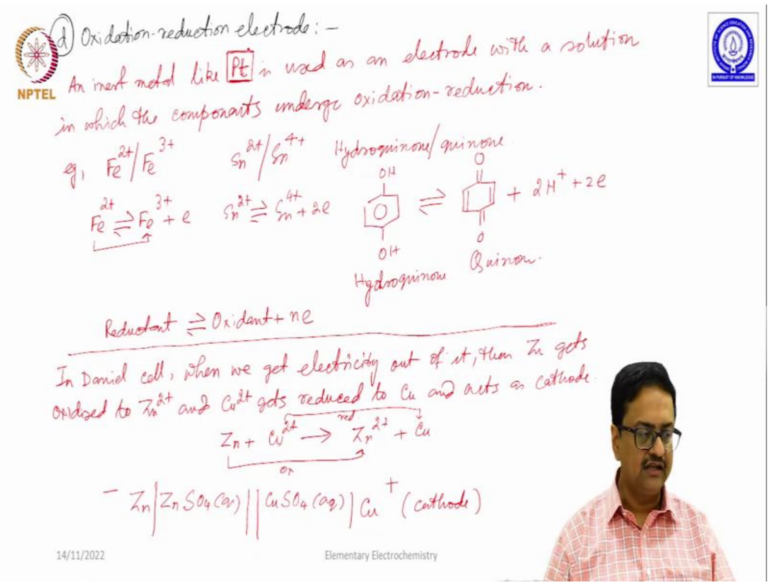

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Hydroquinone Quinone.

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$$Zn + Cu^{2+} \xrightarrow[\text{ox}]{\text{red}} Zn^{2+} + Cu$$

$$^{-}\ Zn | ZnSO_4(aq) || CuSO_4(aq) | Cu\ ^{+}\ (\text{cathode})$$

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So, what you will do is you take one of the electrodes and we name it as electrode 1 and the second electrode and name it as electrode 2, these two electrodes can be anything irrespective of the nature of those electrodes. So, one of the electrode can be suppose a metal-metal ion electrode and the other electrode can be a red ox electrode which can be coupled together to form a cell.

So, what one has to do is individually one has to know the E0 when the reduction mode for the cell and the E0 reduction mode for that cell. So, then you compare the values physical values of these two half cells and if suppose, E0 is the value for this half cell is greater than that then one has to found the cell in such a way that the reaction metal ion to metal takes place in that particular cell that means, Mn plus should get reduced to a metal releasing n number of electrons and when does reduction takes place? When does the reduction takes place?

If you go back to my previous slide, you see the reduction is here. That is copper is getting reduced and the reduction has taken place at cathode and oxidation is taking place at anode. So, then if we encounter a situation like this where electrode 1, has higher reduction potential compared to electrode 2, then the corresponding cell that one has to found should have electrode 2 on left hand side, which will then be anode, it will be connected to the electrode 1, which will serve as the cathode.

So, here in electrode 1, you will encounter the reduction of the metal-ion to the corresponding metal releasing n number of electrons whereas, in this electrode 2 some other metal m prime will get oxidized from its say n plus state to m prime, n plus, n oxidation state by releasing n number of electrons. So, I think this may not be very clear presentation as if we assume that this red ox electrode is Ferrous, ferric system. So, then at this electrode oxidation will take place. So, Fe 2 plus will release electrons at the electrode and will get oxidized to Fe 3 plus.

So, this is the oxidation and this is the reduction that will take place. Now, you see this electrode 2 is a metal-metal ion electrode. So, here you have to have in addition to electrode 2 platinum, which is used to conduct electricity, so, you have to apply platinum as the electrode metal and the corresponding electrode reaction is happening between Ferrous and ferric.

If you go back here, you can also see that we said we will have to use the inert element platinum as an electrode to do the electrical component connectivity, and that electrical connectivity will enable you to do this reaction in the cell. So, with this I would like to conclude this lecture and from this point, we will continue in the next class. Thank you.