BioMEMS and Microfluidics

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Lecture – 05

Let us review what we have done last time.

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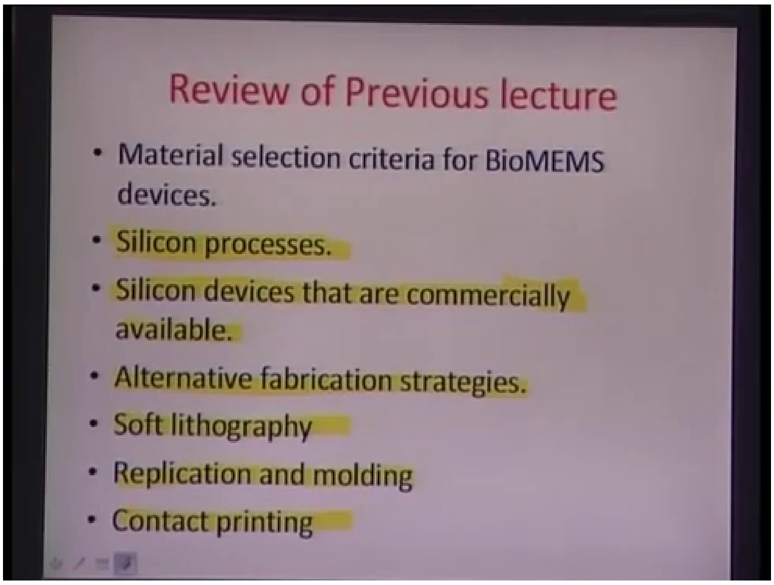

Review of Previous lecture

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

So, we were talking about the various material selection criteria for bioMEMS, biochip kind of devices. And, we talked about issues like optical transparency, bio compatibility, then rapid photo refinability or rapid fabrication, strategies that could be done using these materials. So, these are some of the important selection criteria. 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 the digital micromirror device, accelerometers, and the single chip micro phones; 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. So, we are going to go head on this spree and try to finish the soft lithographic processes today. After which, we will do a little bit of introductory electro chemistry.

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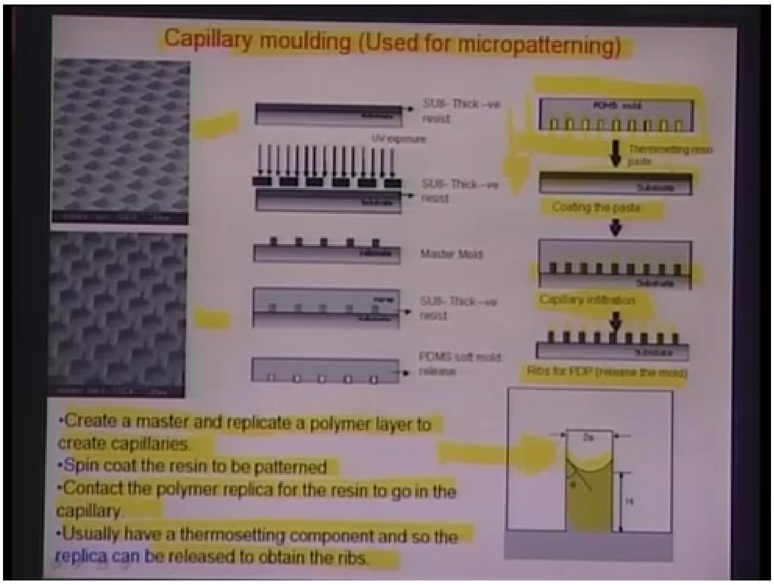

Capillary moulding (Used for micropatterning)

- 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.

So, the next process along the line is capillary moulding; it is again one of the important processes for especially for display technologies sometimes. So, the process steps are very simple. You have again a mold made upon PDMS with these small micro capillaries made by replication and molding techniques. And, essentially then we spin coat thermosetting resin paste on to the surface of a substrate. In this case, substrate may be silicon or a glass wafer. And then, we essentially press this PDMS mold on the top of this thermosetting resin and press it up till the resin actually takes the shape of the small micro capillaries. And, once it is fully…

So, essentially, the PDMS when it sits on the top of this thermosetting resin, it squeezes the material in both directions. And so, there is of course, the material coming out come from these ends and the material also kind of 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 that it leaves intact the resin material filled in these micro capillaries and, this is what is micro capillary molding. It is a very good patterning technique, which can be used to coat polymeric pixels on the top of a substrate.

Now, some of the practical issues that come while doing this is that, 1 – number one 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, essentially, there is a material and… So, these several processes are basically coating the paste capillary infiltration and releasing the mold, so that you are left with the thermosetting resin shaped as small dots. So, these are some of the features and structures; so, which are generated by this process sited from various illustrations. So, the overall process steps are that, you create a master and replicate a polymer layer to create micro capillaries, spin coat the resin to be patterned, contact the polymer replica for resin to go in the capillary with some limitations and restrictions like these kind of formalities; and, usually have a thermosetting component. And so, the replica can be released to obtain the ribs which are thermally set.

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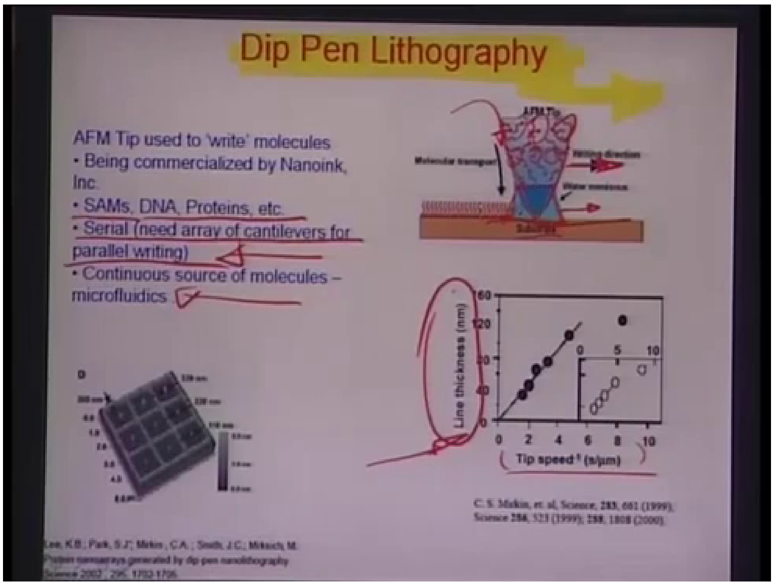

Dip Pen Lithography

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, 1702-1705

The next process is a dip pen lithography. And, in fact, this is again a process wherein we can write selectively molecules on a surface. This process was generated by doctor – by Chad Mirkin's group at Northwestern. And, 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, here this right here is an AFM tip. And, what we do is that, we create some favorable temperature and humidity conditions, so that there is this layer – this mono layer of water. And, we choose the surfaces in a manner that there is a tendency for this water meniscus to adhere more to the AFM tip than the substrate. And so, you can drag it along with the tip as the tip moves around. So, the idea is that, this particular layer as you are seeing here of water is more adherent to this layer AFM tip surface than the subscript on which it is moving. And so, when you are dragging the pen, this moves along with the pen rather than adhering to the substrate. So, why it is used? This is used for transporting molecules.

So, if you have some kind of a constant feed mechanism or delivery mechanism, wherein these small molecules can be delivered rapidly on to this AFM tip; they can use this monolayer to go and set in a particular arranged order on to the substrate of interest. And so, therefore, this process is used for essentially writing molecules. So, it is pretty much like what an ink pen does. And, an ink pen also especially 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 adsorbed on to the paper. And, this is also a similar kind of application with an STM pen doing the same job; instead of ink, this pen writes molecules rather on the surface. So, this is a highly commercial process used rapidly.

