Bio - Microelectromechanical Systems

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Module No. # 01

Lecture No. # 05

Today will be covering lecture 5 and let us review what we have done last time. We were talking about the various material selection criteria for BioMEMS, biochip kind of devices.

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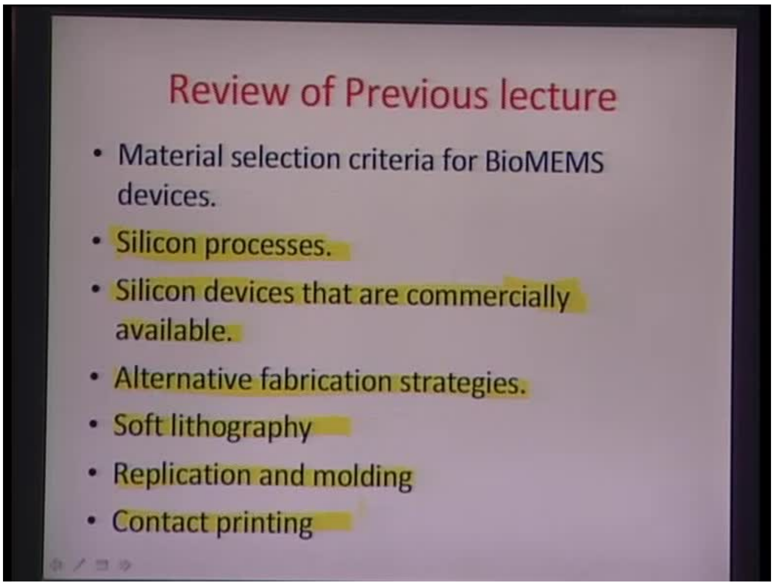

Review of Previous lecture

- Material selection criteria for BioMEMS devices.
- Silicon processes.
- Silicon devices that are commercially available.
- Alternative fabrication strategies.
- Soft lithography
- Replication and molding
- Contact printing

We talked about issues like optical transparency, bio comparability then, rapid photo definability or rapid fabrication strategies that could be done using these materials, so these are some of the important selection criterias.

We also tried to describe some of the basic silicon processes borrowed from the microelectronic industries can be used for MEMS applications. We talked at length about some of the commercially available silicon devices like digital micromere device, esclo meters, the single chip microphones and also the AFM technology - the Atomic Force Microscope technology.

We started with some of the alternative fabrication strategies using polymeric devices and covered some portions on soft lithography like replica molding and contact printing.

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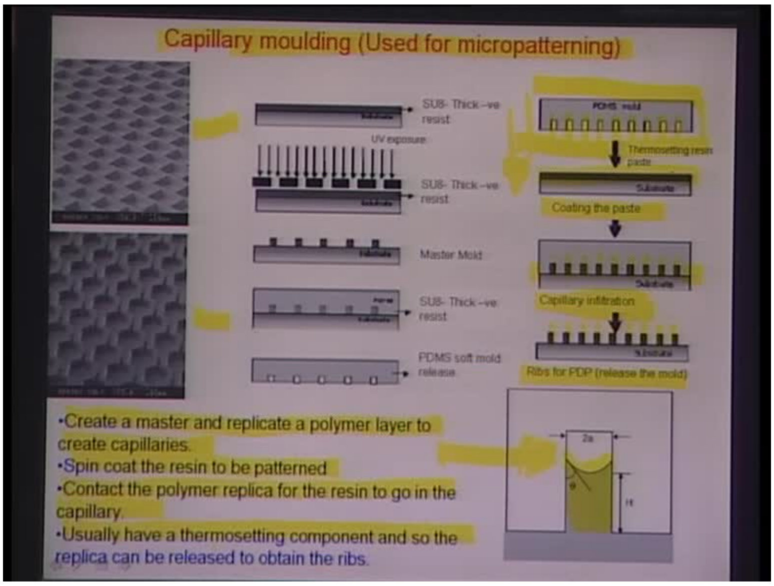

Capillary moulding (Used for micropatterning)

- Create a master and replicate a polymer layer to create capillaries.
- Spin coat the resin to be patterned
- Contact the polymer replica for the resin to go in the capillary.
- Usually have a thermosetting component and so the replica can be released to obtain the ribs.

We are going ahead on this spree and try to finish the soft lithographic processes today, after which will do a little bit of introductory electro chemistry. The next process along the line is capillary molding; once again one of the important process especially for display technologies sometimes.

The process steps are very simple; you have again a mold made up of PDMS with these small micro capillaries made by replication and molding techniques. Then, we spin coat thermo setting resin paste on to the surface of a substrate in this case; substrate may be silicon or a glass wafer.

Then, we essentially press this PDMS mold on the top of this thermo setting resin and press it up till the resin actually takes the shape of the small micro capillaries and once it is fully. Essentially, the PDMS when it sets on the top of this thermo setting resin its squeezes on the material in both directions.

There is of course, the material coming out of these ends and the material also getting filled into these capillaries, as you can see and then, you peel off the PDMS and create the surface of a PDMS by just some preprocessing in a manner direct leaves intact the resin material filled in these micro capillaries and this is what micro capillary molding is, it is very good patterning technique which can be used to core polymeric picks on the top of substrate.

Now, some of the practical issues that come while doing this is number 1 is that there is always a tendency because of surface tensions for this angle theta to be developed between the wall of the micro capillary on the PDMS and the resin material. Several processes are basically, coating the paste capillary infiltration and releasing the mold, so that you are left with thermo setting resin shaped as small dots.

These are some of the features and structures which are generated by this process sited from various illustrations. The overall process steps are that you create a master and replicate a polymer layer to create micro capillaries. Spin coat resin to be patterned. Contact the polymer replica for resin to go in the capillary with some limitations and restrictions like these kind of a normality. Usually have a thermosetting component and the replica can be released to obtain the ribs which are thermally set.

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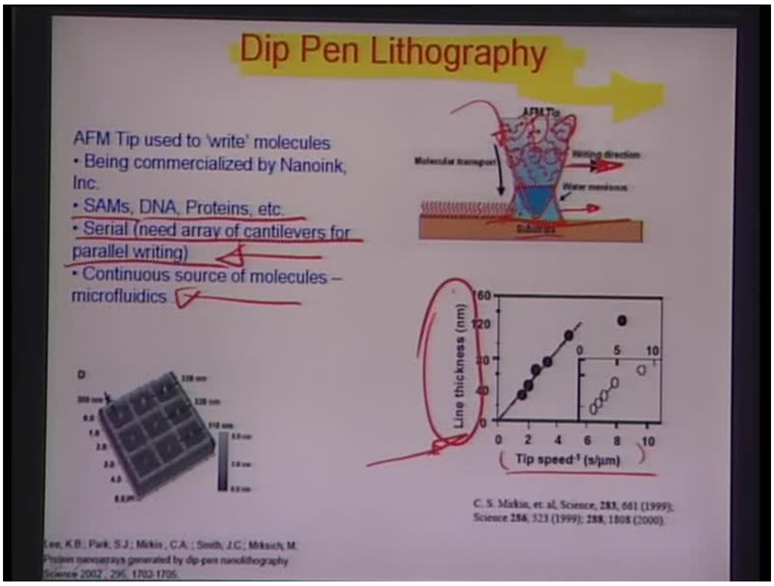

Dip Pen Lithography

AFM Tip used to 'write' molecules
- Being commercialized by Nanoink, Inc.
- SAMs, DNA, Proteins, etc.
- Serial (need array of cantilevers for parallel writing)
- Continuous source of molecules – microfluidics

C. S. Mirkin, et. al, Science, 283, 661 (1999); Science 286, 523 (1999); 288, 1808 (2000)

Lee, K.B.; Park, S.J.; Mirkin, C.A.; Smith, J.C.; Mrksich, M. Protein nanoarrays generated by dip-pen nanolithography Science 2002 , 295, 1703-1705

The next processes Din Pen Lithography and in fact, this is a again the process where we can write selectively molecules on a surface and this process are generated by doctor Chad mikin group at North western. Essentially, if you look at this process there is a substrate which is again coated with some kind of a film which can selectively adhere to molecules may be thiolated DNA and this right here is an s t is an AFM tip. What we do is that we create some favorable temperature and humidity conditions, there is this monolayer of the water and we choose the surfaces in manner that there is a tendency for this water meniscus to adhere more from AFM tip then, the substrate and you can drag it along with the tip as the tip moves around.

The idea is that this particular layer as you are seeing here, water is more adhere to this AFM tip surface then, the substrate on which is it is moving. So, when you are dragging the pen this moves along with the pen rather than adhering to the substrate. Why it is used? This is used for transporting molecules. So, if you have some kind of a constant feed mechanism or the delivery mechanism wherein these small molecules can be delivered rapidly onto these AFM from tip, they can use this monolayer to go and set in a particular arranged order onto the substrate of interest and therefore, this process is used for essentially writing molecules.

It is pretty much like what an ink pen does? An ink pen also specially in a fountain pen there is ink within the tube and it goes through the tip of the pen and due to capillary action of the paper on which it is writing the ink is essentially absorbed onto the paper. This is also similar kind of an application within STM pen doing the same job and instead of ink this pen writes molecules rather on the surface.

This is a highly commercial process used rapidly and in fact, there is a company by the name of Nano ink incorporated where they have commercialized these dip pen lithography technique for a lot of applications, wherein self-assembled monolayers and DNA proteins etcetera rapidly delivered onto such surfaces. Typically, this processes is a serial process but there are some initiatives in which they have to try to make this process parallel wherein there are several such AFM tips which are actually being fed by the molecules all together and then, when this whole probe head moves with the different tips it can be able to write in different tracks and routes these molecules.

There is an initiative where this serialized process is being commercialized for an array of cantilevers for parallel writing. Another challenge here in this mechanism is how the molecules can be rapidly delivered and continuously delivered onto the STM pen and principles of microfluidics are of an use for that purpose.

