Non - Metallic Materials

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Module - 06
Optical and Electrochemical Properties of Non - Metallic Materials
Lecture - 30
Introduction to electrochemistry, Galvanic cells, Cell potentials and Gibbs Energy, Concentration dependence

Welcome to my course Non-Metallic Materials and we are in module number 6, Optical and Electrochemical Properties of Non-Metallic Materials. And, this is lecture number 30, Introduction to electrochemistry, Galvanic cells, Cell potentials, Gibbs Energy and Concentration dependence.

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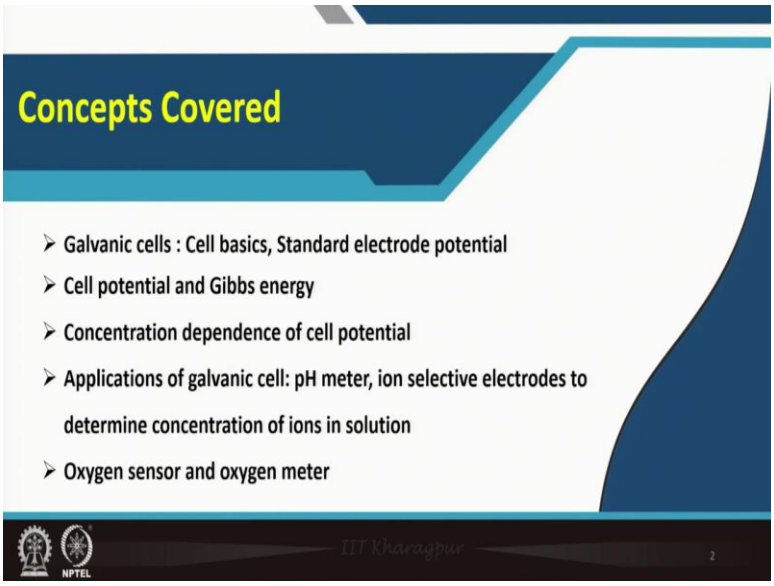

Concepts Covered

- Galvanic cells : Cell basics, Standard electrode potential
- Cell potential and Gibbs energy
- Concentration dependence of cell potential
- Applications of galvanic cell: pH meter, ion selective electrodes to determine concentration of ions in solution
- Oxygen sensor and oxygen meter

So, in this particular lecture first I will introduce the concept of galvanic cells and we will include cell basics, standard electrode potential – what is their function, how they are utilised. Then we will take cell potential and Gibbs energy, how they are related; then we will talk about the concentration dependence of cell potential.

Then we will discuss certain applications of galvanic cells including pH meter, ion selective electrodes to determine the concentrations of ions in the solution in certain applications they are very very important and finally, we will talk about oxygen sensor and oxygen meter in various liquid solutions.

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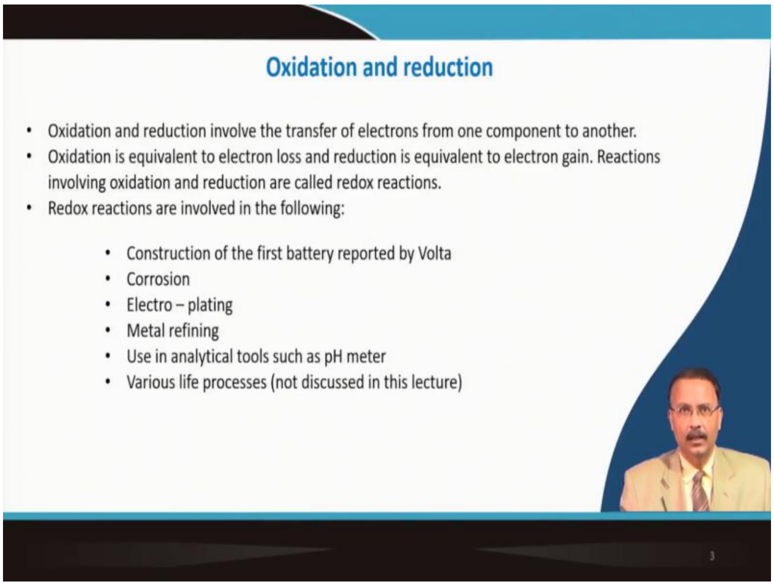

Oxidation and reduction

- Oxidation and reduction involve the transfer of electrons from one component to another.
- Oxidation is equivalent to electron loss and reduction is equivalent to electron gain. Reactions involving oxidation and reduction are called redox reactions.
- Redox reactions are involved in the following:
    - Construction of the first battery reported by Volta
    - Corrosion
    - Electro – plating
    - Metal refining
    - Use in analytical tools such as pH meter
    - Various life processes (not discussed in this lecture)

So, we will start with the basics of oxidation and reduction. Now, as you know, that oxidation and reduction they involve the transfer of electrons from one component to another component.

So, oxidation that is equivalent to loss of electron and reduction is equivalent to the gain of electron and reactions that involved this oxidations and reductions, they are called redox reactions. So, redox reaction they are operative in various applications and that first can be started with the construction of battery which was reported by Volta long back.

Corrosions they are also involved redox reaction. Electro-plating is another important aspects which involve this redox reaction kind of behaviour. In metal refining they are used, they are used in various analytical tools, I will discuss about the pH meter – its construction, its function and various other life processes, they also involve this kind of redox reaction, but this is not part of this particular lecture.

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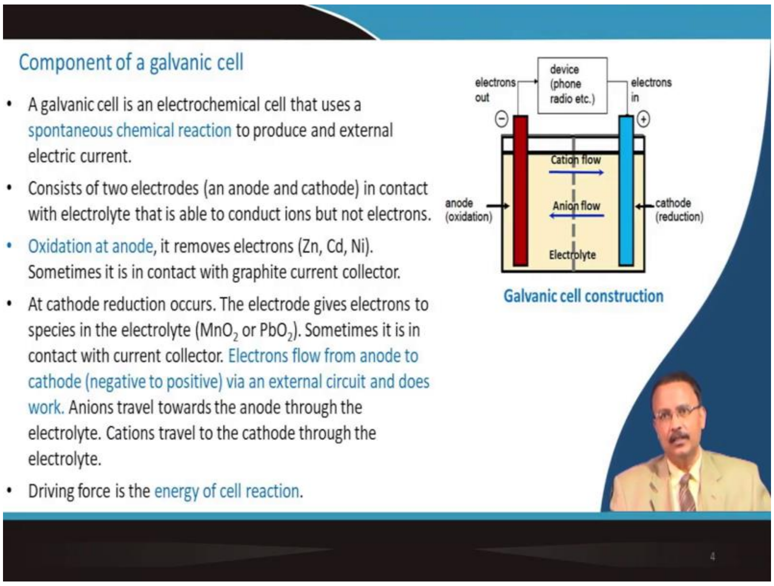

Component of a galvanic cell

- A galvanic cell is an electrochemical cell that uses a spontaneous chemical reaction to produce and external electric current.
- Consists of two electrodes (an anode and cathode) in contact with electrolyte that is able to conduct ions but not electrons.
- Oxidation at anode, it removes electrons (Zn, Cd, Ni). Sometimes it is in contact with graphite current collector.
- At cathode reduction occurs. The electrode gives electrons to species in the electrolyte (MnO_2 or PbO_2). Sometimes it is in contact with current collector. Electrons flow from anode to cathode (negative to positive) via an external circuit and does work. Anions travel towards the anode through the electrolyte. Cations travel to the cathode through the electrolyte.
- Driving force is the energy of cell reaction.