In fact, there is a company by the name of nano ink incorporated, where they have commercialized this dip pen lithography technique for a lot of applications, wherein self-assembled mono layers and DNA, proteins, etcetera are rapidly delivered on to such surfaces. And typically, this process is a serial process, but there are some initiatives in which they have tried to make this process parallel, wherein there are several such AFM tips, which are actually being fed by the molecules altogether. And then, when this whole probe head moves with the different tips, it can able to write in different tracks and routes these molecules. So, there is an initiative, where this serialized process is being currently commercialized for an array of cantilevers for parallel writing.

So, another challenge here in this kind of a mechanism is how the molecules can be rapidly delivered and continuously delivered on to the STM pen. And, principles of microfluidics are off and on used for that purpose. So, if you look at this particular illustration from Mirkin's group, as you can see here that, as a tip speed inverse increases; that means that, the tip speed decreases, the line thickness of these molecules automatically increase; which actually also intuitively makes sense. And so, this is a very important process again, which is kind of grouped into the soft lithography domain.

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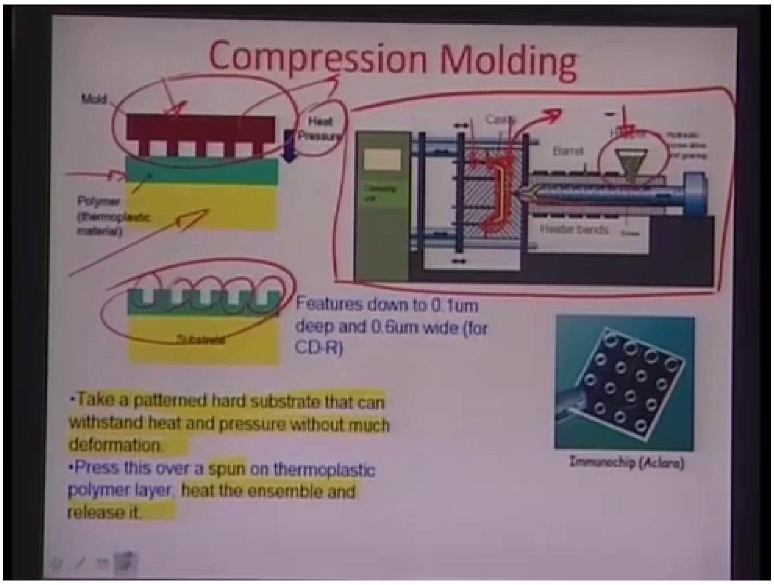

Compression Molding

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 process is compression molding. And, this also forms a foundation of something called nano imprint lithography that we will be just talking in the next slide. So, in this process, again there is a material, which is the substrate. And, thermoplastic material is coated on to the substrate. And, the mold again is prepared and made, which can withstand high heat and pressure. So, this mold can be silicon nitrite or silicon dioxide over maybe a silicon surface or even made with metal, micro machined with some other techniques like EDM – electro discharge machining, ECM, so on and so forth. So, once this mold is pressed on to this thermoplastic material, there is a shaping of this thermoplastic material as the negative for the mold that is used for this squeezing. And then, the idea is that, you remove the mold; and so, whatever remains here is well set; and thus, the features on the mold are trans… – the negatives of the features of the mold are transferred on to this material. This is how you write micro features or structures on to a surface.

So, very common compact disc that we use regularly in our computers are audio equipment, is essentially realized using the compression molding process. And, another very important technique, which is off and on used is injection molding, which is illustrated here in this particular figure. So, if you see this illustration here; there are two dice, which are kind of mating components. And, there is a small gap here in this region between the dice, which is the shape or the feature, which has to be replicated.

So, a polymeric material, which is normally in the solid form is dropped into this Hooper and this least screw essentially transfers the material by first melting it and then constantly feeding it on to this small cavity. And, as the polymer melt goes into the cavity, it stays there and gets cooled off and gets hardened or solidify after which the injection or this mold is kind of separated are opened and the materials is removed. So, you really need a very good surface preprocessing agent here for a proper separation of the polymer that you feed in. So, in fact, this is a very useful process for again micro fabrication.

So, in a nutshell, these processes are about taking a patterned hard substrate, which is capable of a standing heat and pressure with minimal deformation. And, essentially, thermoplastic materials spun over some kind of a wafer is molded by compressing the mold on to this particular thermoplastic film. And then, the sample is heated, so that it sets up the thermoplastic material and the mold is removed eventually.

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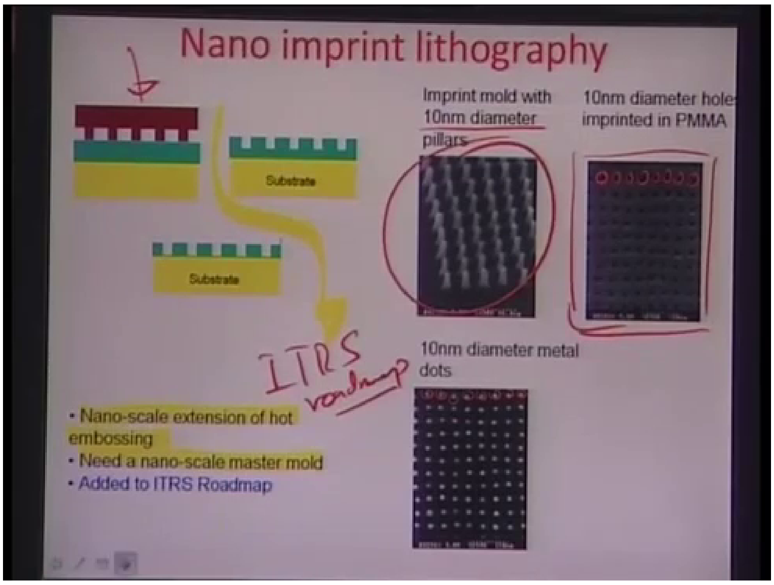

Nano imprint lithography

Imprint mold with 10nm diameter pillars

10nm diameter hole imprinted in PMMA

10nm diameter metal dots

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

So, another very important process, which comes almost immediately from compression molding is nano imprint lithography. And, I would like to just illustrate that, this process has also been made or being included in the ITRS road map especially for end of the road devices. Here… As you see here, the same processes compression molding is used, but on a much smaller scale on a submicron scale. These are some illustrations of what nano imprint lithography can do. In fact, this is actually a set of pillars, which are about 10 nanometers in size. And, there is an array of such pillars, which are made using a nano imprint mold.

You could do a variety of other processes like this particular illustration is that, of a PMMA, which is also a e-beam resist wherein this 10 nanometer diameter holes have been made. And, an array of these holes have been realized on to the polymethyl methacrylate. And, these are through holes. So, this can be used a shadow mask for processes like deposition, where this mold is put over a wafer and material like gold or platinum is deposited through this shadow mask, so that the small tiny dots here are each of about 10 nanometers in diameter, because they can go through this particular hole on the PMMA. So, the shadow mask is later on removed and you have an array of this fine dots. And, these are used off and on for a lot of micro-nano scale electronics. So, in a nutshell, again nano imprint lithography is the extension of the hot embossing process. And, all you need is a nano scale master for this. And, specially, this process has been added on very recently to the ITRS road map.