If we look at on this particular illustration from micron scope, as you can see here that as the tip speed inverse increases that means, as the tip speed decreases the line thickness of these molecules automatically increase which also intuitively make sense. So, this is the very important processes again which is grouped into the lithography domain.

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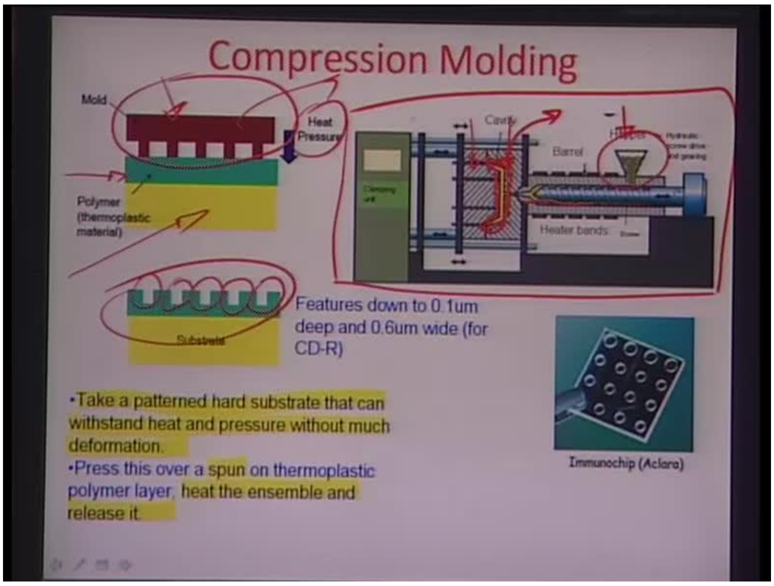

Compression Molding

Features down to 0.1um deep and 0.6um wide (for CD-R)

- Take a patterned hard substrate that can withstand heat and pressure without much deformation.
- Press this over a spun on thermoplastic polymer layer, heat the ensemble and release it.

Another very important processes compression molding and this also forms foundation of something called Nano imprint lithography will be just talking in the next slide. In this process there is a material which is the substrate and thermo plastic material is coated onto the substrate and mold is prepared and made, which can with stand high heat and pressure. This mold can be silicon nitrate, silicon dioxide over may be a silicon surface or even made with material micro machined with some other techniques like EDM Electro Discharge Machine, ECM so on so forth.

Once this mold is pressed onto this thermo plastic material there is a shaping of this thermo plastic material as the negative for the mold that is, used for this squeezing. Then the idea is that you removed the mold and whatever remains here is well set and thus the negative of the features on the mold are transferred onto this material this is how you write micro features or structures onto a surface.

The very common compact disk that we use regularly in our computers or audio equipment’s is essentially realized using a compression molding process and another very important technique which is often on used injection molding which is illustrated here in this particular figure.

If you see this illustration here, you know there are 2 dies which are kind of mating components and there is small gap here in this region between the dyes which is the shape or the feature which has to be replicated. So, polymeric material which is normally in the solid form is dropped into this Hooper and this leads screw essentially transfers the material by first melting it and then, constantly feeding it onto this small cavity and as polymer goes into the cavity.

It stays there and gets cooled off and gets hard and solidified after which the injection or this mold is separated or opened and the material is removed. So, you really need a very good surface preprocessing agent here for a proper separation of the polymer that you feed in.

In fact this is the very useful process for again micro fabrication, so in a nutshell this processes are about taking a patterned hard substrate which is capable of withstand heat and pressure without with minimal deformation. Essentially, a thermo plastic material spun over some kind of a wafer is molded by compressing the mold on to this particular thermo plastic film and then assemble is heated, so that sets up thermo plastic material and the mold is removed eventually.

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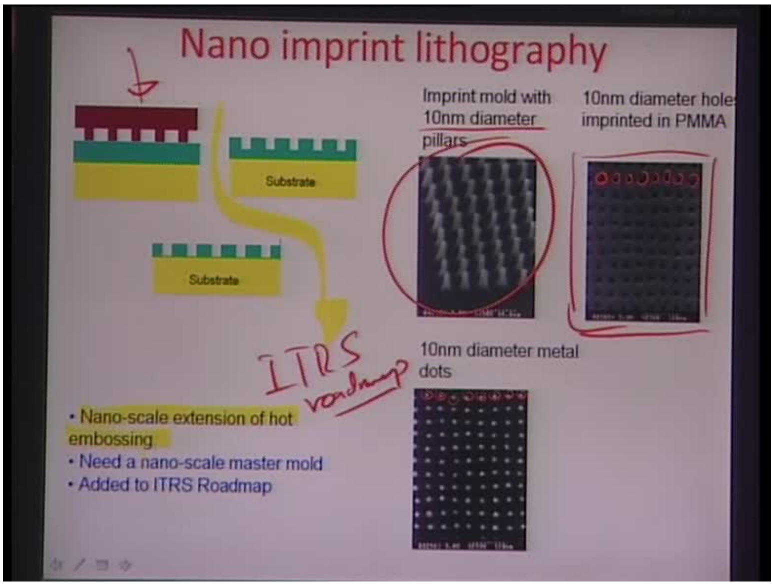

Nano imprint lithography

- Nano-scale extension of hot embossing
- Need a nano-scale master mold
- Added to ITRS Roadmap

Another very important process which comes almost immediately from compression molding is Nano imprint lithography. I would like to illustrate that this process has also been made or be included in the ITRS road map especially, for the end of road devices.

As you see here that the same processes compression molding is used but on a much smaller scale - on a sub-micron scale - these are some illustrations of what Nano imprint lithography can be do.

In fact this is actually say of pillars which are about 10 Nano meters in size and this is an array of pillars which are made using Nano imprint mold. A variety of other processes like this particular illustration is that of PMMA which is also an e beam resist, when this 10 Nano meter diameter holes have been made and an array of these holes have been realized onto the poly methyl methacrylate and these are through holes.

This can be used as shadow masks or processes like deposition where this mold is put over wafer and material like gold or platinum is deposited through this shadow mask that the small tiny dots here are each of about 10 Nano meters in diameters, because they can go through this particular hole on the PMMA.

The shadow mask is later on removed and you have an array of this fine dots and these are used off and on for lot of micro Nano scale electronics. In a nutshell, Nano imprint lithography is the extension of the hot embossing process and all you need is a Nano scale master for this and especially, this process has been added on recently to the ITRS road map.

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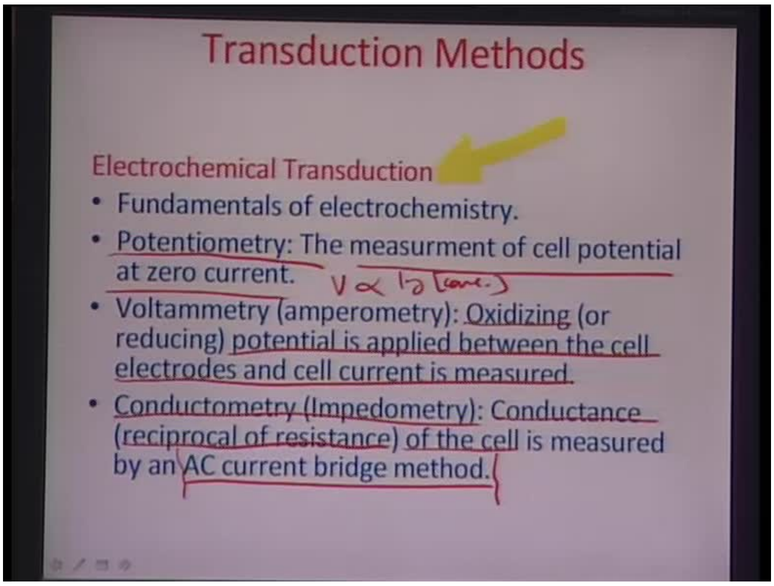

Transduction Methods

Electrochemical Transduction

- Fundamentals of electrochemistry.
- Potentiometry: The measurment of cell potential at zero current. $V \propto \lg\,(conc.)$
- Voltammetry (amperometry): Oxidizing (or reducing) potential is applied between the cell electrodes and cell current is measured.
- Conductometry (Impedometry): Conductance (reciprocal of resistance) of the cell is measured by an AC current bridge method.

This brings us to the end of the type of polymeric methods available for micro fabrication processes. We will now turn back to our initial line of thought sensor which we covered even last lecture and before. We would look into a little bit of fundamentals of electro chemistry or electro chemical sensing and essentially, if you look at the different transaction types I would just like to retrade this from the last few lectures that the electro chemical transaction can be characterized into potentiometry which is the measurement of cell potential at zero current.

If I may just add, it is method is which the voltage is to proportional to the log of concentration of the analyte of interest. Voltammetry, where the oxidizing and reducing potential of a material to sense the material. Conductometry, where you are rapidly monitoring the conductance change - conductance is again the reciprocal of resistance of the electrochemical cell - by using the conductance you can find out whether there is any change in the concentration of the analyte or you can use AC current bridge method, wherein impedance measured at a certain frequency can be seen and the change can be monitored for gauging the rapidly increasing, decreasing concentration of a certain analyte.