Galvanic cell construction

So, first let us have a look of the components of a typical galvanic cell. So, this galvanic cell is basically an electrochemical cell, which uses a spontaneous chemical reaction and eventually it produces electric current. So, that, you can use in various devices the current that is generated.

So, fundamentally it consist of two electrode – one we call anode and another one is called is cathode, and both these electrodes are in contact with electrolyte that actually transport this ions, but not electrons. So, if electrons are transported through them, then we call this is the short circuit. So, electron is always pass through the external circuit, but internally within the electrolyte only the ions they are transported.

Oxidation reaction that actually takes place in the anode and it involves removal of electron from the anode typically zinc, cadmium, nickel, etcetera is used. Sometimes these anodes are in contact with a current collector and I will discuss it in other lectures part of this module that sometimes graphite current collectors are used.

In cathode usually the reduction occurs. So, electron gives this in this electrode electrons are contributed. So, in the species of the electrolyte that contributes electron sometimes it is oxide like manganese oxide, lead oxide that is used. We will see in case of batteries. We use manganese oxide or lead oxide as cathode.

And, also like your anode sometimes the current collectors are used along with the cathode part and electron flows from anode to cathode. So, from negative to positive electron flow is there via an external circuit. It does not flow through the electrode as I told.

And, an-ions basically travel towards anode. So, the anion in the electrolyte that travels towards the anode side through the electrode electrolyte and cations basically travels through the electrolytes. So, there is a separative, which separates the cathode and anode. And, the driving force is the energy of this cell reaction that will talk.

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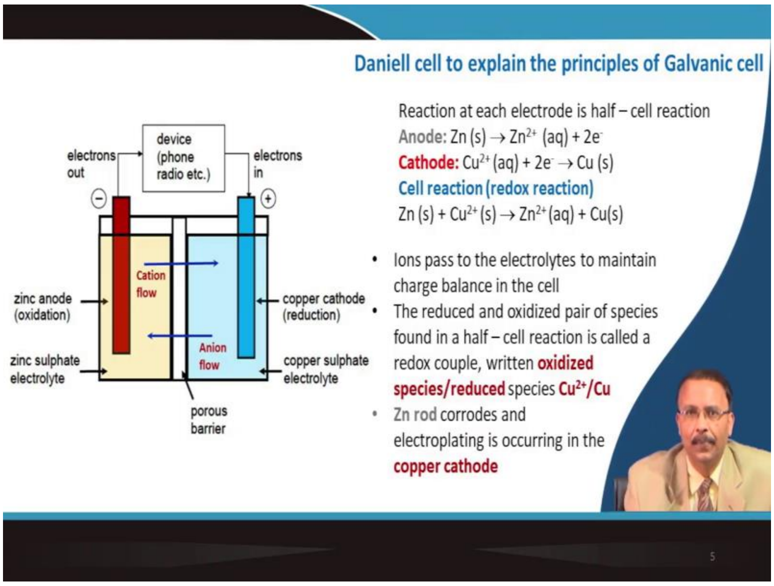

Daniell cell to explain the principles of Galvanic cell

Reaction at each electrode is half – cell reaction

Anode: $Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$

Cathode: $Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$

Cell reaction (redox reaction)

$Zn\ (s) + Cu^{2+}\ (s) \rightarrow Zn^{2+}\ (aq) + Cu(s)$

- Ions pass to the electrolytes to maintain charge balance in the cell
- The reduced and oxidized pair of species found in a half – cell reaction is called a redox couple, written **oxidized species/reduced** species **Cu^{2+}/Cu**
- Zn rod corrodes and electroplating is occurring in the **copper cathode**

So, first we can describe a Daniel cell and a reaction in each of this component involving anode and cathode we call this is a half cell reaction. So, in anode as you can see that solid zinc I have used as anode and copper we have used as cathode. Why particularly zinc and copper is used as anode and cathode respectively we will talk about it.

So, in anode zinc is oxidised. So, it forms zinc ion in aqueous solution and gives 2 electron depends on its valency and in cathode it takes this electron and actually copper ion, which is there in the electrolyte that is electroplated on the cathode surface. So, the cell reaction you can write solid zinc plus copper ion in the solution.

This should be solution. It forms a zinc ion that is also in the solution and copper is electroplated. So, ions passes to the through the electrolyte to maintain the charge balance in the cell. And, the reduced an oxidised pairs of this species found in this half cell reaction that is called a redox couple.

So, it is usually written oxidised species and with a slash reduced species. So, in case of say for example, copper it is Cu 2 plus oblique copper. And, in this particular cell reaction zinc rod corrodes and electroplating occurs in the copper cathode site.

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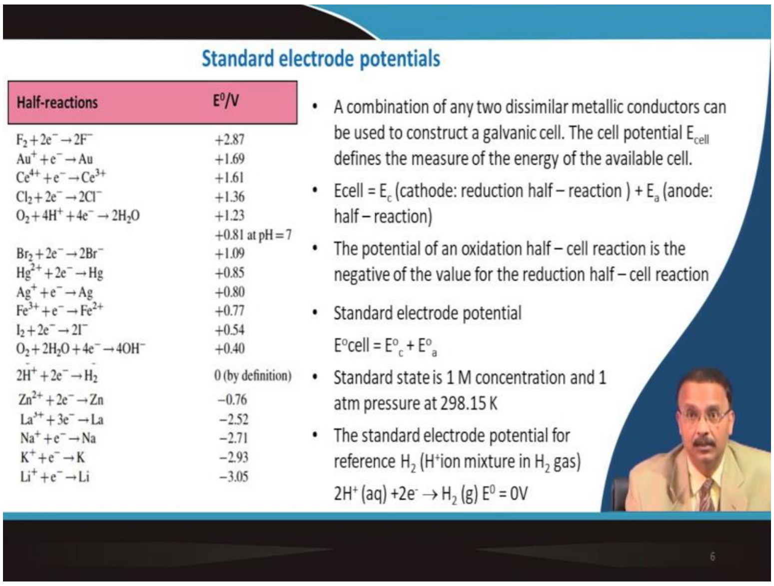

Standard electrode potentials

Half-reactions	E^0/V
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Au^+ + e^- \rightarrow Au$	+1.69
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23
	+0.81 at pH = 7
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.85
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40
$2H^+ + 2e^- \rightarrow H_2$	0 (by definition)
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$La^{3+} + 3e^- \rightarrow La$	−2.52
$Na^+ + e^- \rightarrow Na$	−2.71
$K^+ + e^- \rightarrow K$	−2.93
$Li^+ + e^- \rightarrow Li$	−3.05

- A combination of any two dissimilar metallic conductors can be used to construct a galvanic cell. The cell potential E_{cell} defines the measure of the energy of the available cell.
- Ecell = E_c (cathode: reduction half – reaction) + E_a (anode: half – reaction)
- The potential of an oxidation half – cell reaction is the negative of the value for the reduction half – cell reaction
- Standard electrode potential

  $E^o cell = E^o_c + E^o_a$
- Standard state is 1 M concentration and 1 atm pressure at 298.15 K
- The standard electrode potential for reference H_2 (H^+ion mixture in H_2 gas)

  $2H^+ (aq) + 2e^- \rightarrow H_2 (g)\ E^0 = 0V$

So, a standard electro potential that is there for almost all types of the ions in consent. So, in principle combination of any two dissimilar metallic conductor can be used to construct a galvanic cell. And, the cell potential which I have defined as E cell that defines the measure of the energy of the available cell.