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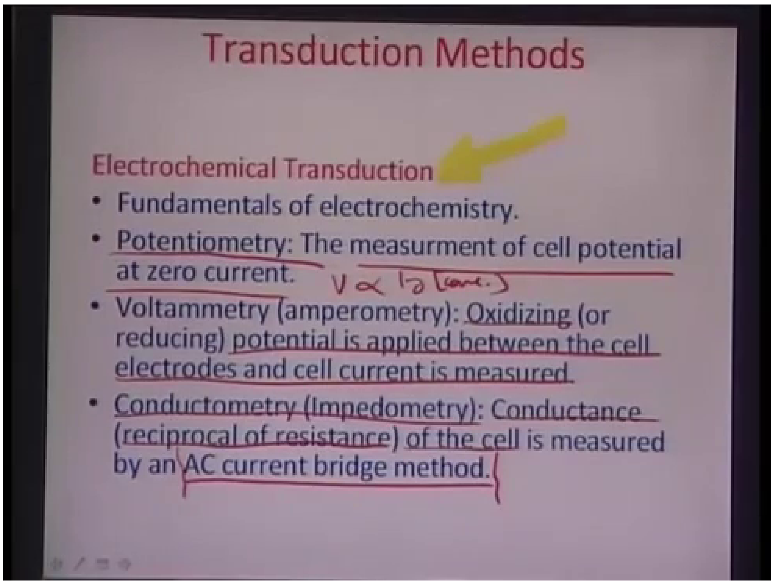

Transduction Methods

Electrochemical Transduction

- Fundamentals of electrochemistry.
- Potentiometry: The measurment of cell potential at zero current.

$V \propto \lg(\text{conc.})$

- 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.

So, this kind of 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 and sensors, which we have done, which we covered even last lecture and before. And, we would look into a little bit of fundamentals of electrochemistry or electrochemical sensing. And, essentially, if you look at again the different transduction types, I would just like to reiterate this from the last lectures – last few lectures that, the electrochemical transduction can be characterized into potentiometry, which is the measurement of cell potential at zero current. And, if I may just add, it is a method in which the voltage is proportional to the log of concentration of the analyte of interest. Voltammertry, where you use 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; and by using the conductance, you can find out whether there is any change in the concentration of the analyte. Or, you can use this using an AC current bridge method, wherein impedance measured at a certain frequency can be seen and the change can be monitored for gauging the concentration – the rapidly increasing or decreasing concentration of a certain analyte.

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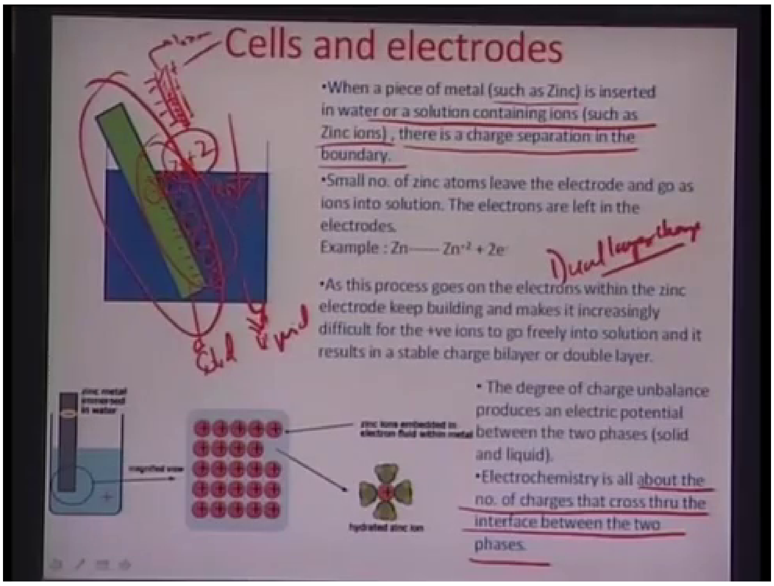

Cells and electrodes

- 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 : $Zn \text{——} Zn^{+2} + 2e^-$
- 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.

So, let us look into a little bit of fundamental aspects of what happens really when we dip a metal rod inside a solution. So, when a piece of a metal such as let us say zinc in this case is inserted in water or maybe a solution, which contains zinc ions, there is an immediate charge separation in the boundary. And, this I think I illustrated in one of my lectures 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 oxidized states are created. And simultaneously, the electron, which is liberated – in this case, in case of zinc, it is two electrons are rapidly concentrated around this particular area of the electrode.

So, it is a self-stopping processes, because by the principle of electro neutrality, this combination cannot hold beyond a certain level of negative charge; it would automatically try to stop this process of zinc going into solution and creating electrons. But, once the zinc goes into the solution, there is also another effect, which is happening that, the water from the surroundings kind of comes between the zinc and this negative charge on the electrode and forms a thin dielectric layer. So, essentially, we are talking about a very small capacitance, which results from the positive charges in terms of zinc ions, which is in the solution and the negative electrons separated by a small monolayer of water. Now, this layer can be asked in as about 10 nanometers; but, this is self-stopping process essentially develops something called a dual layer of charge. And, all electrochemistry is essentially about the number of charges that cross through this interface dual layer between the two phases: solid and the liquid.

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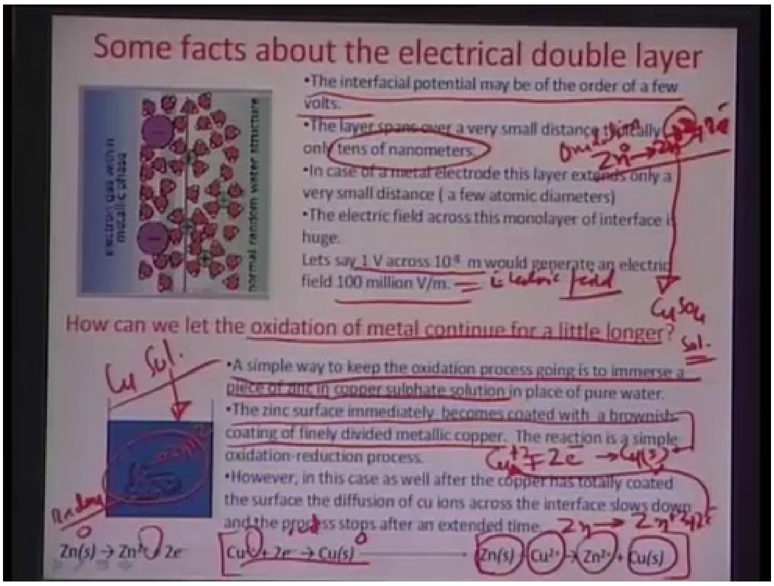

Some facts about the electrical double layer

- 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. = i.e. electric field

How can we let the oxidation of metal contiue 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.

$Zn(s) \rightarrow Zn^{2+} + 2e^-$ $Cu^{2+} + 2e^- \rightarrow Cu(s)$ ——→ $Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$

Oxidation $Zn \rightarrow Zn^{+2} + 2e$

$CuSO_4$ Sol.

Cu Sol.