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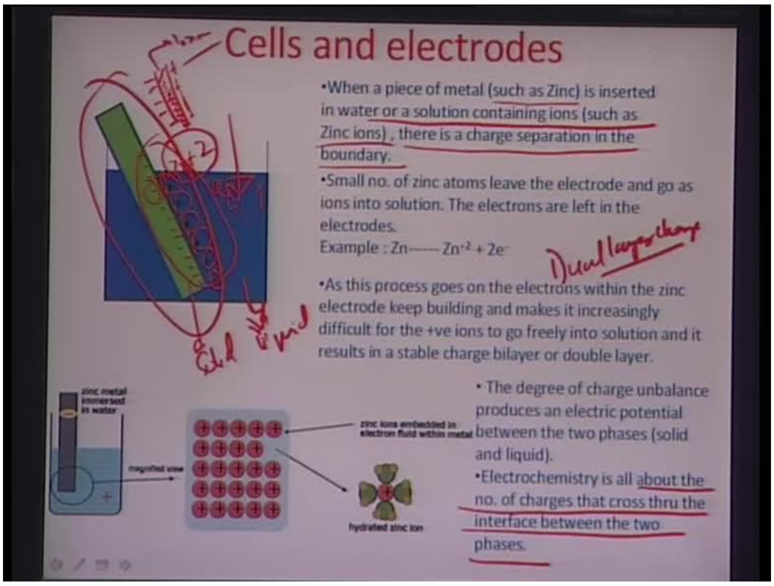

Cells and electrodes

- When a piece of metal (such as Zinc) is inserted in water or a solution containing ions (such as Zinc ions), there is a charge separation in the boundary.
- Small no. of zinc atoms leave the electrode and go as ions into solution. The electrons are left in the electrodes.
  Example : Zn—— $Zn^{+2} + 2e^-$
- As this process goes on the electrons within the zinc electrode keep building and makes it increasingly difficult for the +ve ions to go freely into solution and it results in a stable charge bilayer or double layer.
- The degree of charge unbalance produces an electric potential between the two phases (solid and liquid).
- Electrochemistry is all about the no. of charges that cross thru the interface between the two phases.

Dual layer charge

Let us look into a little bit of fundamental aspects of what happens really when a dip metal rod inside solution. So, when a piece of a metal such as let us say zinc in this case is inserted in water or may be a solution which contains zinc ions, there is a immediate charge separation in the boundary - I think I illustrated of one of my lecture before - that whatever processes take place at this interface lead to the rapid development of metals from the electrode going into the solution as metal plus ions.

Some oxidize state are created; simultaneously, the electron which is liberated, in this case of zinc is to 2 electrons, are rapidly concentrated around this particular area of the electrode. It is the cells stopping processes because by the principle of electron equality, this combination cannot hold beyond a certain level of negative charged, it would automatically try to stop the this process of zinc going to solution and creating electrons.

Once the zinc going to the solution there is also another effect which is happening that the water from surroundings comes between the zinc and this negative charge on the electrode and forms a thin dielectric layer. Essentially, we are talking about a very small capacitance which results from the positive charges of zincs ions which is in the solution and the negative electros separated by a small monolayer of water.

Now, this layer can be as thin as about 10 nanometers but, this self-stopping processes develops something called a dual layer of charge and all electro chemistry is about the number of charges that cross through this interface dual layer between the two phases solid and the liquid.

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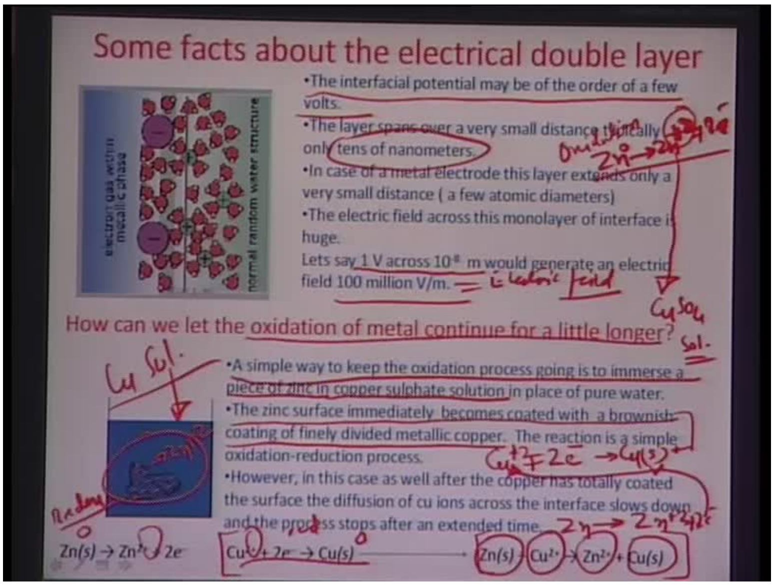

Some facts about the electrical double layer

- The interfacial potential may be of the order of a few volts.
- The layer spans over a very small distance typically only tens of nanometers.
- In case of a metal electrode this layer extends only a very small distance (a few atomic diameters)
- The electric field across this monolayer of interface is huge.

Lets say 1 V across 10^{-8} m would generate an electric field 100 million V/m.

How can we let the oxidation of metal continue for a little longer?

- A simple way to keep the oxidation process going is to immerse a piece of zinc in copper sulphate solution in place of pure water.
- The zinc surface immediately becomes coated with a brownish coating of finely divided metallic copper. The reaction is a simple oxidation-reduction process.
- However, in this case as well after the copper has totally coated the surface the diffusion of cu ions across the interface slows down and the process stops after an extended time.

$Zn(s) \rightarrow Zn^{2+} + 2e$ $\quad$ $Cu^{2+} + 2e \rightarrow Cu(s) \longrightarrow Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$

Once this concept is clear, let us look into a little more detail of what may happen to the electrical double layer. Essentially, the interfacial potential in such a double layer maybe of the order of a few volts which essentially makes the electric fields very high, because if you consider the span or the special separation of the positive and negative charges it is not more about 10's of nanometers. Therefore, 1 volt across about 10 to the power minus 8 meters would make about 100 million volts per meter.

That is how high the electric field is really going to be in such a double layer what happens is - let us say - another illustration here, if a piece of zinc is dipped in copper solution. Let us first consider why or how can this oxidation of the metal which we were seeing in the last case where zinc was been converted into Zn plus 2, can be increased for a little longer. As we know this is again by diffusion, this process where the zinc is going into water as plus 2, because of the principles of electro neutrality there is only a finite amount of oxidation can be happen.

How can I extend the oxidation time is the question and this is the very important for developing a basic understanding of what electro chemical sensing is all about, that is why it is important to go through some of these concepts. So, a simple to keep the oxidation process going is to immerse the piece of zinc from water into rather solution of copper sulfate. Copper again is an electrically active material and also there is a tendency of zinc to displace copper from its solution.

This generates something called redox couple, wherein the first process that take places is. Let me first say what is going to happen if such a zinc is dissolved inside the copper surface solution, immediately it becomes coated with a brownish coating of finely divided metallic copper onto the surface. If you look at why this is happening essentially, the copper which was present in the copper plus 2 state in the Cu.

So, 4 solution gets reduced by taking electrons which have been generated in this metal as the zinc tries to move out as Zn plus 2. Therefore, the 2 electrons which are already present in this particular lump of zinc, by virtue of the oxidation of zinc and by the by, how do we know what is oxidizing? Just a little bit of basics here that the valence of a material should increase for an oxidation process to happen.

Oxidation signified by, here the valance is 0, here as you see this plus 2 because plus 2 electrons are gone out, so oxidation is essentially the increase in the valance of the material. Copper goes from a copper plus 2 state into a simple copper, may be in the solid form. This is the bound deposit that we are talking about and the zinc on the other hand, gets converted into Zn plus 2 and leaves 2 electrons back in this surface which is easily donated away to the copper ion to get converted into copper solid.

If I look at this equation together, it becomes something like that the zinc has the potential of displacing copper plus 2 from its solution to make into solid copper deposited on the surface and the zinc in turn gets oxidize. So, this is also known as a redox reaction because one element here, the copper is getting reduced, mind you that the valance is changing from plus 2 to 0 in the solid state.

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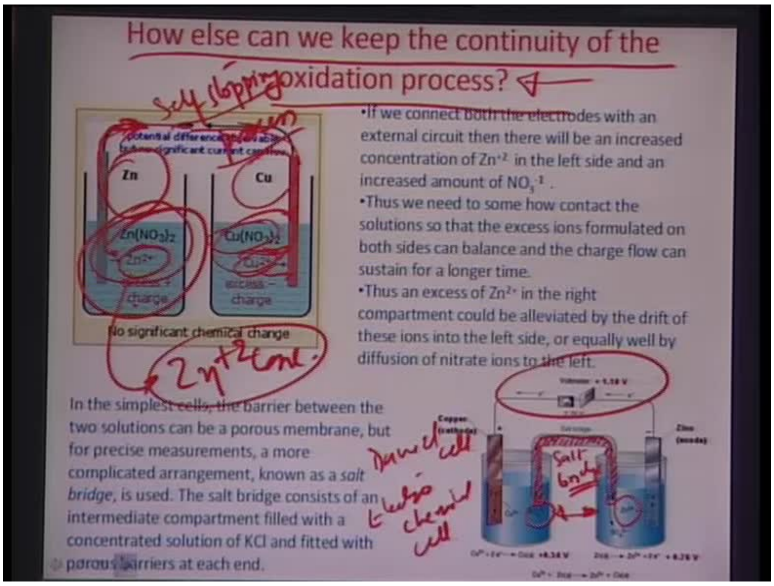

How else can we keep the continuity of the oxidation process?

- If we connect both the electrodes with an external circuit then there will be an increased concentration of Zn^{+2} in the left side and an increased amount of NO_3^{-1} .
- Thus we need to some how contact the solutions so that the excess ions formulated on both sides can balance and the charge flow can sustain for a longer time.
- Thus an excess of Zn^{2+} in the right compartment could be alleviated by the drift of these ions into the left side, or equally well by diffusion of nitrate ions to the left.

In the simplest cells, the barrier between the two solutions can be a porous membrane, but for precise measurements, a more complicated arrangement, known as a *salt bridge*, is used. The salt bridge consists of an intermediate compartment filled with a concentrated solution of KCl and fitted with porous barriers at each end.

One component the zinc is getting oxidize where the valance is changing from 0 to plus 2. These two acquaint together it is also known as a reduction, oxidation or redox mechanism well. The next obvious question that anybody would ask is that how we can keep the continuity of the oxidation process going on so, once we have this process a little bit extended. The next goal is how we can keep this process to go on, so one way of doing it would be the - let us say - we have something which is able to be displays into the solution as ions and something wherein it is able to displays the ionic state into the solid state form. Zinc here, as you see getting oxidize to Zn plus 2 and going into the solution and copper from this copper nitrate getting reduced and going is a deposit onto the copper electrode.