So, if you want to estimate E cell that is the half cell potential of cathode. So, reduction half cell reaction plus E a that is anode half cell energy; so, E c plus E a. So, the potential of an oxidation half-cell reaction is actually the negative of the value of the reduction half-cell reaction.

So, all these values are tabulated is they are all reduction half-cell potential. So, if you go for the oxidation half-cell then this value is negative of the value that has been reported. We can define a standard electrode potential which is defined at E 0 cell, which is E 0 cathode plus E 0 anode. So, this standard condition is one molar concentration of the species 1 atmospheric pressure and temperature is 298.15 Kelvin.

So, the standard electrode potential for the reference electrode we have taken some kind of reference with respect to that we can have this reduction potential defined. So, usually that is hydrogen, which is hydrogen ion mixture in hydrogen gas. So, that is considered to be 0 and that is by definition.

So, the reaction for this is this hydrogen ion in aqueous it takes electron and it forms hydrogen gas. So, that is the reaction involved and the standard electrode potential is considered to be 0. And, with respect to that you can define the other species either as anode or cathode.

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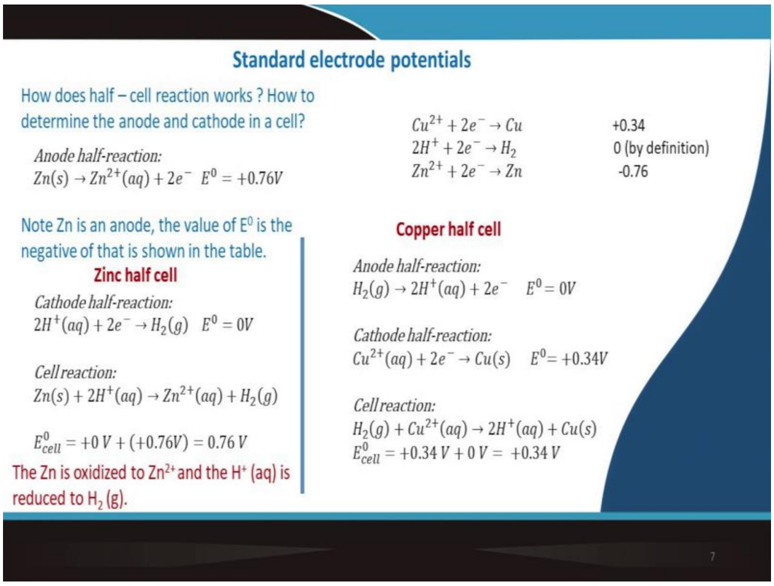

Standard electrode potentials

How does half – cell reaction works ? How to determine the anode and cathode in a cell?

Anode half-reaction:
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \quad E^{0} = +0.76V$

$Cu^{2+} + 2e^{-} \rightarrow Cu$	+0.34
$2H^{+} + 2e^{-} \rightarrow H_2$	0 (by definition)
$Zn^{2+} + 2e^{-} \rightarrow Zn$	-0.76

Note Zn is an anode, the value of E^0 is the negative of that is shown in the table.

Zinc half cell

Cathode half-reaction:
$2H^{+}(aq) + 2e^{-} \rightarrow H_2(g) \quad E^{0} = 0V$

Cell reaction:
$Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

$E^{0}_{cell} = +0\,V + (+0.76V) = 0.76\,V$

The Zn is oxidized to Zn^{2+} and the H^{+} (aq) is reduced to H_2 (g).

Copper half cell

Anode half-reaction:
$H_2(g) \rightarrow 2H^{+}(aq) + 2e^{-} \quad E^{0} = 0V$

Cathode half-reaction:
$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \quad E^{0} = +0.34V$

Cell reaction:
$H_2(g) + Cu^{2+}(aq) \rightarrow 2H^{+}(aq) + Cu(s)$
$E^{0}_{cell} = +0.34\,V + 0\,V = +0.34\,V$

So, now the question is that how this half cell reaction actually works? And how one can determine which one is anode and which one is cathode in a full cell? So, that thing you need to know. So, if you consider a cell a, which is having zinc, zinc solid, so, when it is oxidised then it forms zinc ion and it gives electron back to the back to the circuit.

So, the potential here is as I told it is negative of the value which is defined in standard electrode potential. So, it was minus 0.76. So, it is actually plus 0.76. So, zinc is considered as an anode, the value of the standard electrode potential is negative that was shown in the table. So, that therefore, it is plus 0.76.

And, in the cathode reaction where you are taken care of a standard hydrogen electrode the reaction that is taking place is something related to that which already, I have defined, and standard electrode potential is 0. So, the cell reaction you can add this two up, zinc solid plus hydrogen ion in aqueous condition, it is giving in fact it is corrode engine.

So, zinc ion in aqueous solution it is come, and hydrogen gas is evolved. So, if you want to estimate the standard electrode potential E 0 cell then it is 0 for hydrogen and plus 0.76 for zinc. So, it will give you 0.76 volt. So, here zinc is oxidised, so, zinc ion is formed and hydrogen in aqueous solution is getting reduced to H 2 gas.

Now, if you consider copper then from the standard electrode potential, the value was plus 0.34 and this is the reaction for the standard hydrogen electrode, and this is the reaction as I have just said for zinc. So, if you consider the copper half cell now, so, here you can see the anode half cell reaction, here hydrogen will be in the anode side. So, that is 0.

And, cathode half cell reaction is plus 0.34, where copper plus ion, which is in the aqueous solution that is taken this electron which is evolved by hydrogen and the full cell reaction is given by this relation and you can estimate the standard electrode potential to be plus 0.34 volt.

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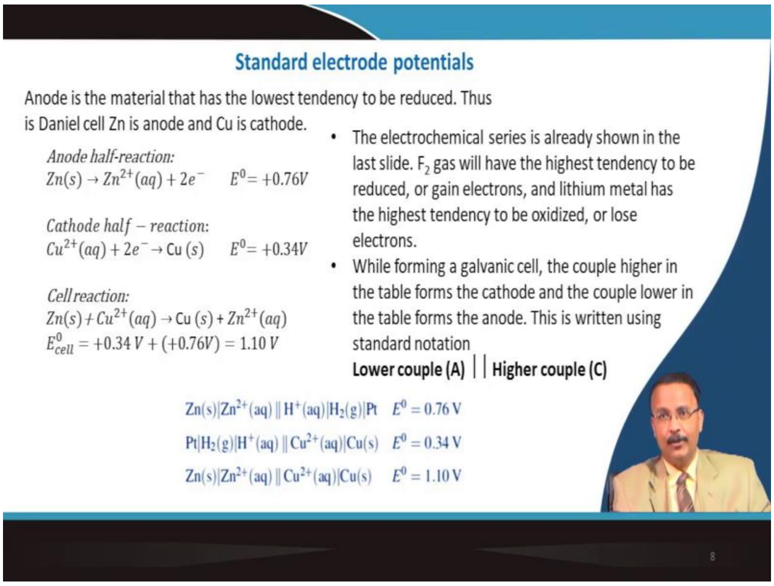

Standard electrode potentials

Anode is the material that has the lowest tendency to be reduced. Thus is Daniel cell Zn is anode and Cu is cathode.