Reduction

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

$Zn \rightarrow Zn^{+2} + 2e$

So, once this concept is clear, let us look it into a little bit more detail of what may happen to the electrical double layer. So, essentially, the interfacial potential in such a double layer may be of the order of few volts, which essentially makes the electric field very high, because if you consider the span or the spacial separation of the positive and negative charges, it is not more than about 10s of nanometers. So, therefore, 1 volt across about 10 to the power minus 8 meters would make about a 100 million volts per meter. That is how high the electric field is really going to be in such a double layer. What happens…

Let’s say if another illustration here; if a piece of zinc is you know dipped in copper solution. So, let us first actually consider why it is… – why or how can this oxidation of the metal, which we were seeing in the last case, where zinc was being converted into Zn^{+2} can be increased for a little longer. So, as we know, this is again driven by diffusion – this process, where this zinc is going into water as plus 2. And, because of the principle of electro neutrality, there is only a finite amount of oxidation that can happen. So, how can I extend the oxidation time is the question. And, this is very important for developing a basic understanding of what electrochemical sensing is all about. That is why it is important to go through these – some of these concepts.

So, a simple way to keep the oxidation process going is to immerse the piece of zinc from water into rather a solution of copper sulphate. So, copper again is an electrically active material. And also, there is a tendency of zinc to displace copper from its solution. So, this generates something called a redox couple, wherein the first process that takes place is… So, let me first say what is going to happen if such a zinc is dissolved inside the copper sulphate solution. So, immediately becomes coated with the brownish coating of finely divided metallic copper on to the surface. And, if you look at why this is happening, essentially the copper, which was present in the Cu^{+2} – in the $CuSO_4$ solution, gets reduced by taking electrons, which have been generated in this metal as the zinc tries to move out as Zn^{+2} . And so, therefore, the two electrons, which are already present in this particular lump of zinc by virtue of the oxidation of zinc…

By the by why – how do we know what is oxidizing? Just a little bit of basics here that, the valency of a material should increase for an oxidation process to happen. So, oxidation is signified by… Here the valency is 0; here as you see this plus 2, because plus 2 electrons have gone out. So, oxidation is essentially the increase in the valency of the material. So, copper goes from a copper plus 2 state into simple copper maybe in the solid form. This is the brown deposit that we are talking about. And, the zinc on the other hand gets converted into Zn^{+2} and leaves two electrons back in this surface, which is easily donated away to the copper ion to get converted into copper solid. So, if I look at this equation together, it becomes something like that, that the zinc has a potential of displacing Cu^{+2} from its solution to make into solid copper deposited on the surface. And, the zinc in turn gets oxidized. So, this is also known as a redox reaction, because one element here – the copper is getting reduced; mind you that, the valency is changing from plus 2 to 0 in the solid state; and, one component – the zinc is getting oxidized, where the valency is changing from 0 to plus 2. So, these two are going together. So, it is also known as a reduction oxidation or redox mechanism.

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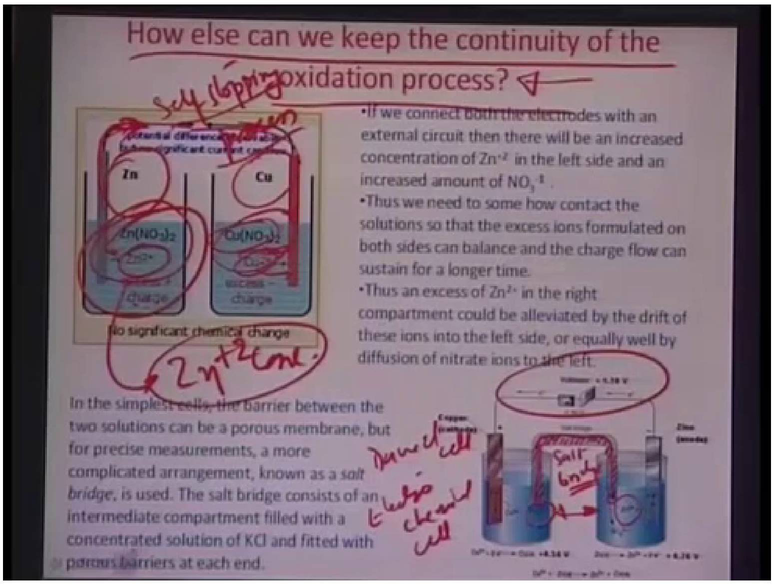

How else can we keep the continuity of the oxidation process?

- 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.

The next obvious question that anybody would ask is that, how can we 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 that, let us say we have something, which is able to be displaced into the solution as ions; and something wherein it is able to displace the ionic state into the solid form. So, zinc here as you see getting oxidized to Zn plus 2 and going into the solution; and, copper from this copper nitrate, getting reduced and going as a deposit on to the copper electrode. So, 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 process will only happen finitely, because after a while, there would be an increase in the Zn^{+2} concentration inside this particular solution, because of which there would be no further transportation of zinc into this solution as Zn^{+2}. So, in effect, what would happen is that, the ionic concentration of Zn^{+2} would 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.

So, can I do something to make this process continue? The answer is yes. So, what we do here is that, we create a charge balance back by connecting the two solutions together as well by something called a salt bridge. So, essentially, this is something wherein it contains two plugs at both the ends; and, there is ion exchange solvent; and, there is a continuous exchange of the increase let us say SO_4^{-2} ion on one side in the copper sulphate solution with the increased Zn^{+2} ion on other side with the zinc sulphate solution. And so, therefore, this creates the charge balance between the two cells or two half cells. And, this process goes on for some time. So, this is also known as an electrochemical cell – electrochemical cell. And, in fact, this is also called as a Daniell cell.

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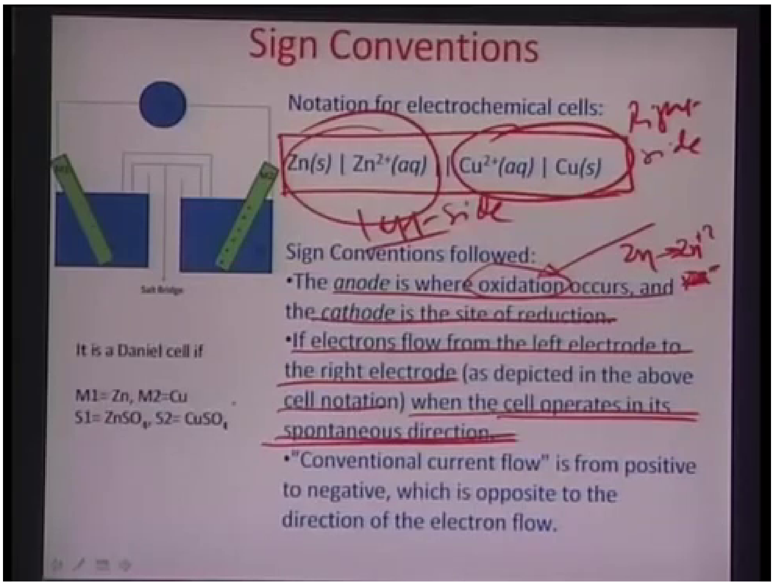

Sign Conventions

Notation for electrochemical cells:

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

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.

It is a Daniel cell if

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

So, what I would like to illustrate here is that, there is a sign convention, which is used for writing such half cells. So, the convention, which is followed here is essentially the anode is where the oxidation would occur; and, the anode is represented in the convention more on to the left side. So, anode is where oxidation takes place. So, zinc is converted into Zn^{+2} , is really called the anode, because we consider the… It is solution perspective of it as if it is giving positive ions into the solution. And, cathode is where reduction is happening. This right side of this particular convention is the cathode. And of course, there is an electron flow from the left electrode to the right from the electrode, which provides oxidation to the electrode, which provides reduction. And, the current essentially is the opposite of the flow of electrons, because it is conventional to consider current flow as positive. So, 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 the spontaneous direction.