If I connect both these electrodes together then the electron which is liberated here can flow all the way through to this particular electrode and it can easily reduce the copper here, but this will only happen finitely because after avail there would be an increase in this Zn plus 2 concentration inside this particular solution because of which there would be no further transportation of zinc into the solution as Zn plus 2. In effect what would happen is that the ionic concentration of Zn plus 2 increase here and it would stop this electron flow process because there is no more oxidation taking place and it would be a self-stopping process.

Can I do something to make this process continue? The answer is yes, what we do here is that we create charge balance back by connecting the two solutions together as well by something called as a salt bridge. Essentially, this is something wherein you know it contains 2 plugs at both the ends and there is a ion exchange solvent and there is a continues exchange of the increase - let us say - So 4 minus 2 ions on one side in the copper sulfate solution with the increase Zn plus 2 ion on other side, with this zinc sulphate solution. Therefore, this creates the charge balance between the 2 cells or 2 of cells and this process goes on for some time.

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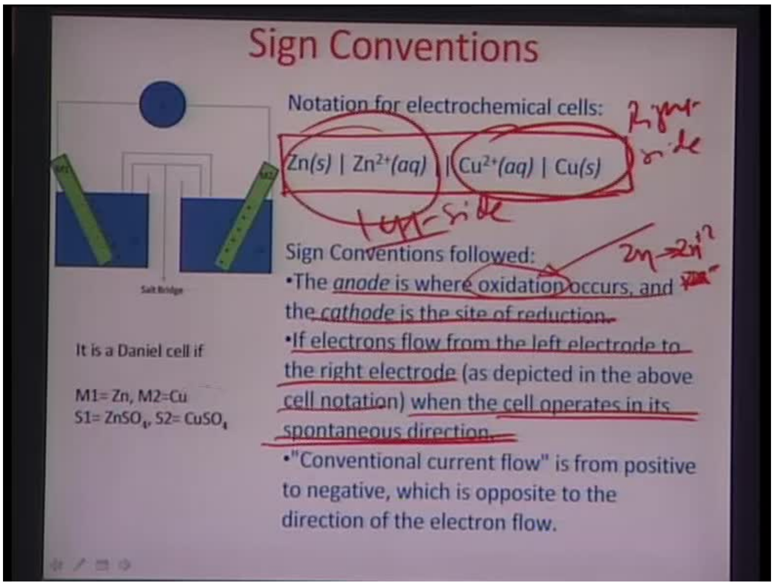

Sign Conventions

Notation for electrochemical cells:

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

It is a Daniel cell if

M1= Zn, M2=Cu
S1= $ZnSO_4$, S2= $CuSO_4$

Sign Conventions followed:

- The *anode* is where oxidation occurs, and the *cathode* is the site of reduction.
- If electrons flow from the left electrode to the right electrode (as depicted in the above cell notation) when the cell operates in its spontaneous direction.
- "Conventional current flow" is from positive to negative, which is opposite to the direction of the electron flow.

This is also a known as an electro chemical cell and in fact this is also called as a Daniel cell. So, what I would like to illustrate here is that there is a sign convention which is used for writing such half cells. The convention which is followed here is essentially, the anode is where the oxidation would occur and the anode is presented in the convention mode on to the left side.

Anode is where oxidation takes place, so zinc is converted into Zn plus 2 is really called the anode, because we considered the solution perspective of it as if it giving positive ions into the solution. Cathode is where reduction is happening this right side of this particular convention is the cathode. Of course, there is an electron flow from the left electrode to the right from the electrode which provides oxidation to the electrode which provide reduction. The current is the opposite of the flow of electrons because it is conventional to consider current flow as positive.

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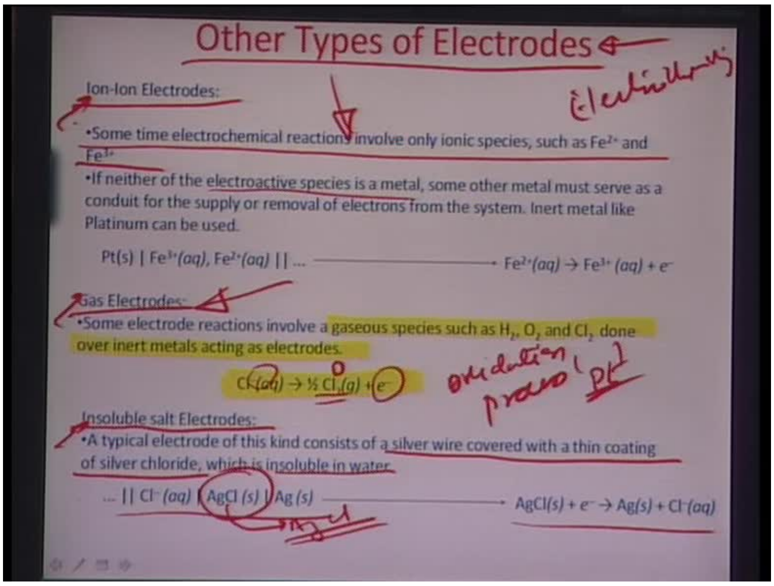

Other Types of Electrodes

Electrochemistry

Ion-Ion Electrodes:

- Some time electrochemical reactions involve only ionic species, such as Fe^{2+} and Fe^{3+}
- If neither of the electroactive species is a metal, some other metal must serve as a conduit for the supply or removal of electrons from the system. Inert metal like Platinum can be used.

$Pt(s) \mid Fe^{3+}(aq), Fe^{2+}(aq) \mid\mid ...$ ⟶ $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

Gas Electrodes:

- Some electrode reactions involve a gaseous species such as H_2, O_2 and Cl_2 done over inert metals acting as electrodes.

$Cl^-(aq) \rightarrow \frac{1}{2} Cl_2(g) + e^-$

oxidation process (Pt)

Insoluble salt Electrodes:

- A typical electrode of this kind consists of a silver wire covered with a thin coating of silver chloride, which is insoluble in water.

$... \mid\mid Cl^-(aq) \mid AgCl(s) \mid Ag(s)$ ⟶ $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$

The current would flow from the cathode to the anode it is in the opposite direction, so this is what happens when the cell operates in a spontaneous direction. Following this sign convections there can be other kind of electrodes which can work out in pretty much similar way. These electrodes would be essentially off and on use for electro chemistry later on where will talk about how to sense analyte using some of these basic electro chemical principles.

The other form of electrode which exists in ion-ion electrode where as you have seen in the last illustration, we talked about really 2 solutions 1 oxidizing, another reducing and 2 different solutions 1 in copper, 1 is zinc with a copper and zinc electro respectively each of the solution.

Here, we are talking about 2 different oxidation states of the same material. In one state ion here is available is a Fe plus 2 and in another state it is available as Fe plus 3. Assuming that if this Fe plus 3 is the oxidized form of the material and Fe plus 2 is also oxidized form of material but essentially, with the difference of 1 electron between them there is still an electron flow from the anode side to the cathode side and this is working set of electrodes and a flow cell and a batteries.

We are talking about that sometimes the electrochemical reaction involve only ionic species, such as plus 2 plus 3 form in this case. If neither of the electro active species is a metal, we need something to provide the connectivity. So, in this case we use an inert metal which is platinum let us say and this acts as a conduit for providing or for picking of the electron from the anode side and placing it onto the cathode side.

The other types of electrodes that are available are gas electrodes as can be illustrated here in this particular example. Here, instead of liquid species we are concerned with a gaseous reaction, it is gaseous species such as - let us say - a hydrogen oxygen chlorine etcetera. If you look at this particular reaction what is again happening is an oxidation process wherein the chlorine which had a minus charge here is getting converted into a 0 valance state or a gas form and at the cost of one electron, one electron is eliminated from the chlorine, it is an oxidation processes essentially.

Some material here like platinum are again used as the conduit for electrical activity or for promoting connections between 2 or more cells, but the material itself is inert and it does not participate in the electro chemical reaction or the electro chemical process. Another form of electrode here is the insoluble salt electrode, here the concept is little different. Let us say, if we are talking about an AgCl electrode - silver chloride electrode, normally a silver chloride is an insoluble salt in water, so if you put AgCl it precipitate as crystal.

Problem in that case what we do with the electro chemical sensing or electro chemical cell design. In that case what we do is you take a silver wire and cover with a thin coating of silver chloride and that formulates good scheme of ion exchange even though the salt considered is highly insoluble in water.

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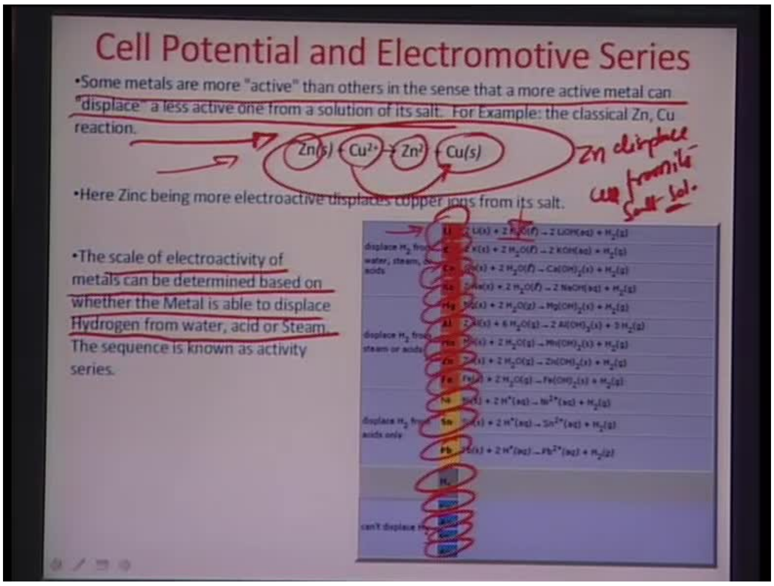

Cell Potential and Electromotive Series

- Some metals are more "active" than others in the sense that a more active metal can "displace" a less active one from a solution of its salt. For Example: the classical Zn, Cu reaction.