Anode half-reaction:
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^0 = +0.76V$

Cathode half − reaction:
$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s)$ $E^0 = +0.34V$

Cellreaction:
$Zn(s) + Cu^{2+}(aq) \rightarrow Cu\ (s) + Zn^{2+}(aq)$
$E^0_{cell} = +0.34\ V + (+0.76V) = 1.10\ V$

- The electrochemical series is already shown in the last slide. F_2 gas will have the highest tendency to be reduced, or gain electrons, and lithium metal has the highest tendency to be oxidized, or lose electrons.
- While forming a galvanic cell, the couple higher in the table forms the cathode and the couple lower in the table forms the anode. This is written using standard notation

Lower couple (A) || Higher couple (C)

$Zn(s)|Zn^{2+}(aq) \| H^+(aq)|H_2(g)|Pt$ $E^0 = 0.76\ V$
$Pt|H_2(g)|H^+(aq) \| Cu^{2+}(aq)|Cu(s)$ $E^0 = 0.34\ V$
$Zn(s)|Zn^{2+}(aq) \| Cu^{2+}(aq)|Cu(s)$ $E^0 = 1.10\ V$

Now, anode is the material that has the lowest tendency to be reduced thus in the Daniel cell we have used zinc as anode and copper you can use at cathode now. So, again you can write the anode half cell reaction. So, zinc solid is getting corroded the standard electrode potential is 0.76 for this two dissimilar electrode material cathode half cell reaction is given by copper 2 plus and it is taking electron getting electroplated.

So, this is 0.34. So, the total cell reaction is given by zinc in solid state copper it is taking from the electrolyte and copper is electroplated and zinc is getting corroded. So, two different salt solution are there in the anode compartment and in the cathode compartment, usually the sulphate salts are used, which is separated by a salt bridge which allow the cat-ions to passed, but not the electron to be passed.

So, the electrochemical series whatever I have already shown in the previous slide, you can see the fluorine gas will have the highest tendency to be reduced or gain electrons and lithium metal is highest tendency to be oxidised or loose electron. So, while following the galvanic cell the couple higher in the table forms in the cathode and the couple lower in the table than the standard hydrogen forms the anode.

And, this is actually written as a standard notation lower couple and couple means that this oxidised species and the reduced species the redox couple and this is the separation by the electrolyte and the higher couple.

So, if you take the zinc half-cell, the standard electrode potential is 0.76 and if you take copper half cell the standard electrode potential is 0.34 and if you take this full cell zinc and copper eventually you are forming a battery and you will get 1.10 volt. And, this concept I will use because in other lectures will be talking about primary battery, we will talk about rechargeable secondary ion battery. So, these concepts will use thoroughly.

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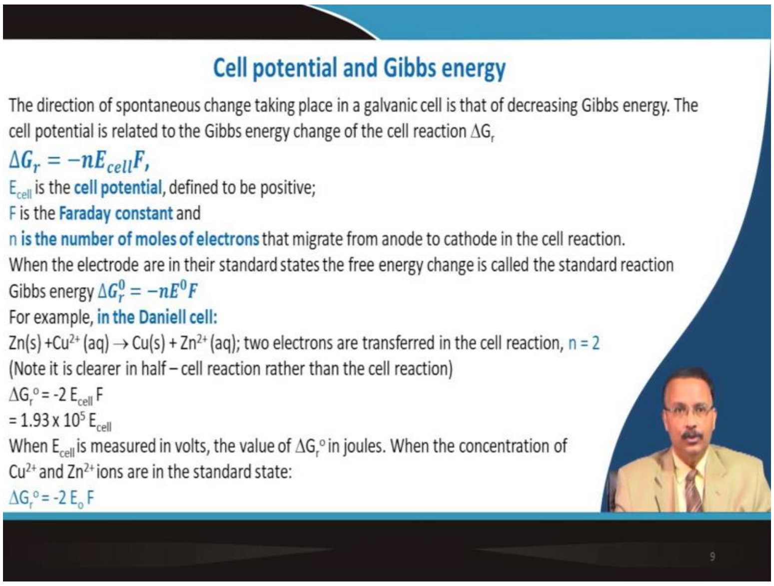

Cell potential and Gibbs energy

The direction of spontaneous change taking place in a galvanic cell is that of decreasing Gibbs energy. The cell potential is related to the Gibbs energy change of the cell reaction ΔG_r

$\Delta G_r = -nE_{cell}F,$

E_{cell} is the **cell potential**, defined to be positive;

F is the **Faraday constant** and

n **is the number of moles of electrons** that migrate from anode to cathode in the cell reaction.

When the electrode are in their standard states the free energy change is called the standard reaction Gibbs energy $\Delta G_r^0 = -nE^0F$

For example, **in the Daniell cell:**

$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$; two electrons are transferred in the cell reaction, n = 2

(Note it is clearer in half – cell reaction rather than the cell reaction)

$\Delta G_r^o = -2\ E_{cell}\ F$

$= 1.93 \times 10^5\ E_{cell}$

When E_{cell} is measured in volts, the value of ΔG_r^o in joules. When the concentration of Cu^{2+} and Zn^{2+} ions are in the standard state:

$\Delta G_r^o = -2\ E_o\ F$

So, the cell potential that is related to the Gibbs energy because as I told that the direction of the spontaneous change that is taking place in a galvanic cell is the whole idea is to reduce or decrease the Gibbs energy. So, cell potential is of course, related to the Gibbs energy change, which I have denoted as del G r and this is related negative term is there minus n is the number of moles of electron that migrates from anode to cathode in the cell reaction.

And, then you have E cell and this E cell is a cell potential and it defines to be positive because the overall the energy change should be negative to make it spontaneous and F is the Faraday constant. So, in the standard reaction condition; that means, 1 mole concentration temperature is 298 degree Kelvin and pressure if you take 1 atmosphere, then the free energy change is given by this relation.

So, you can calculate for the Daniel cell you know the full cell reaction is something like this. And, here 2 electron that is apparent from the half-cell reaction; so, two electrons are transferred and that depends on the valency of the cation that is taking part in the reaction.

So, you can estimate by this and put the value of the Faraday constant and you will get this number 1.93 into 10 to the power 5 into respective E cell, which will depend on the type of the 2 metal couple. So, when E cell you are measuring in volt the value of this energy change is in joule and when the concentration of copper 2 plus and zinc 2 plus ions are in the standard state; that means, 1 molar concentration. So, this equation is valid in the standard case.