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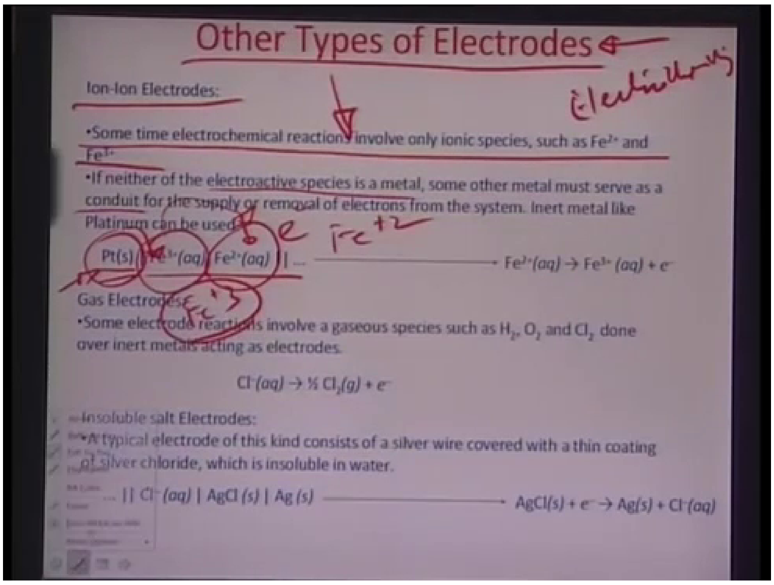

Other Types of Electrodes

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.

$Pt(s) | Fe^{3+}(aq), Fe^{2+}(aq) || \ldots \longrightarrow Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

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.

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

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.

$\ldots || Cl^-(aq) | AgCl(s) | Ag(s) \longrightarrow AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$

So, following these sign conventions, there can be other kind of electrodes, which can work out in pretty much similar way. And, these electrodes would be essentially off and on used electrochemistry later on, where we will talk about how to sense analytes using some of these basic principles electrochemical principles. So, the other form of electrode, which exists is an ion electrode, where when you talk about… As you have seen in the last illustration, we talked about really two solutions: one – oxidizing and another reducing; and, two different solutions – one in copper, one in zinc; with the copper and a zinc electrode respectively each of the solutions.

Here, we are talking about two different oxidation states of the same material. So, in one state, iron here is available as Fe^{+2} and in another state, it is available as Fe^{+3} . So, assuming that, if this Fe^{+3} is the oxidized form of the material and Fe^{+2} is also the oxidized form of the material, but essentially with the difference of one electron between them. There is still an electron flow from the anode side to the cathode side. And, this is essentially again a working set of electrodes and a flow cell essentially and batteries. So, essentially… So, we are talking about that, sometimes electrochemical reactions involve only ionic species such as in this case, the plus 2, plus 3 form. And, if neither of the electroactive species is metal; instead of… So, 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 picking up the electron from the anode side and placing it on to the cathode side.

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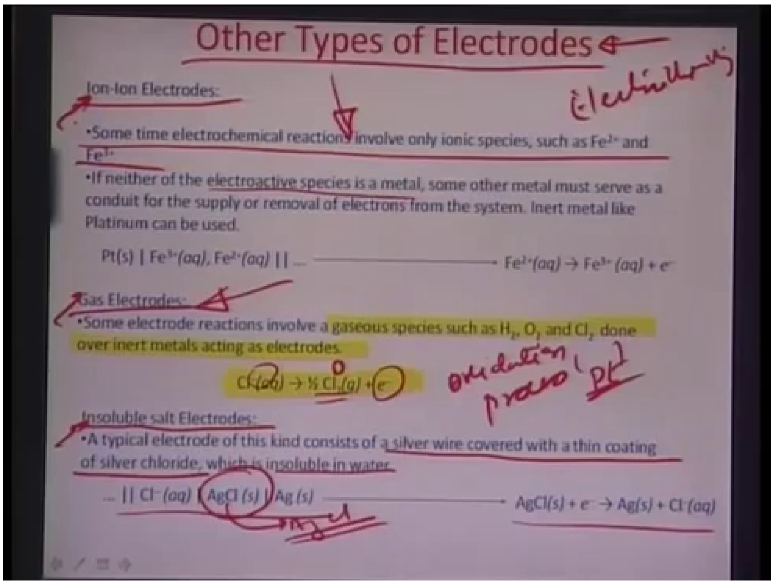

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Gas Electrodes:

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$Cl^-(aq) \rightarrow \frac{1}{2}\overset{0}{Cl_2}(g) + e^-$

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 other types of electrodes that are available are gas electrodes as can be illustrated here in this particular example. So, here instead of a liquid species, we are concerned with a gaseous reaction. So, it is a gaseous species such as let us say hydrogen, oxygen, chlorine, etcetera. And, 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 zero valance state or a gas form and at the cost of one electron; one electron is eliminated from the chlorine. So, it is an oxidation processes essentially. So, some materials here like platinum are again used as a conduit for electrical or for promoting connections between two or more cells; but, the metal itself, material itself is inert and it does not participate in the electrochemical reaction or the electrochemical process.

Another form of electrode here is the insoluble salt electrode. Here the concept is a little different like let us say if we are talking about AgCl electrode – a silver chloride electrode; so, normally, silver chloride is an insoluble salt in water. So, if you put a AgCl, it precipitates as crystal. So, the problem is in that case what you do with the electrochemical sensing or electrochemical cell design. So, in that case, essentially, what you do is you take a silver wire and cover this with the thin coating of silver chloride. And, that formulates a good scheme of ion exchange even though the salt is considered is highly insoluble in water. So, these are some of the types of electrodes that are used off and on for electrochemical sensing apart from the conventional metal electrolyte electrodes.

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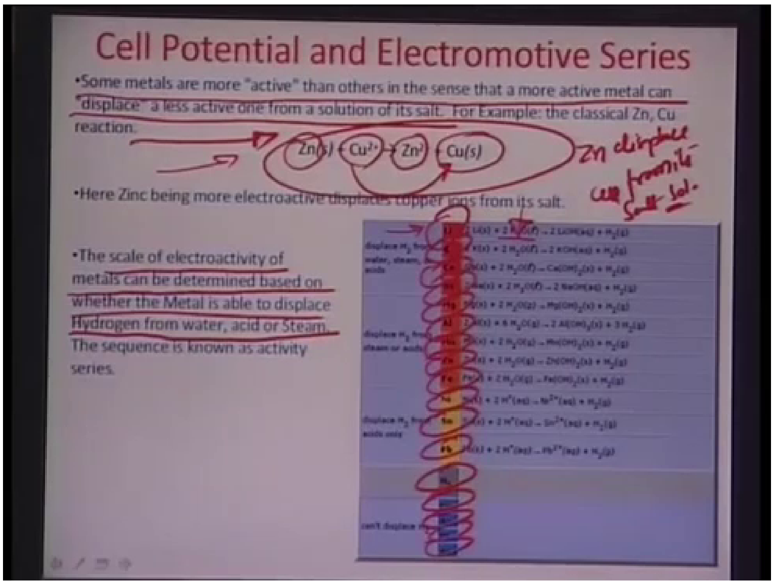

Cell Potential and Electromotive Series

- 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.

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

- 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.

Zn displace Cu from its Salt sol.