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

Zn displace Cu from its salt sol.

- Here Zinc being more electroactive displaces copper ions from its salt.
- The scale of electroactivity of metals can be determined based on whether the Metal is able to displace Hydrogen from water, acid or Steam. The sequence is known as activity series.

These are some of the types of electrodes that are used off and on for electro chemical sensing apart from the conventional metal electrolyte electrodes. Another very interesting factor is that some metals are more active than others in the sense that they provide or they can displace less active one from a solution of salt. Like let us say, if we consider zinc copper case or if we consider Daniel cell, as we saw here that there the zinc was getting displace or getting oxidized and going into the solution and was really displacing the copper plus 2 state as a deposit onto the electrode.

Zinc was able to clearly displace copper from its salt solution, I can consider zinc to be more electro active then copper ions. Based on these ability of materials to displace each other from their solution state, there is a scale of electro activity especially of metals which have been formulated on the ability of the metal to displace hydrogen form water steam or acid. Either if you take H 2 O in any form be it in steam or be it in equilibrium with an acid or be it in the water state.

How the metal can displace hydrogen or how actively it can displace hydrogen also gives it a position up the ladder on the electro activity series. Why hydrogen? Because a common scale is needed, it is like a references scale. So, if it is compared with respect to the hydrogen it gets compared with each other by that process. If it is way upon the electro activity series it can easily display something which is below it on to the same series that is how the series are being made. Some fundamental basics of electro chemistry are important for understanding how really measurements can be made in electro chemical sensing.

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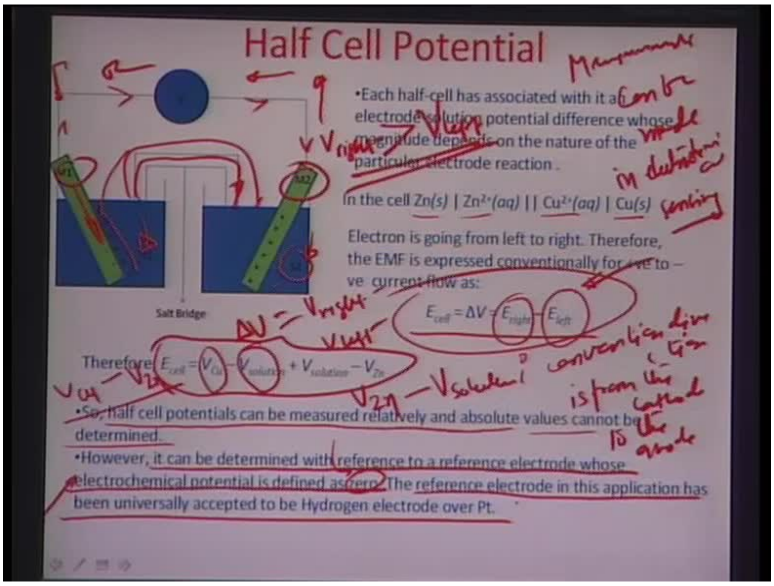

Half Cell Potential

•Each half-cell has associated with it an electrode-solution potential difference whose magnitude depends on the nature of the particular electrode reaction.

In the cell $Zn(s) \mid Zn^{2+}(aq) \mid\mid Cu^{2+}(aq) \mid Cu(s)$

Electron is going from left to right. Therefore, the EMF is expressed conventionally for +ve to –ve current flow as:

$$E_{cell} = \Delta V = E_{right} - E_{left}$$

Therefore $E_{cell} = V_{Cu} - V_{solution} + V_{solution} - V_{Zn}$

•So, half cell potentials can be measured relatively and absolute values cannot be determined.

•However, it can be determined with reference to a reference electrode whose electrochemical potential is defined as zero. The reference electrode in this application has been universally accepted to be Hydrogen electrode over Pt.

Let us again look at the same example of Daniel cell, so you have a metal electrode, you have salt solution, M1 is the type of metal here then, you have another metal M2 in its salt solution S2. You have interconnected them using the salt bridge and you are trying to take a readout of the total current between the 2 electrodes and obviously, if M1 is the anode then the electron flow would be from M1 to M2.

Let us say, M1 in this case zinc is zinc plus 2 and M2 in this cases copper plus 2 and copper. So, M2 and S2 are essentially copper and copper plus 2, and M1 and S1 are zinc and zinc plus 2. If you consider that total EMF, this particular cell would have its EMF of the right side of right cell minus the EMF on the left cell - this is more, so because as you know currents conventional direction is from the cathode to the anode.

In other words, the current really is going in this particular direction, so if the current is going in this direction we can safely assume the potential here we right is higher than the potential in the left side. Delta v which is the responsible for movement of this electrons is V right minus V left, as you can see here. If we consider what E right or the V right is it is nothing but the voltage provided by the copper minus voltage of the sulphate solution S2. Similarly, V left is voltage provided by the zinc minus voltage of zinc sulphate solution.

Therefore, overall EMF of this particular cell can essentially be represented as the right V copper of the electrode minus left V zinc of the electrode. The solution really do not play much of a role more, because a salt bridge which keeps on interconnecting and neutral or making the solution electro neutral are all points of time.

One thing is very obvious here that the half-cell potentials can only be measured relatively and absolute values cannot be determined irrespective of how hard you try and how really can you do it because, for that the electric double layer which is responsible for this potential to build up is a very small layer. A small piece of metal in this 100 Nano meters or 10 Nano meter domain and get a relative potential of the electrode with respect to the solution surrounding the electrode, so only the other way is relative measurement.

However, this problem can be averted by making a reference electrode and defining that as an electrochemically in active electrode, with a 0 electrochemical potential. Although in principle such an electrode would have some potential, but if we consider scale where in this potential is signified or represented zero potential then, this can be a reference electrode for considering the individual potentials of different metal electrodes with respect to it.

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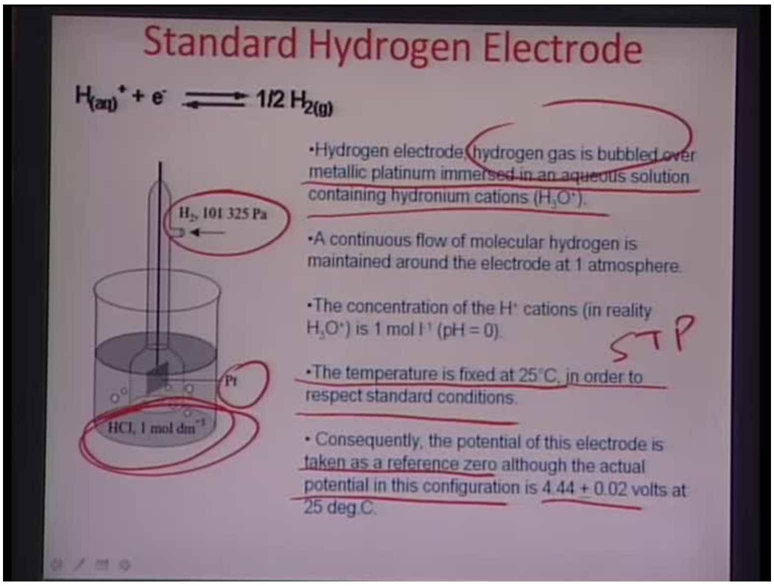

Standard Hydrogen Electrode

$H_{(aq)}^{+} + e^{-} \rightleftharpoons 1/2\ H_{2(g)}$

- Hydrogen electrode: hydrogen gas is bubbled over metallic platinum immersed in an aqueous solution containing hydronium cations (H_3O^+).
- A continuous flow of molecular hydrogen is maintained around the electrode at 1 atmosphere.
- The concentration of the H^+ cations (in reality H_3O^+) is 1 mol l^{-1} (pH = 0).
- The temperature is fixed at 25°C, in order to respect standard conditions.
- Consequently, the potential of this electrode is taken as a reference zero although the actual potential in this configuration is 4.44 ± 0.02 volts at 25 deg.C.

So, reference electrodes in this application has been universally accepted to be the standard hydrogen electrode which is essentially something like this, where there is a platinum and there is 1 molar solution of HCL in water and hydrogen is bubbled through this particular electrode at pressure of about 101 325 Pascal’s or 1 atmosphere, Essentially, there is a potential which is created. Basically, the standard hydrogen electrode now therefore, is something which is realized by metallic platinum immersed in an aqueous solution containing hydronium ions H 3 O plus which is formulated by gain 1 molar HCL in water and hydrogen gases slowly bubbled for this at 1 atmosphere pressure.

Temperature is fixed to be again 25 degree Celsius in order to get standard conditions called the standard temperature pressure STP conditions and consequently, the potential for this electrode is taken has a reference 0 although the actual potential in this configuration comes out to be 4.4 plus minus 0.02 volts at 25 degrees Celsius.

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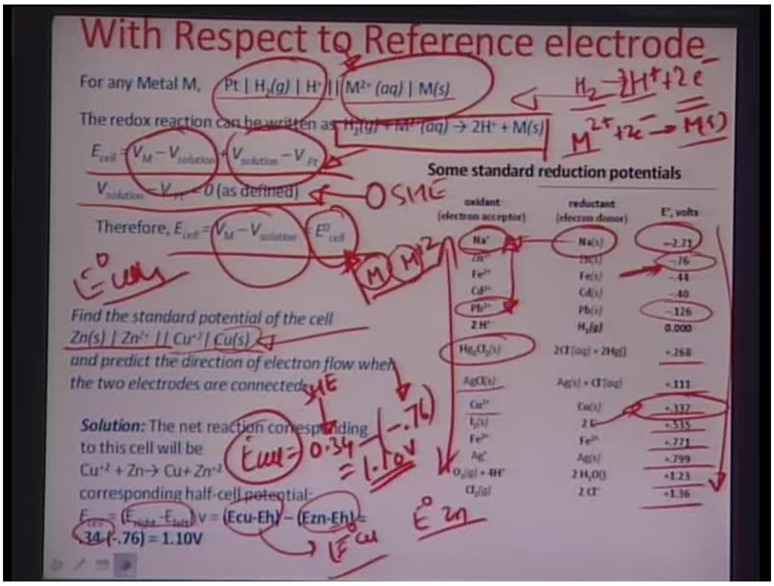

With Respect to Reference electrode

For any Metal M, Pt | $H_2(g)$ | H^+ || $M^{2+}(aq)$ | $M(s)$

The redox reaction can be written as $H_2(g) + M^{2+}(aq) \rightarrow 2H^+ + M(s)$

$E_{cell} = (V_M - V_{solution}) + (V_{solution} - V_{Pt})$

$V_{solution} - V_{Pt} = 0$ (as defined)

Therefore, $E_{cell} = V_M - V_{solution} = E^0_{cell}$

Find the standard potential of the cell
$Zn(s)$ | Zn^{2+} || Cu^{+2} | $Cu(s)$
and predict the direction of electron flow when the two electrodes are connected.