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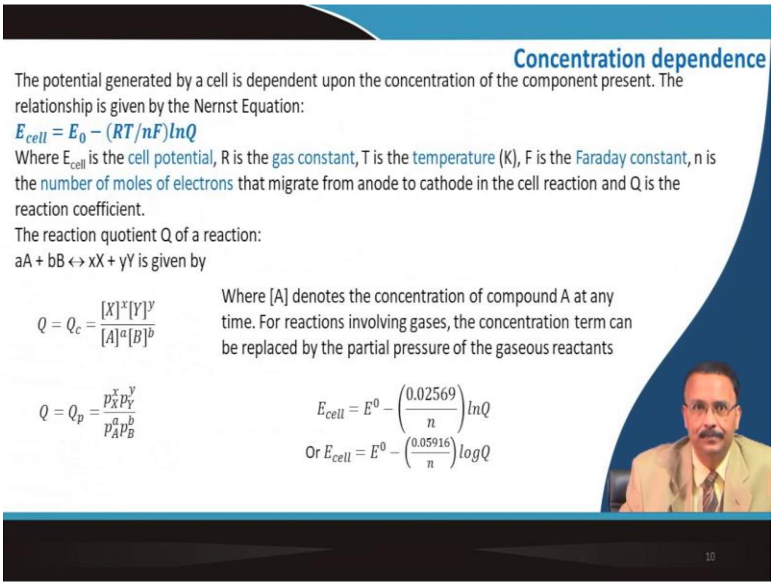

Concentration dependence

The potential generated by a cell is dependent upon the concentration of the component present. The relationship is given by the Nernst Equation:

$$E_{cell} = E_0 - (RT/nF)lnQ$$

Where E_{cell} is the cell potential, R is the gas constant, T is the temperature (K), F is the Faraday constant, n is the number of moles of electrons that migrate from anode to cathode in the cell reaction and Q is the reaction coefficient.

The reaction quotient Q of a reaction:

$aA + bB \leftrightarrow xX + yY$ is given by

$$Q = Q_c = \frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

Where [A] denotes the concentration of compound A at any time. For reactions involving gases, the concentration term can be replaced by the partial pressure of the gaseous reactants

$$Q = Q_p = \frac{p_X^x p_Y^y}{p_A^a p_B^b}$$

$$E_{cell} = E^0 - \left(\frac{0.02569}{n}\right) lnQ$$

Or $E_{cell} = E^0 - \left(\frac{0.05916}{n}\right) logQ$

Now, not always this concentration is maintained which is standard. So, the potential which is generated by the cell is dependent on the concentration of the component, which is present in the galvanic cell. And, this relation is given by the known Nernst equation; already I have described it in one of my early lectures. So, E cell is E 0 minus RT by nF into lnQ.

So, here the terminologies are already defined R is the gas constant, T is the temperature, F is the Faraday constant and n is the number of moles of electron that migrate from anode to cathode of the cell reaction and Q is known as the reaction coefficient. So, if you take a typical reaction that is taken place aA plus bB mole is given you x mole of X and y mole of capital Y.

So, you can calculate this reaction coefficient that is the concentration of the product divided by concentration of the reactant. So, for example, concentration of a is the concentration of compound A at any time and if the gases are involved then this is replaced by respective partial pressure of the gaseous reactant. So, you can now have this value of the E cell which is not only the standard potential which we have evaluated then you have this term.

I have just put the value of R, temperature is standard 298, we have taken number of electrons is still there. So, this value is the combination of this standard constant values and if you can take in ln you can take also in 10 base log and for 10 base log following relation is valid.

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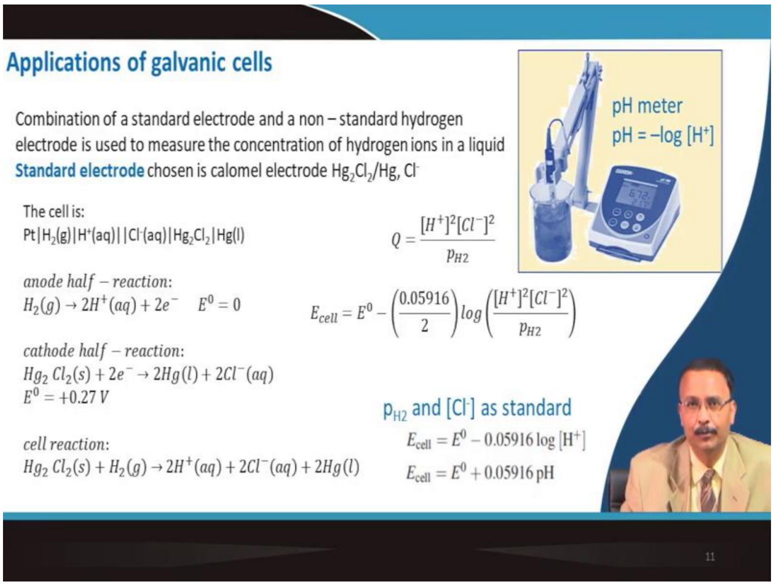

Applications of galvanic cells

Combination of a standard electrode and a non – standard hydrogen electrode is used to measure the concentration of hydrogen ions in a liquid

Standard electrode chosen is calomel electrode $Hg_2Cl_2/Hg, Cl^-$

The cell is:

$Pt|H_2(g)|H^+(aq)||Cl^-(aq)|Hg_2Cl_2|Hg(l)$

$$Q = \frac{[H^+]^2[Cl^-]^2}{p_{H2}}$$

anode half – reaction:

$H_2(g) \rightarrow 2H^+(aq) + 2e^- \quad E^0 = 0$

$$E_{cell} = E^0 - \left(\frac{0.05916}{2}\right) log\left(\frac{[H^+]^2[Cl^-]^2}{p_{H2}}\right)$$

cathode half – reaction:

$Hg_2\,Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$

$E^0 = +0.27\ V$

cell reaction:

$Hg_2\,Cl_2(s) + H_2(g) \rightarrow 2H^+(aq) + 2Cl^-(aq) + 2Hg(l)$

p_{H2} and $[Cl^-]$ as standard

$E_{cell} = E^0 - 0.05916 \log [H^+]$

$E_{cell} = E^0 + 0.05916\, pH$

So, having known this concept we can have several application of the galvanic cell and one of this galvanic cell application is well known to you in terms of the pH meter where negative logarithm of hydrogen ion concentration is measured. So, for measuring this thing a combination of a standard electrode and a non-standard hydrogen electrode is used because eventually you are measuring the hydrogen ion concentration in a liquid.

So, the standard electrode which is used is a calomel electrode which is Hg 2 Cl 2 by Hg in chlorion concentration. So, the cell is you can define like this. So, this is the current collector Pt. Hydrogen gas is there, hydrogen ion in aqueous solution is there and that is separated by chloride ion in aqueous solution and your standard electrode material.

So, you can write a half cell reaction for hydrogen standard condition it is 0 by definition and cathode reaction is given by this where electron it is adopted by this cathode material it is getting reduced to form mercury and chloride ion and the standard electrode potential will be plus 0.27 volt. So, Q you can calculate by the relation I have shown, and in the reactant, it is only the partial pressure of hydrogen.