Another very interesting factor is that, some metals are more active than others in the sense that, they provide – they can displace a less active one from a solution of its salt. Like let us say if we consider the zinc-copper case or if we consider the Daniell cell; as we saw here that, the zinc was displacing or was getting displaced or getting oxidized and going into the solution and was really displacing the copper plus 2 state as a deposit – a copper deposit on to the electrode. So, zinc was able to clearly displace copper from its salt solution. So, I can consider zinc to be more electroactive than copper ions. So, based on these kind of 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 from water, steam or acid. So, it is essentially that, if you take H_2O in any form, be it steam or be it kind of in equilibrium with an acid or be it just in water state; how the metal can displace hydrogen or how actively it can displace hydrogen also gives it a position up to the ladder on the electro activity series. Why hydrogen? Because a common scale is needed for… It is like a reference scale. So, if it is compared with respect to the hydrogen, it gets compared with each other by that process. So, if it is way up on the electroactivity series, it can easily display something, which is below it on the same series. That is how these series are being made.

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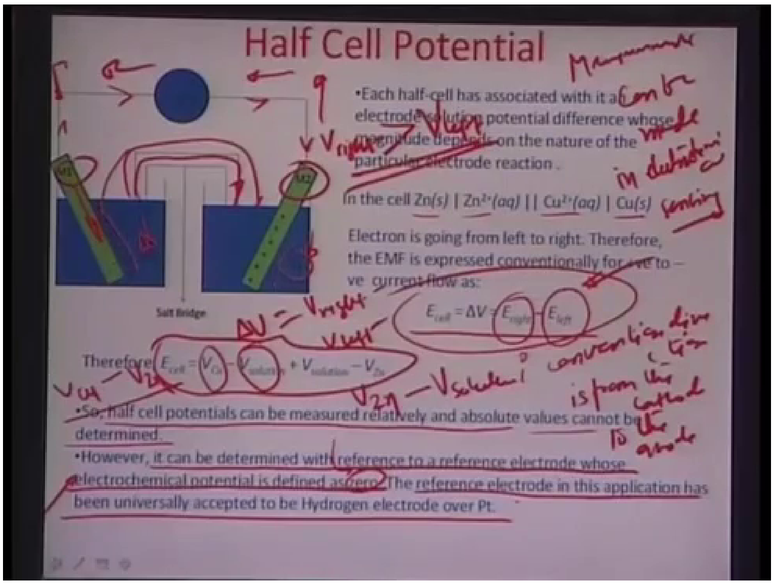

Half Cell Potential

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

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.

Some fundamental basics of electrochemistry are important for understanding how really measurements can be made in electrochemical sensing. So, let us again look at the same example of Daniell cell. So, you have a metal electrode; you have a solution – salt solution. You have the M1 is the type of metal here. And, you have another metal M2 in its salt solution S 2. And, you have connected them or interconnected them using this salt bridge and you are trying to take read out of the total current across – between the two electrodes. And obviously, if M1 is the anode; then, the electron flow would be from M1 to M2. So, let us say M1 in this case zinc – Zn^{+2} . And, M2 in this case is Cu^{+2} and copper. So, M2 and S2 are essentially copper and copper plus 2. And, M1 and S1 are essentially zinc and zinc plus 2.

So, if you consider the total EMF that, this particular cell would have… It is essentially the EMF of the right side of the cell or the right cell minus the EMF on the left cell. This is more so because as you know, currents conventional the correction 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 that, the potential here we write is higher than the potential in the left side. And, the delta v, which is responsible for movement of these electrons, is essentially V right - V left as you can see here.

If we consider what really the E right or the V right is, it is nothing but the voltage provided by the copper minus voltage of the sulphate solution S2. And similarly, V left is voltage provided by the zinc minus voltage of the zinc sulphate solution. And therefore, the total 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. So, the solutions really do not play much of a role; and more so, because there is a salt bridge, which keeps on interconnecting and neutral are making the solution electroneutral at all points of time. So, 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 the very factor is that, the double layer – the electric double layer, which is responsible for this potential to build up is a very small layer. So, you cannot again a small piece of metal in this 100 nano meters or 10 nanometer domain and get a relative potential of the electrode with respect to the solution surrounding the electrode. So, the only other way is a relative measurement.

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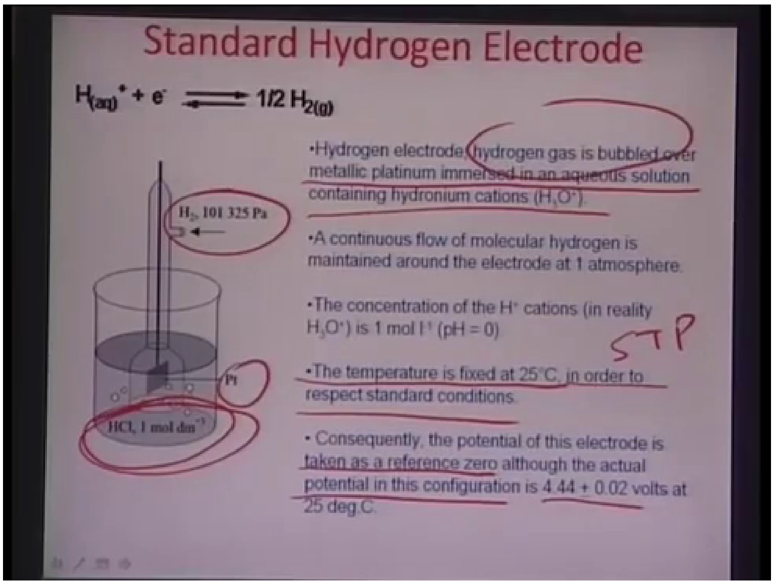

Standard Hydrogen Electrode

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

- 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.

STP

However, this problem can be averted by making a reference electrode and defining that as an electrochemically inactive electrode; so, with a zero electrochemical potential. Although in principle, such electrode would have some potential. But, if we consider a scale, wherein this potential is signified or represented as a zero potential; then, this can be a reference electrode for considering the individual potentials of different metal electrodes with respect to it. So, this reference electrode 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 a one molar solution of HCl in water; and, hydrogen is bubbled through this particular electrode at about – pressure of about 101325 Pascals or 1 atmosphere.

Essentially there is a potential, which is created. So, basically the standard hydrogen electrode now, therefore, is something, which is realized by a metallic platinum immersed in an aqueous solution containing hydronium ions – H_3O plus, which is formulated by again 1 molar HCl in water. And, hydrogen gas is slowly bubbled for this at 1 atmosphere pressure. And, temperature is fixed to be again 25 degree Celsius in order to get standard conditions. Let us call the standard temperature pressure STP conditions. And, consequently, the potential for this electrode is taken as the reference 0 although the actual potential in this configuration comes out to be about 4.4 plus minus 0.02 volts at 25 degree Celsius.