Solution: The net reaction corresponding to this cell will be
$Cu^{+2} + Zn \rightarrow Cu + Zn^{+2}$
corresponding half-cell potential:
$E_{cell} = (E_{right} - E_{left})$ v = (Ecu-Eh) – (Ezn-Eh) =
.34-(-.76) = 1.10V

Some standard reduction potentials

oxidant (electron acceptor)	reductant (electron donor)	E°, volts
Na^+	$Na(s)$	−2.71
Zn^{2+}	$Zn(s)$	−.76
Fe^{2+}	$Fe(s)$	−.44
Cd^{2+}	$Cd(s)$	−.40
Pb^{2+}	$Pb(s)$	−.126
$2H^+$	$H_2(g)$	0.000
$Hg_2Cl_2(s)$	$2Cl^-(aq) + 2Hg(l)$	+.268
$AgCl(s)$	$Ag(s) + Cl^-(aq)$	+.111
Cu^{2+}	$Cu(s)$	+.337
$I_2(s)$	$2I^-$	+.535
Fe^{3+}	Fe^{2+}	+.771
Ag^+	$Ag(s)$	+.799
$O_2(g) + 4H^+$	$2H_2O(l)$	+1.23
$Cl_2(g)$	$2Cl^-$	+1.36

Lets actually move onto the aspect of how we can calculate, how we can predict what is the current level, what is the potential difference between appear or a combination of such electrode solutions and how we can predict the flow of current? Again as we know that for any metal solution combination the total E cell is represented by E right minus E left. The right is essentially, as in this particular case the cathode and the left is the anode right.

If we consider an electrode where we are talking on 1 side of the standard hydrogen electrode right and the other side a to be the particular metal of interest. So, how we can really right this redox couple is the question? Here for instance ion this particular cell when we are writing the combination of a metal solution and metal with respect to the standard hydrogen electrode with platinum as the conduit, hydrogen is getting oxidized at the cost of realizing two electrodes. These two electrons are gathered together by the metal which converts from the plus 2 state into the solid metal.

This redox reaction can be also written as H 2 plus M 2 plus makes 2 H plus M S as can be illustrated in this particular equation here, for this particular cell again E cell is represented as the voltage on the right side minus the voltage on the left side. Essentially it is the voltage of metal minus voltage of solution plus voltage of solution minus voltage of platinum.

We define this voltage of solution minus platinum to be 0 because there is a scale of the SHE of the Standard Hydrogen Electrode and therefore, the E cell comes out to be nothing but V M minus V solution and we call this the absolute potential of the particular metal-metal ion combination.

Very useful to find out we can actually get the couple of these E 0 cells for a different combination of different metals and its salt solution and these have been illustrated here in this table. Like for example if there is a conversion of sodium ion into solid sodium there is an E 0 with respect to the standard hydrogen electrode of minus 2.71, the minus here indicates that rather the sodium gets oxidized like zinc as we have illustrated before when you connected to a hydrogen electrode.

Similarly, zinc has a negative potential and this course all the way have to led so up to led all these different metal are more electro active then hydrogen and they displace hydrogen from its plus state or oxidized state and reduces into gaseous state when connected to a standard hydrogen electrode.

The potentials are reverse and positive when you connect the standard hydrogen electrode to a below these like Makri chloride silver chloride, copper cuprous kind of solutions so on so forth. It is very easy to find out the standard potential of the cell and also predict the electron flow direction, if this scale here with respect to the SHE has already been formulated. Like in the case of the Daniel cell if we look at there is an electrode here which is the anode convert into Zn plus 2 an electrode which is the cathode converting from copper plus or cuprous state into copper 0 state, so for the standard cell potential in this case would really be actually nothing but E right minus E left, which is E copper minus E copper sulphate minus E zinc minus E zinc sulphate and these are nothing but, also E 0 copper and E 0 zinc.

If you look at this particular electro active series here, the E 0 copper comes out to be about 0.34. So, it comes out to be about 0.34 and the E 0 zinc here as you are seeing comes out to be minus 0.76, so this is copper, this is the zinc (Refer Slide Time: 43:27). The total E cell can be represented as E right which is 0.34, E 0 right I am sorry, with respect to the standard hydrogen electrode minus E left which is minus 0.76 another words it would be 1.10 volt, this is essentially the total EMF of the cell. You consider the individual electrodes with respect to the SHE or Standard Hydrogen Electrode and then, make a combination of these two easily finds out, what is the potential or the particular cell.

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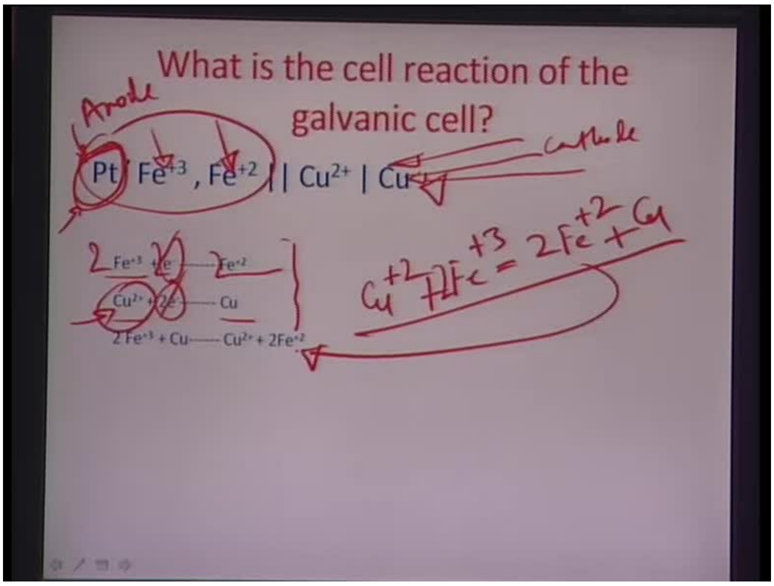

What is the cell reaction of the galvanic cell?

$Pt \mid Fe^{+3}, Fe^{+2} \parallel Cu^{2+} \mid Cu$

$Fe^{+3} + e \longrightarrow Fe^{+2}$

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

$2Fe^{+3} + Cu \longrightarrow Cu^{2+} + 2Fe^{+2}$

Some other numerical examples, this is the very interesting example again wherein, you are considering an ion electrode. There is a ferric and a ferrous state here plus 3 and plus 2 and you are coupling it to a copper and cuprous state. Here, this actually is the cathode where there is in reduction process going on and this is the anode, where there is an oxidation going on.

What would be the cell reaction in this case? The cell reaction would be that the Fe 3 converts into their Fe plus 2 state by giving 1 electron. Again, as I had earlier illustrated platinum here is an inert non-participative metal which just a conduit, which takes out the electron on the charge from this particular solution. On the cuprous side the Cu 2 plus gets be reduced into Cu giving to one electron. In order to balance these two, we can easily write the final solution as Cu plus 2 plus Fe plus 3 twice should be able to give you twice Fe plus 2 plus Cu.

This is just for the purpose of charge balance, so you have to generate 2 electrons here, for these two electrons to compensate for the two electrons which are needed to reduce the copper to its copper plus copper 0 state. This is how the final cell reaction of this particular galvanic cell would look like.

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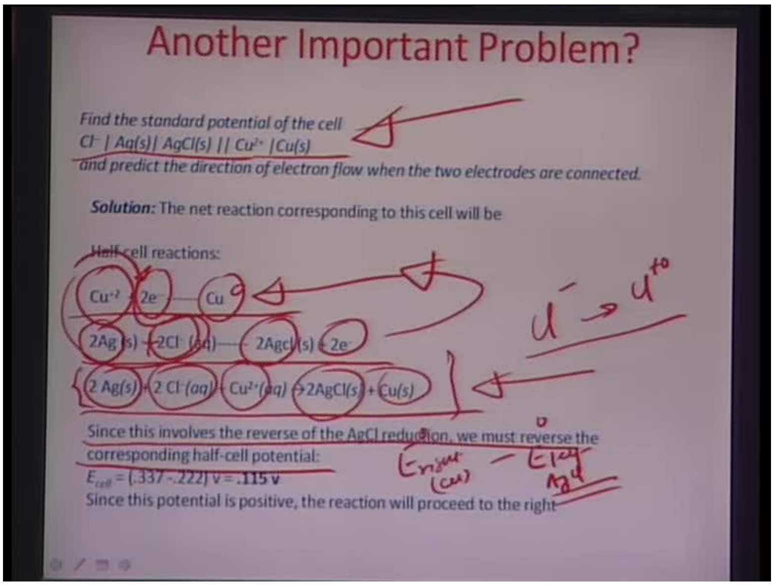

Another Important Problem?

Find the standard potential of the cell
$Cl^- \mid Ag(s) \mid AgCl(s) \parallel Cu^{2+} \mid Cu(s)$
and predict the direction of electron flow when the two electrodes are connected.