So, you can estimate the concentration of E cell is equal to E 0; E 0 already you have defined. This constant term will be there – number of electron is 2. Therefore, n is equal to 2 and log of Q that you can write like this. Now, if you take partial pressure of hydrogen and chloride ion as standard then you can have E cell is equal to E 0 into this constant term will be there and you can have a relation with log of H plus.

And, this value as you know; it is a negative logarithm of hydrogen ion concentration. So, eventually with hydrogen ion concentration you get a relation with the measured cell potential and in fact it is done automatically inside the equipment. So, depending on the hydrogen ion concentration always you get in terms of the millivolt which is internally converted to the pH of the solution it is displayed as you can see it here.

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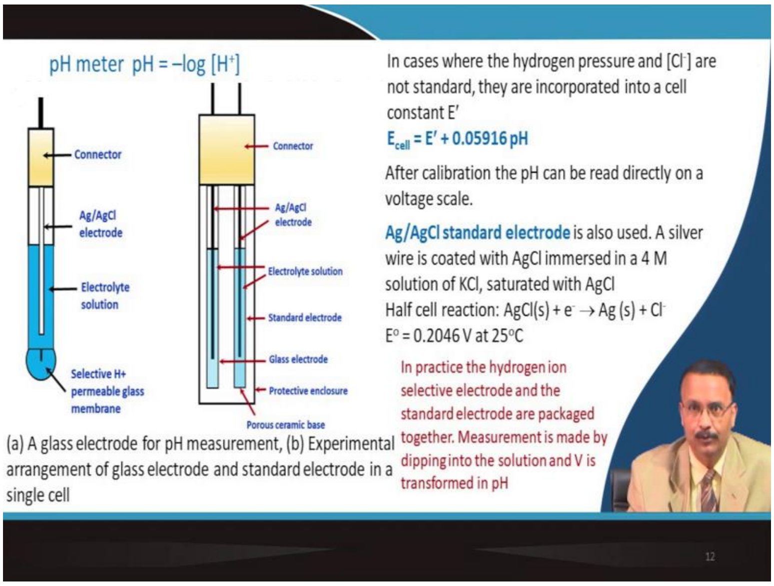

pH meter pH = $-\log [H^+]$

(a) A glass electrode for pH measurement, (b) Experimental arrangement of glass electrode and standard electrode in a single cell

In cases where the hydrogen pressure and $[Cl^-]$ are not standard, they are incorporated into a cell constant E′

$E_{cell} = E' + 0.05916\ pH$

After calibration the pH can be read directly on a voltage scale.

Ag/AgCl standard electrode is also used. A silver wire is coated with AgCl immersed in a 4 M solution of KCl, saturated with AgCl

Half cell reaction: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$

$E^o = 0.2046$ V at 25°C

In practice the hydrogen ion selective electrode and the standard electrode are packaged together. Measurement is made by dipping into the solution and V is transformed in pH

So, the pH meter the negative concentration of hydrogen ion is being determined and it is calibrated with the voltage. So, the electrode is something similar to this, which many of you are familiar with. So, this is a glass electrode for pH measurement, and this is actually the experimental arrangement of the glass electrode and the standard electrode in the same package.

So, when the hydrogen pressure and chloride ion as I said is not standard, they are incorporated into the cell by a constant because the constant term only change. So, E cell will not be E 0, but E prime plus 0.05916 pH value of the solution. So, one can calibrate the pH and directly read on a voltage scale.

So, not always this calomel electrode is used sometimes the silver – silver chlorides standard electrode is also used. So, there is silver wire is coated with silver chloride and it is typically dipped in a 4 molar concentration solution of KCl, which is saturated with AgCl. So, this is the half-cell reaction.

And, in practice this membrane is a hydrogen ion selective membrane is used. So, that only hydrogen ion passes. So, it is permeable to hydrogen ion selective glass membrane is used and the standard electrode are packaged together, and measurement is done by dipping the electrode into a solution and directly you can read the value.

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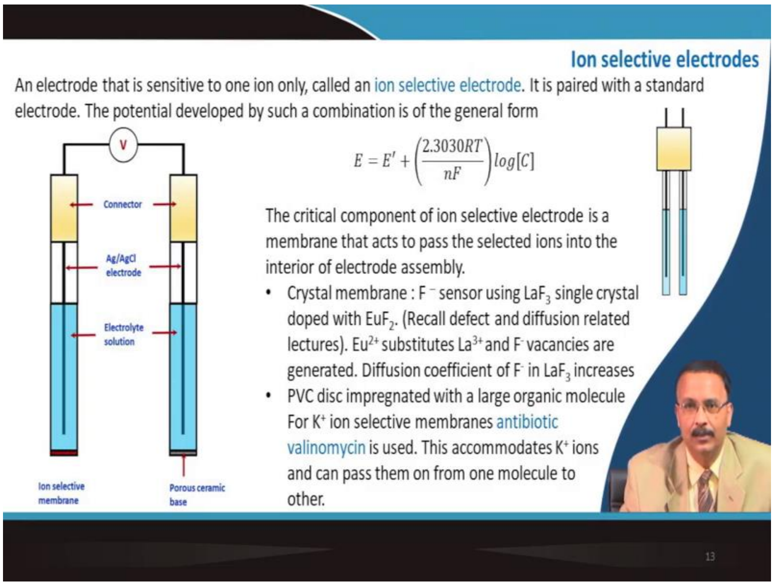

Ion selective electrodes

An electrode that is sensitive to one ion only, called an ion selective electrode. It is paired with a standard electrode. The potential developed by such a combination is of the general form

$$E = E' + \left(\frac{2.3030RT}{nF}\right) log[C]$$

The critical component of ion selective electrode is a membrane that acts to pass the selected ions into the interior of electrode assembly.

- Crystal membrane : F^- sensor using LaF_3 single crystal doped with EuF_2. (Recall defect and diffusion related lectures). Eu^{2+} substitutes La^{3+} and F^- vacancies are generated. Diffusion coefficient of F^- in LaF_3 increases
- PVC disc impregnated with a large organic molecule For K^+ ion selective membranes antibiotic valinomycin is used. This accommodates K^+ ions and can pass them on from one molecule to other.

So, not only this hydrogen ion, but various ion selective electrodes one can make to know the concentration of a particular ion for a specific purpose. So, it is selective to that particular ion and the reaction is something similar to this. So, it is no longer hydrogen ion concentration, but the concentration of that particular ion.

So, I have cited two examples the feature is something similar to this as you can see that one is ion selective membrane is here and another one is a normal porous ceramic base. So, that is used. So, this is also packaged in the form of this type and the crystal that is used say for floating sensor is lanthanum fluoride single crystal, which is duped with uranium fluoride. And, you can recall that lanthanum is substituted by europium Eu 2 plus.

So, it will create, it is the accepted dopant it will create, fluorine vacancies and diffusion coefficient of fluorine in lanthanum fluoride will increase. So, it is selective to fluorine ion. Similarly, PVC can also be used where potassium ion is selective membrane and in that case PVC it is coated with an antibiotic valinomycin. This accommodates potassium ions and that can pass from one molecule to other to serve the purpose and you can measure the concentration of this.