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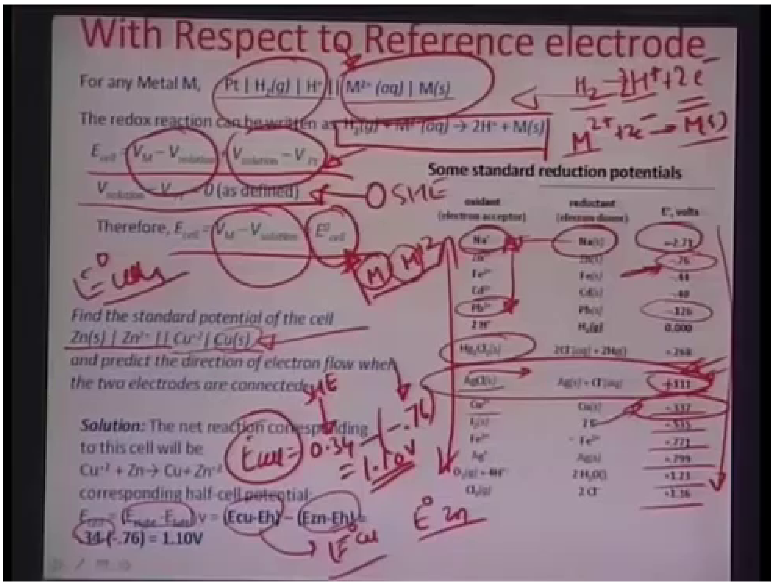

With Respect to Reference electrode

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

So, let us actually move on to the aspect of how we can calculate, how we can predict what is the current level – what is the potential difference between a pair or a combination of such electrode solutions; and, how we can predict the flow of current. So, again as you know that, for let us say any metal solution combination, the total E_{cell} is represented by E right minus E left. And, the right is essentially as in this case – this particular case, the cathode and the left is the anode. So, if you consider an electrode, we are talking on one side of the standard hydrogen electrode and the other side to be the particular metal of interest. So, how can we really right this redox couple is the question. So, here for instance, in this particular cell, when we are writing a combination of the metal solution and a metal with respect to the standard hydrogen electrode with platinum as the conduit; hydrogen is getting oxidized at the cost of releasing two electrons. And, these two electrons are gathered together by the metal, which converts from the plus 2 state into the solid metal. So, this redox reaction can be also written as H_2 plus M_2 plus makes 2 H plus – 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. So, essentially, it is the voltage of metal minus voltage of solution plus voltage of solution minus voltage of platinum. So, we define this voltage of solution minus platinum to be zero because there is a scale of the SHE or the standard hydrogen electrode. And therefore, the E_{cell} comes out to be nothing but B M minus B solution. And, we call this the absolute potential of the particular metal ion combination; so, very useful again to find out. We can actually get a couple of these E0 cells for a different combination of different metals and its salt solution. And, these have been kind of 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 goes all the way up to lead. And so, lead – up to lead, all these different metals are more electroactive than hydrogen. And so, 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 below these mercury chloride, silver chloride, copper – cuprous kind of solutions, so on and so forth. So, it is very easy now to find out the standard potential of the cell and also the predict the electron flow direction.

If this scale here with respect to the SHE as already been formulated like in the case of the Daniell cell of we look at, there is an electrode here, which is the anode converting into Zn^{+2} . And, an electrode, which is the cathode converting from copper plus or cuprous state into copper zero 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. And, if you look at this particular electroactive series here, the E 0 copper comes out to be about 0.34 and the ink… And so, it comes 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. So, the total E cell can be represented as E_{right}, which is 0.34 – E 0 right with respect to the standard hydrogen electrode minus E left, which is minus 0.76. On the other words, it would be 1.10 volt. So, this is essentially the total EMF of the cell. So, you consider the individual electrodes with respect to the SHE or standard hydrogen electrode and then make a combination of these two to easily find out what is the potential of the particular cell.

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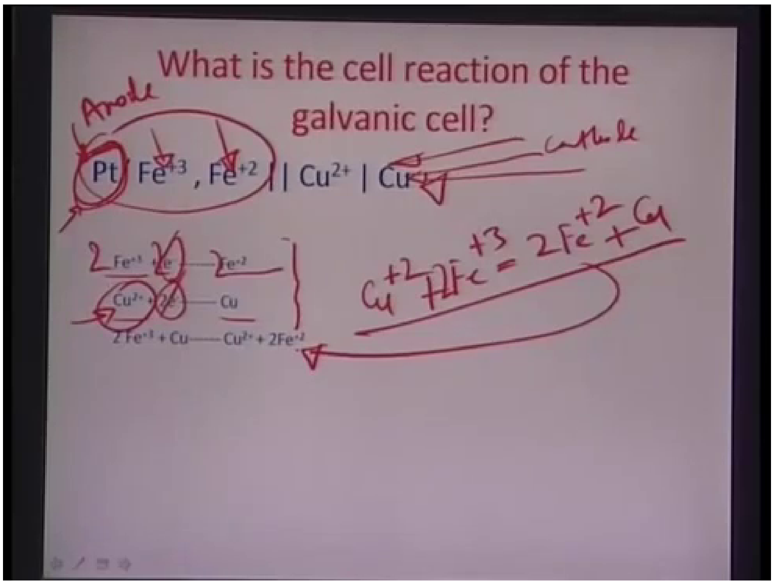

What is the cell reaction of the galvanic cell?

Anode

Pt | Fe^{+3} , Fe^{+2} || Cu^{2+} | Cu

cathode

$2Fe^{+3} + e$ —— Fe^{+2}

$Cu^{2+} + 2e$ —— Cu

$2Fe^{+3} + Cu$ —— $Cu^{2+} + 2Fe^{+2}$

$Cu^{+2} + 2Fe^{+3} = 2Fe^{+2} + Cu$

Some other numerical examples; this is a very interesting example again wherein you are considering an ion-ion electrode. So, there is a ferric and a ferrous state here – plus 3 and plus 2. And, you are coupling it to copper and cuprous state. Here this actually is the cathode, where there is a reduction process going on; and, this is the anode, where this is an oxidation going on. So, what would be the cell reaction in this case? So, the cell reaction would be that, the Fe 3 converts into the Fe plus 2 state by giving one electron. $2Fe^{+3}+2e \rightarrow 2Fe^{+2}$ Mind you again as I had earlier illustrated, platinum here is an inert non-participative metal, which is just a conduit, which takes out the electron and the charge from this particular solution. And, on the cupric side – on the cuprous side, the Cu 2 plus gets reduced in to Cu giving two electrons. $\begin{matrix} 2++2e \rightarrow Cu \\ Cu^{\square} \end{matrix}$ So, 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.

$$\begin{matrix} 2++2Fe^{+2} \\ 2Fe^{+3}+Cu \rightarrow Cu^{\square} \end{matrix}$$

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

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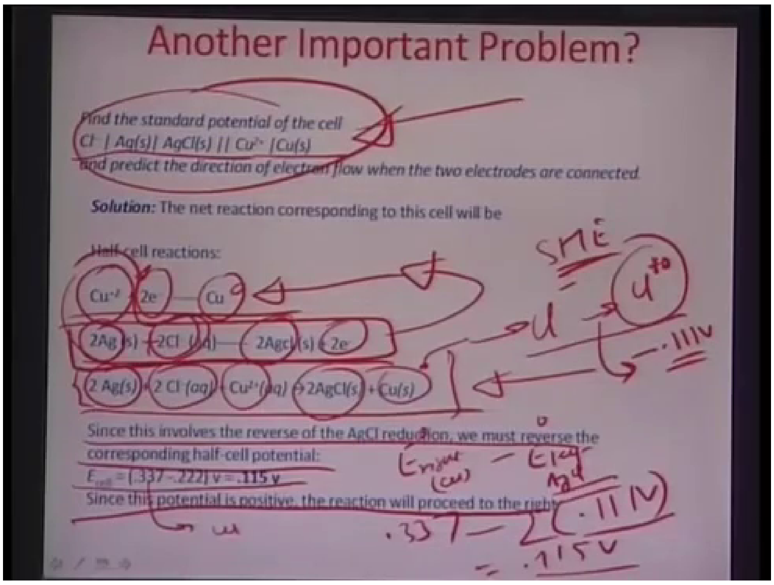

Another Important Problem?