Solution: The net reaction corresponding to this cell will be

~~Half~~-cell reactions:

$Cu^{+2} + 2e^- \longrightarrow Cu$

$2Ag(s) + 2Cl^-(aq) \longrightarrow 2AgCl(s) + 2e^-$

$2\,Ag(s) + 2\,Cl^-(aq) + Cu^{2+}(aq) \rightarrow 2AgCl(s) + Cu(s)$

Since this involves the reverse of the AgCl reduction, we must reverse the corresponding half-cell potential:

$E_{cell} = (.337 - .222)\,V = .115\,V$

Since this potential is positive, the reaction will proceed to the right

There are few more illustrations here, this is a very interesting problem for the case of the silver chloride electrode get be can copulate and formulate redox couple with a cupreous copper combination. In this case, the standard potential of the cell can be calculated by considering the reactions, so the right side again, there is the cathode which is a conversion of the cupreous Cu plus 2 form to Cu 0 of two electrons which is liberated in the process. In the silver chloride side if you look at, you have this twice Ag or twice silver plus two times chlorine minus giving 2 AgCl, effectively you have oxidizing the chlorine or you are trying to make the chlorine electron less and generate two electrons here.

These two couple together would formulate redox reaction wherein, twice silver plus twice Cl minus plus Cu 2 plus especially these three would react to give 2 AgCl and Cu. So, this is essentially the cell reaction that would happen.

If I want to generate what is the standard potential of this particular cell, so as this process involves essentially, there is reduction in the chlorine state or a oxidation in the chlorine state. Therefore it would be the E right, which is E copper in this particular case minus E, sorry, 0 left which is E AgCl in this particular case.

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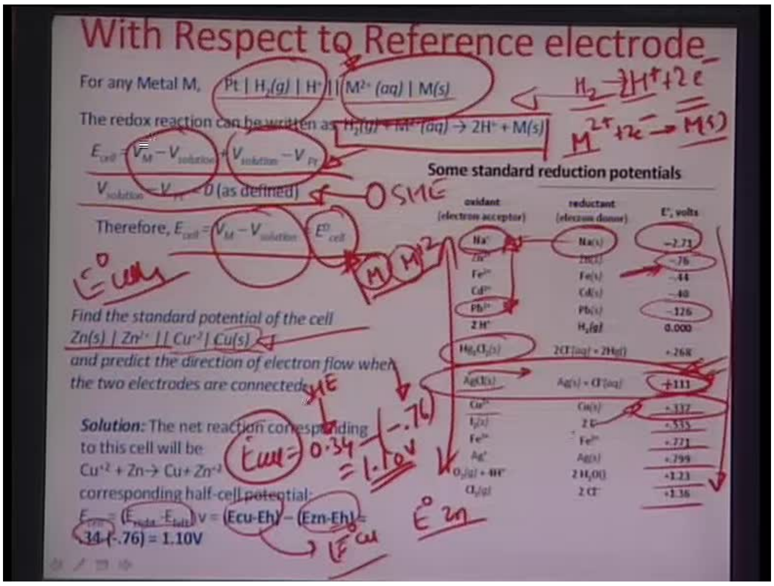

With Respect to Reference electrode

For any Metal M, $Pt \mid H_2(g) \mid H^+ \mid\mid M^{2+}(aq) \mid M(s)$

The redox reaction can be written as $H_2(g) + M^{2+}(aq) \rightarrow 2H^+ + M(s)$

$E_{cell} = (V_M - V_{solution}) + (V_{solution} - V_{Pt})$

$V_{solution} - V_{Pt} = 0$ (as defined)

Therefore, $E_{cell} = V_M - V_{solution} = E^0_{cell}$

Find the standard potential of the cell
$Zn(s) \mid Zn^{2+} \mid\mid Cu^{+2} \mid Cu(s)$
and predict the direction of electron flow when the two electrodes are connected.

Solution: The net reaction corresponding to this cell will be
$Cu^{+2} + Zn \rightarrow Cu + Zn^{+2}$
corresponding half-cell potential:
$E_{cell} = (E_{right} - E_{left})\,v = (E_{Cu}-E_h) - (E_{Zn}-E_h) = .34-(-.76) = 1.10V$

Some standard reduction potentials

oxidant (electron acceptor)	reductant (electron donor)	E°, volts
Na^+	$Na(s)$	−2.71
Zn^{2+}	$Zn(s)$	−.76
Fe^{2+}	$Fe(s)$	−.44
Cd^{2+}	$Cd(s)$	−.40
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$2H^+$	$H_2(g)$	0.000
$Hg_2Cl_2(s)$	$2Cl^-(aq) + 2Hg(l)$	+.268
$AgCl(s)$	$Ag(s) + Cl^-(aq)$	+.111
Cu^{2+}	$Cu(s)$	+.337
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Ag^+	$Ag(s)$	+.799
$O_2(g) + 4H^+$	$2H_2O(l)$	+1.23
$Cl_2(g)$	$2Cl^-$	+1.36

$H_2 \rightarrow 2H^+ + 2e$

$M^{2+} + 2e \rightarrow M(s)$

0 SHE

E^0_{cell}

SHE

$E_{Cu} = 0.34 - (-.76) = 1.10V$

E^0_{Zn}

E^0_{Cu}

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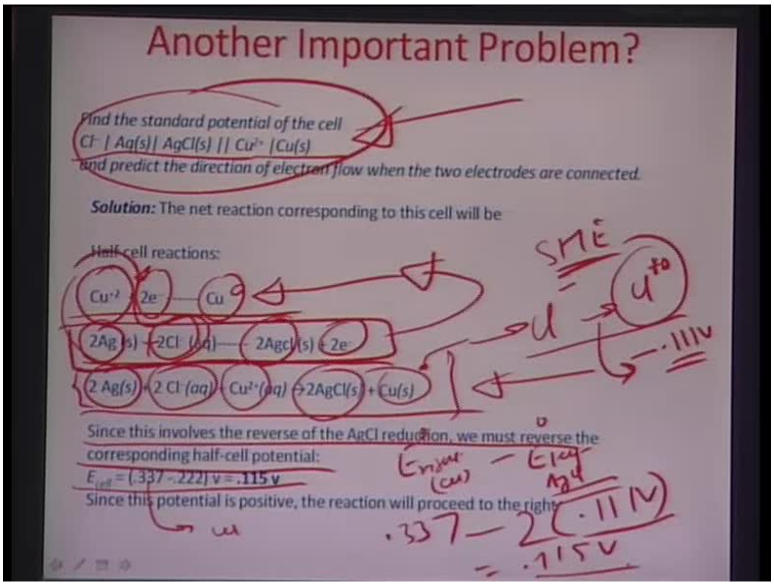

Another Important Problem?

Find the standard potential of the cell
$Cl^- \mid Ag(s) \mid AgCl(s) \mid\mid Cu^{2+} \mid Cu(s)$
and predict the direction of electron flow when the two electrodes are connected.

Solution: The net reaction corresponding to this cell will be

Half-cell reactions:

$Cu^{+2} + 2e^- \rightarrow Cu$

$2Ag(s) + 2Cl^-(aq) \rightarrow 2AgCl(s) + 2e^-$

$2Ag(s) + 2Cl^-(aq) + Cu^{2+}(aq) \rightarrow 2AgCl(s) + Cu(s)$

Since this involves the reverse of the AgCl reduction, we must reverse the corresponding half-cell potential:

$E_{cell} = (.337 - .222)\,v = .115\,v$

Since this potential is positive, the reaction will proceed to the right

SHE

u^{+0}

.111V

$E^0_{right\,(Cu)} - E^0_{left\,(Ag)}$

$.337 - 2(.111V)$

$= .115V$

Essentially, if you look at table before where we are talking about the standard reduction potentials, this particular illustration here represents the reduction of AgCl. The reduction of AgCl is given with respect to a standard hydrogen electrode to be plus 0.111 volts. Therefore, if you look at the potential here, you have two times this particular reaction and in the opposite sense that means here, the Cl minus is oxidized to a Cl plus 0 states. So, the E cell potential of this should be exactly minus 0.11 volts.

This processes happening in the reverse manner and would have normally happened if you coupled to a standard hydrogen electrode. The E cell potential here is essentially, 0.337 that is the potential E 0 of the copper or the right side of this particular representation here or a notation here minus twice 0.111 volts, so it comes out to be 0.115 volts.

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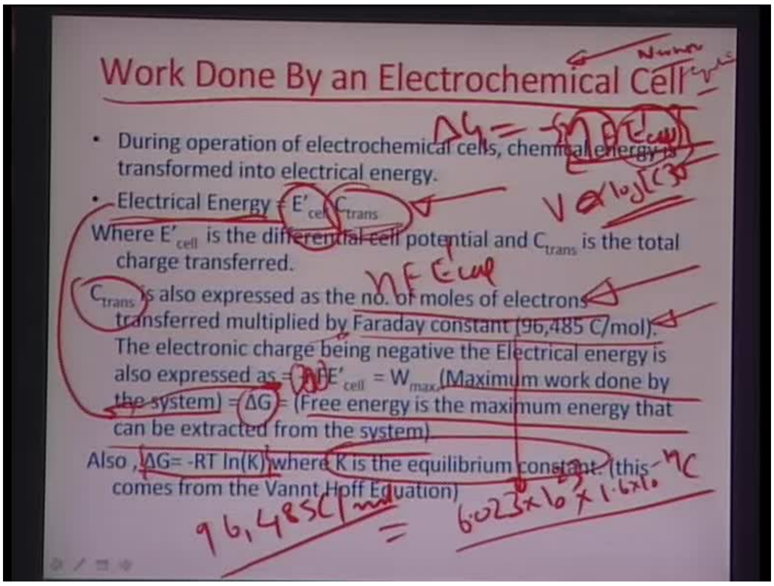

Work Done By an Electrochemical Cell

- During operation of electrochemical cells, chemical energy is transformed into electrical energy.
- Electrical Energy = $E'_{cell}\,C_{trans}$

Where E'_{cell} is the differential cell potential and C_{trans} is the total charge transferred.