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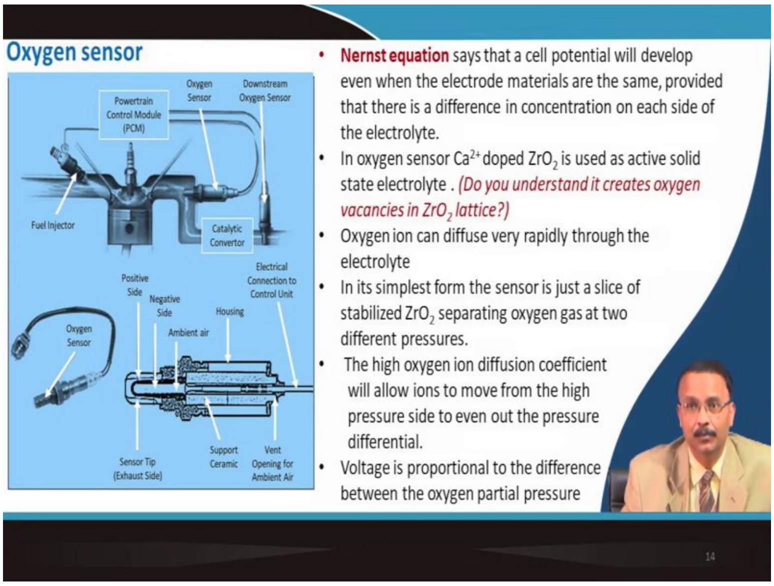

Oxygen sensor

- **Nernst equation** says that a cell potential will develop even when the electrode materials are the same, provided that there is a difference in concentration on each side of the electrolyte.
- In oxygen sensor Ca^{2+} doped ZrO_2 is used as active solid state electrolyte . *(Do you understand it creates oxygen vacancies in ZrO_2 lattice?)*
- Oxygen ion can diffuse very rapidly through the electrolyte
- In its simplest form the sensor is just a slice of stabilized ZrO_2 separating oxygen gas at two different pressures.
- The high oxygen ion diffusion coefficient will allow ions to move from the high pressure side to even out the pressure differential.
- Voltage is proportional to the difference between the oxygen partial pressure

Now, the final part is quite interesting it is a oxygen sensor and oxygen sensor is used for effective combustion in the IC engine or petrol engines and you know precise combustion of petrol is important. So, the oxygen content needs to be known. So, this is a typical assembly which is used.

And you have one oxygen sensor here before the catalytic converter because you want all the carbonaceous hydrocarbons material is completely burnt into carbon dioxide and H 2 and no more carbon monoxide, which is thrown in the ambient to increase the pollution level. So, you have a catalytic converter.

So, oxygen concentration here will tell you whether this is completely burnt and whether you have any un-burnt carbon. So, this two oxygen sensor value the oxygen concentration that is measured in a normal car engines. So, again the Nernst equation says that it is not only two dissimilar electrodes, but even if the electrodes are same in this case it is porous platinum and the electrolyte is a zerconia based electrolyte which is a good oxygen transport media.

And, if you can change the oxygen partial pressure in both the end then voltage will be generated. So, by calibrating this voltage with oxygen ion partial pressure partial pressure of the oxygen you can eventually tell that what is the content of oxygen. So, the whole important thing is to develop this ZrO 2, which again is calcium doped.

So, again from your previous knowledge on the defect you know it is a accepted dopant replacing zirconium which is plus 4 state. So, it will create lot of oxygen vacancies and this oxygen ions can diffuse very rapidly through the electrolyte. So, in a simplest form the sensor is just a slice of the stabilised ZrO_2 separating oxygen gas at two different pressure.

The high oxygen ion diffuse diffusion coefficient will allow the ions to move from high pressure side to even out the pressure difference differential and voltage is proportional to the difference between the oxygen partial pressure.

So, this is the actual oxygen sensor and in fact this is a cross-section effect and heating is required otherwise oxygen diffusion will not take place. So, it is equipped by a heater platinum plates are used as an electrode in both the sides, only the concentration variation will give you the voltage to measure.

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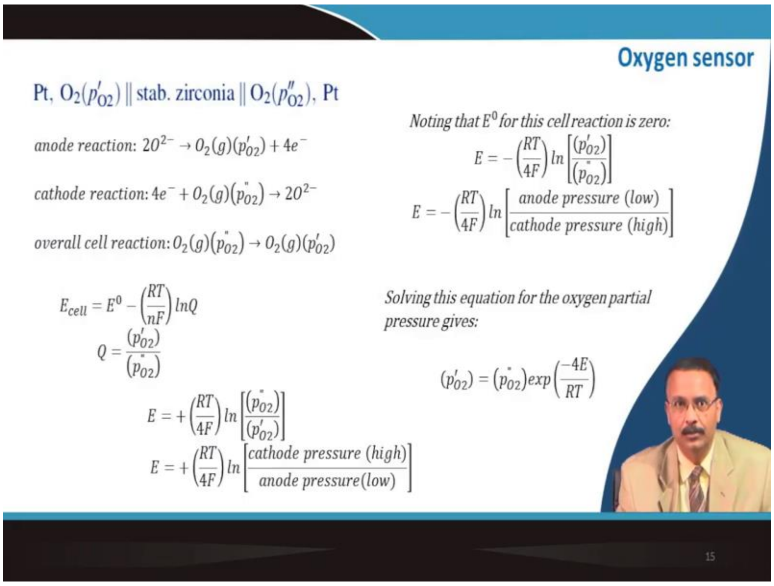

Oxygen sensor

$\text{Pt}, O_2(p'_{O2}) \,\|\, \text{stab. zirconia} \,\|\, O_2(p''_{O2}), \text{Pt}$

anode reaction: $2O^{2-} \rightarrow O_2(g)(p'_{O2}) + 4e^-$

cathode reaction: $4e^- + O_2(g)(p''_{O2}) \rightarrow 2O^{2-}$

overall cell reaction: $O_2(g)(p''_{O2}) \rightarrow O_2(g)(p'_{O2})$

$$E_{cell} = E^0 - \left(\frac{RT}{nF}\right) lnQ$$

$$Q = \frac{(p'_{O2})}{(p''_{O2})}$$

$$E = +\left(\frac{RT}{4F}\right) ln\left[\frac{(p''_{O2})}{(p'_{O2})}\right]$$

$$E = +\left(\frac{RT}{4F}\right) ln\left[\frac{\text{cathode pressure (high)}}{\text{anode pressure(low)}}\right]$$

Noting that E^0 for this cell reaction is zero:

$$E = -\left(\frac{RT}{4F}\right) ln\left[\frac{(p'_{O2})}{(p''_{O2})}\right]$$

$$E = -\left(\frac{RT}{4F}\right) ln\left[\frac{\text{anode pressure (low)}}{\text{cathode pressure (high)}}\right]$$

Solving this equation for the oxygen partial pressure gives:

$$(p'_{O2}) = (p''_{O2}) exp\left(\frac{-4E}{RT}\right)$$

So, these are the similar equation the cell is something like this porous platinum in one end, oxygen is in one particular partial pressure and you have a stabilised zirconia and then oxygen at second another partial pressure. So, you can define the anode reaction and cathode reaction and overall cell reaction. You can estimate what is the cell potential and the value of Q is the partial pressure ratio.