C_{trans} is also expressed as the no. of moles of electrons transferred multiplied by Faraday constant (96,485 C/mol). The electronic charge being negative the Electrical energy is also expressed as $= -nFE'_{cell} = W_{max}$ (Maximum work done by the system) $= \Delta G$ = (Free energy is the maximum energy that can be extracted from the system)

Also , $\Delta G = -RT\ln(K)$ where K is the equilibrium constant. (this comes from the Vannt Hoff Equation)

Nernst equation

$\Delta G = -nFE'_{cell}$

$V \propto \log[C]$

nFE_{cell}

$96{,}485\ C/mol = 6.023 \times 10^{23} \times 1.6 \times 10^{-19}\ C$

Since this potential is positive is the reaction will proceed to right. The next illustration as again very interesting problem wherein, we talk about the work done by an electro chemical cell, we are slowly trying to gage the voltage equation which is also known as nernst equation.

Here, we first try to derive this equation so that we can have a direct relationship between the voltage and the log of concentration. In fact, this is preliminary level study for the potentiometry as an area of sensing or diagnostics. Let us first talk about what is the electrical energy that is spent when bunch of electrons or bunch of charges is moved from one side of the cell to the other side. There is an EMF of the particular cell - let us say - E dash cell here is the EMF of that particular cell against to which there is total amount of charge transfer of C trans magnitude. Against the potential Ecell there about C coulomb of charge that are being moved. So, the total amount of electrical energy in this case would be represented as E dash cell times of C trans.

Essentially, charge into potential is the total work done or the electrical energy spent. C trans or the total amount of charge can also be represented as the number of moles of electron which is being transferred in the process into the total charge per mole of the electron, which is also known as Faraday constant F 96,485 coulomb, this gets generated by multiplying 1 mole size which is 6.023 into10 to the power times of the electronic charge which is 1.6 into 10 to the power of minus 19 coulomb. So, this is essentially 1 mole of electrons total amount of charge.

If we want to write this electrical energy with these particular notations the number of moles of charge transferred and the Faraday constant, we can easily write this electrical energy to be n F E dash cell. We can think about that maximum work that is done by the system and because it is a work done, we are considering a negative sign here and is also equal to the free energy of the system delta G - this is the gibbs free energy - which is the maximum work that is the system can do or has a potential of doing.

The free energy can be easily equated to minus n F E dash cell. This is the amount of work which has been already done in order to transfer n F charges through a potential E dash cell in particular illustration, delta G can be equated to minus n f E dash cell. There is another very common illustration coming from the Van't Hoff equation, where the delta G is equated to the equilibrium constant of any reaction K as minus RT L n K. We will be actually coming to this little bit later probably in a next slide.

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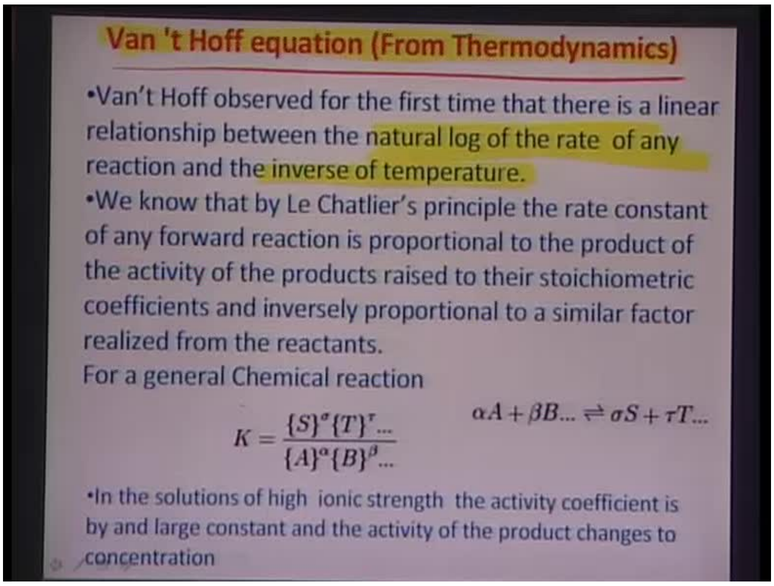

Van 't Hoff equation (From Thermodynamics)

- Van't Hoff observed for the first time that there is a linear relationship between the natural log of the rate of any reaction and the inverse of temperature.
- We know that by Le Chatlier's principle the rate constant of any forward reaction is proportional to the product of the activity of the products raised to their stoichiometric coefficients and inversely proportional to a similar factor realized from the reactants.

For a general Chemical reaction

$$\alpha A + \beta B ... \rightleftharpoons \sigma S + \tau T ...$$

$$K = \frac{\{S\}^{\sigma}\{T\}^{\tau}...}{\{A\}^{\alpha}\{B\}^{\beta}...}$$

- In the solutions of high ionic strength the activity coefficient is by and large constant and the activity of the product changes to concentration

Let us first talk about how this Van't Hoff equation comes into picture from thermo dynamics. So, Van 't Hoff observed for the first time, if you really plot the natural log of the rate of any reaction with respect to the inverse of temperature and this actually he found for a system of gases. There is a strange kind of linear relationship between the two, this can be illustrated more in this particular curve as you are looking at. So, this is essentially the access which represents the natural log of K, where K is the equilibrium constant.

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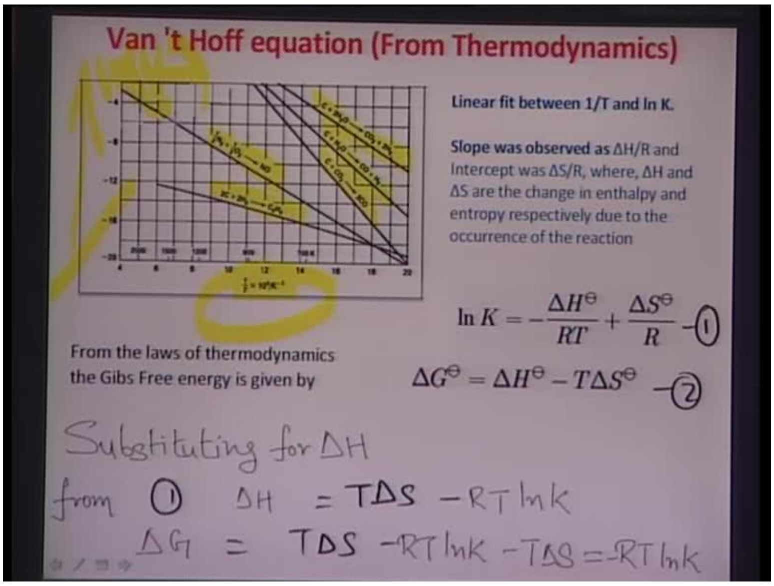

Van 't Hoff equation (From Thermodynamics)

Linear fit between 1/T and ln K.

Slope was observed as ΔH/R and Intercept was ΔS/R, where, ΔH and ΔS are the change in enthalpy and entropy respectively due to the occurrence of the reaction

$$\ln K = -\frac{\Delta H^{\ominus}}{RT} + \frac{\Delta S^{\ominus}}{R} \quad ①$$

From the laws of thermodynamics the Gibs Free energy is given by

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} \quad ②$$

Substituting for ΔH

from ① $\Delta H = T\Delta S - RT \ln K$

$\Delta G = T\Delta S - RT \ln K - T\Delta S = -RT \ln K$

You are plotting this with respect to inverse of temperature, so for different gas systems - system of gases all these are equilibrium processes essentially - he found out that there is a linear relationship between the inverse of temperature and the log of K.

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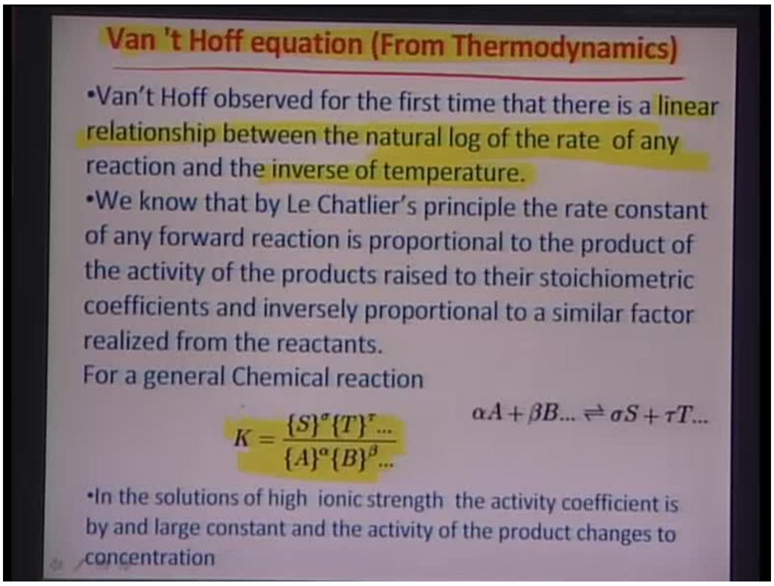

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For a general Chemical reaction

$$\alpha A + \beta B ... \rightleftharpoons \sigma S + \tau T ...$$

$$K = \frac{\{S\}^{\sigma}\{T\}^{\tau}...}{\{A\}^{\alpha}\{B\}^{\beta}...}$$

- In the solutions of high ionic strength the activity coefficient is by and large constant and the activity of the product changes to concentration

What is really the equilibrium constant; this comes from another illustration called the Le Chatlier’s principle, the rate constant of any equilibrium process of any forward reaction is proportional to activity of products which are created by reaction raise to the power their stoichiometric coefficients.

In this particular case an alpha mole of A’s reacting beta moles of B to generate, let us say, sigma moles of S and tau moles of T. By the Le Chatlier’s principle the equilibrium constant for the forward reaction is generated as S, the activity of S to the power sigma into activity of T to the power tau by activity of T to the power alpha into activity of b to the power of beta. We would like to continue this and some other illustrations probably in the next lecture, thank you.