And, E 0 in the reaction is 0 because as you understand as there is no couple here both are platinum. So, you the value of E, you can solve it and you get the partial pressure of oxygen at one side with respect to the another and eventually you can make a calibration curve to know the precise concentration of oxygen in air well mixture ratio.

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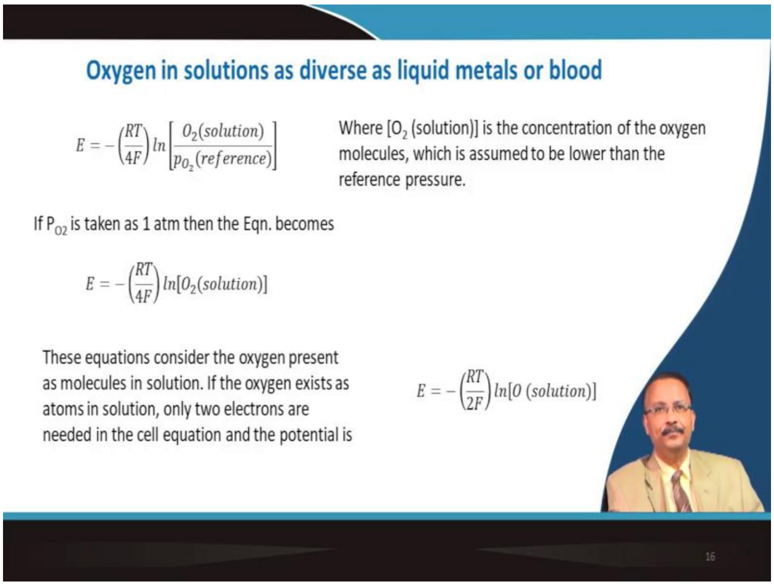

Oxygen in solutions as diverse as liquid metals or blood

$$E = -\left(\frac{RT}{4F}\right) ln\left[\frac{O_2(solution)}{p_{O_2}(reference)}\right]$$

Where $[O_2$ (solution)] is the concentration of the oxygen molecules, which is assumed to be lower than the reference pressure.

If P_{O2} is taken as 1 atm then the Eqn. becomes

$$E = -\left(\frac{RT}{4F}\right) ln[O_2(solution)]$$

These equations consider the oxygen present as molecules in solution. If the oxygen exists as atoms in solution, only two electrons are needed in the cell equation and the potential is

$$E = -\left(\frac{RT}{2F}\right) ln[O\ (solution)]$$

Something similar to this is slightly modified version is to know the oxygen concentration in solution. It is a very diverse application. Nowadays in the COVID-19 pandemic it is very important for you to know the oxygen ion concentration in the blood stream. The similar kind of principle is also adopted here.

So, you can measure the oxygen concentration in solution with respect to a reference oxygen which is usually kept at one atmosphere in earlier case as well as in this case. If it is not a molecule, but in atomic form this reaction is slightly changed, because the number of electron is different.

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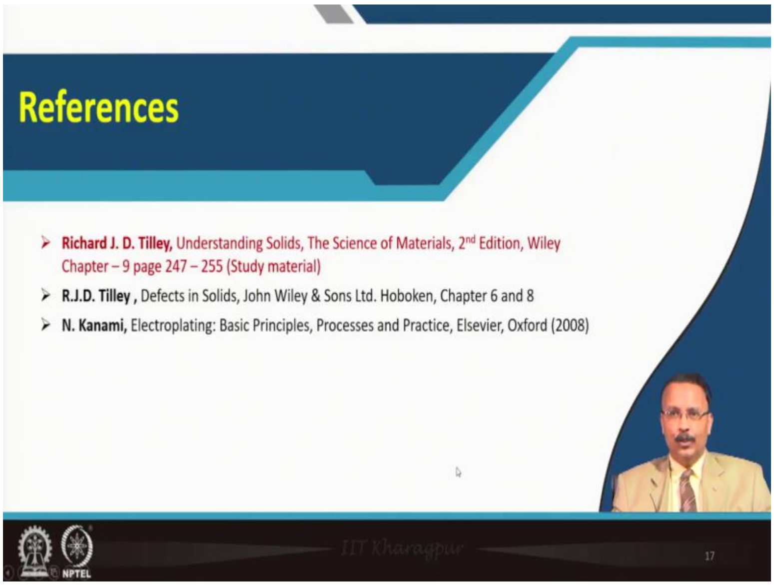

References

- **Richard J. D. Tilley,** Understanding Solids, The Science of Materials, 2nd Edition, Wiley Chapter – 9 page 247 – 255 (Study material)
- **R.J.D. Tilley ,** Defects in Solids, John Wiley & Sons Ltd. Hoboken, Chapter 6 and 8
- **N. Kanami,** Electroplating: Basic Principles, Processes and Practice, Elsevier, Oxford (2008)

So, the study material for this particular part is a book by Tilley chapter number 9 and also the Defect in the Solids are important as you have seen that we use lot of defect related equation in the solid electrolyte or making the membranes. So, the knowledge of defect is important and there is a good book by Kanami which is on Electroplating.

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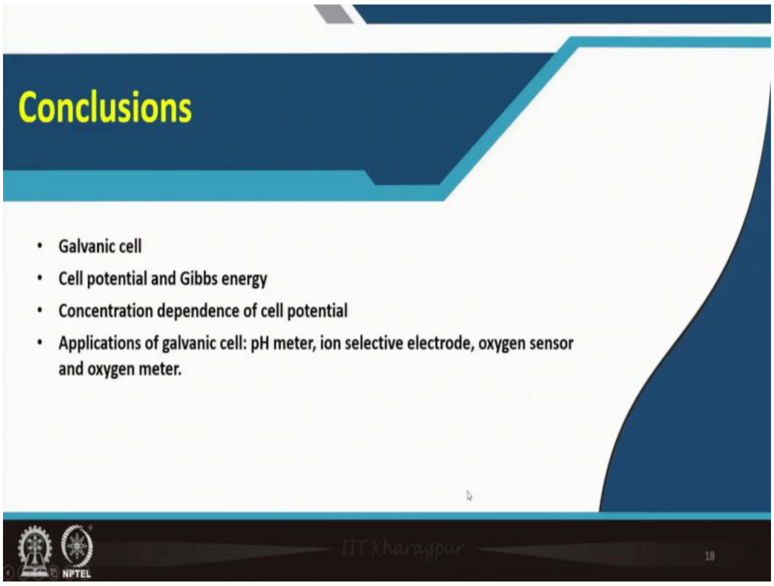

Conclusions

- Galvanic cell
- Cell potential and Gibbs energy
- Concentration dependence of cell potential
- Applications of galvanic cell: pH meter, ion selective electrode, oxygen sensor and oxygen meter.

So, in this particular lecture we introduced about the galvanic cell, we talked about the cell potential and Gibbs energy, we talked about the concentration dependence of with the cell potential, which is important for oxygen sensor or oxygen meter and several applications I have illustrated which include the pH meter, ion selective electrode, oxygen sensor and oxygen meter.

Thank you for your attention.