Find the standard potential of the cell
$Cl^- \mid Ag(s) \mid AgCl(s) \mid\mid Cu^{2+} \mid Cu(s)$
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} $2e^-$ — Cu

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

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

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 where we can couple it and form a redox couple with the cuprous copper combination. And, in this case, the standard potential of the cell can be calculated by considering the reactions. So, the right side again is the cathode – is a conversion of the $Cu^{2+} + 2e \rightarrow Cu$. And, at the behest of two electrons, which is liberated in the process; and, in the silver chloride side if you look at, you have this $2\,Ag(s) + 2Cl^{-}(aq) \rightarrow 2\,AgCl(s) + 2e$. So, effectively, you are oxidizing the chlorine or you are trying to make the chlorine electron less and generate 2 electrons here. So, these two coupled together would formulate a redox reaction, wherein $2\,Ag(s) + 2\,Cl^{-}(aq) + Cu^{2+}(aq) \rightarrow 2\,AgCl(s) + Cu(s)$. So, this is essentially the cell reaction that would happen.

So, if I want to generate what is the standard potential of this particular cell; so, as this processing was the you know that the. So, essentially there is a reduction in the chlorine state or this oxidation in the chlorine state. So, therefore, it would be the E right, which is E copper in this particular case minus E_0 left, which is E AgCl in this particular case. And, essentially, if you look at the table before, where we are talking about the standard deduction potentials, this particular illustration here represents the reduction of AgCl really. And so, the reduction of the AgCl is given with respect to a standard hydrogen electrode to be plus 0.11 volts. And so, therefore, if you look at the potential here; you have two times this particular reaction and in the opposite cells; that means, here the Cl minus is oxidized to a Cl plus 0 state. So, the E cell potential of this should be exactly minus 0.11 volts. This process is happening in the reverse manner as would have normally happened if you coupled this two a standard hydrogen electrode. So, 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 notation here minus twice 0.111 volts. So, it comes out to be 0.115 volts. So… Since this potential is positive, the reaction will proceed to the right.

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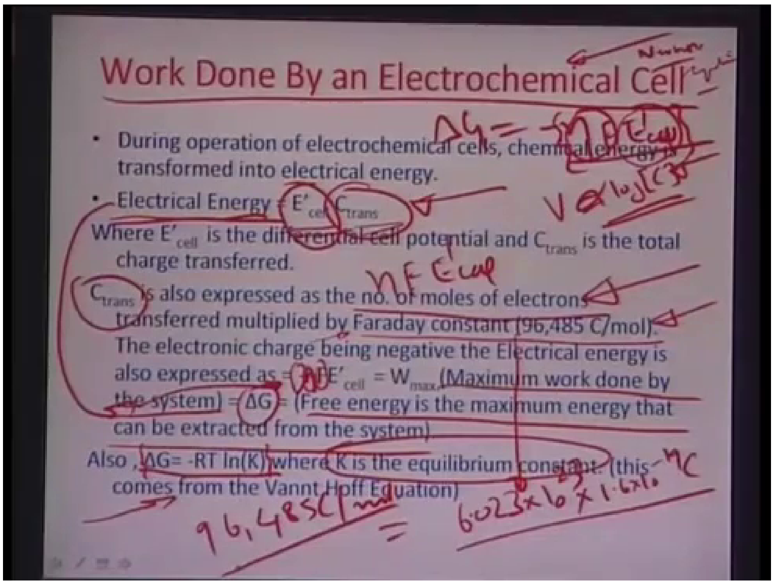

Work Done By an Electrochemical Cell

- 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) = ΔG = (Free energy is the maximum energy that can be extracted from the system)

Also , ΔG= -RT ln(K) where K is the equilibrium constant (this comes from the Vannt Hoff Equation)

$\Delta G = -nFE_{cell}$

$V \propto \log[C]$

nFE_{cell}

$96{,}485\ C/mol = 6.023\times10^{23} \times 1.6\times10^{-19}\ C$

So, the next illustration is again very interesting problem, wherein we talk about the work done by an electrochemical cell. And, we are slowly trying to gauge the voltage equation, which is also known as Nernst equation. And, 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 a preliminary level study for the potentiometry as an area of sensing or diagnostics. So, let us first talk about what is the electrical energy that is spent when bunch of electrons or a bunch of charges is moved from one side of the cell to the other side. So, there is an EMF of the particular cell; let us say E' cell here is the EMF of that particular cell; against which there is kind of total amount of charge transfer of C trans magnitude.

So, against the potential E cell, there are about C Coulombs of charge that are being moved. So, the total amount of electrical energy in this case would be represented as E' cell times of C_{Trans} . So, essentially, charge into potential is the total work done or the electrical energy spent. So, C_{Trans} or the total amount of charge can also be represented as the number of moles of electrons, which is being transferred in the process into the total charge per mole of the electron, which is also known as a Faraday constant – F 96485 coulomb. This gets generated from multiplying 1 mole size, which is $6.023 \times 10^{23} \times the\,electronic\,charg\,e\,, which\,is\,1.6 \times 10^{-19}\,coulomb$. So, this is essentially 1 mole of electrons total amount of charge.

So, if we want to write this electrical energy as with these particular notations, the number of moles of charge transferred and the Faraday constant, we can easily write this electrical energy to be $nF\,E_{cell}^{'}$. So, we can think about that the 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 Gibb's free energy, which is the maximum work that a system can do or has a potential of doing. So, the delta G can be easily equated to… The free energy can be easily equated to $-nF\,E_{cell}^{'}$.

This is the amount of work, which has been already down in order to transfer n F charges through a potential $E_{cell}^{'}$ in a particular illustration. So, the delta G can be equated to $-nF\,E_{cell}^{'}$. And, there is another very common illustration coming from the Van't Hoff equation, where delta G is equated to the equilibrium constant of any reaction K as $-RT\ln K$. And, we will be actually coming to this a little bit later – probably in the next slide.

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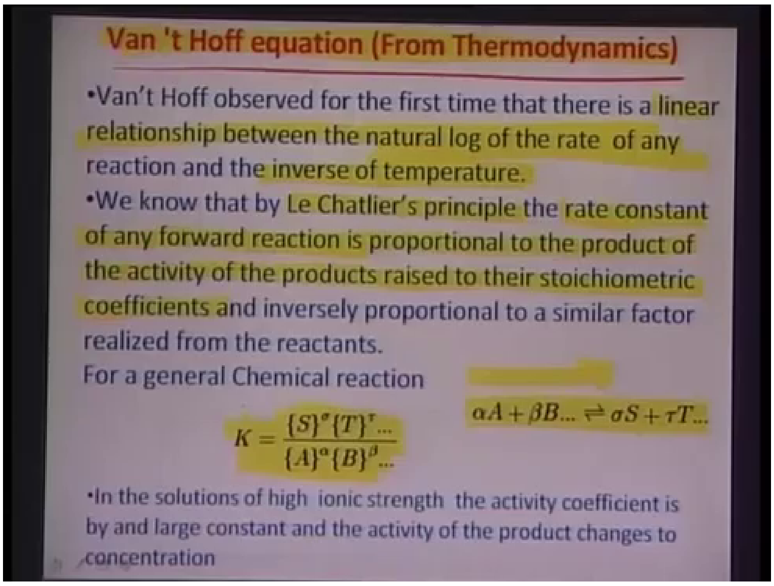

Van 't Hoff equation (From Thermodynamics)

- 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

So, therefore, let us first talk about how this a Van’t Hoff equation comes into picture from thermodynamics. So, the Van’t Hoff observed for the first time that, if you really plot the natural log of the rate of any reaction with respect to the inverse of temperature; and, this actually found for the system of gases. So, there is a strange kind of linear relationship between the two.

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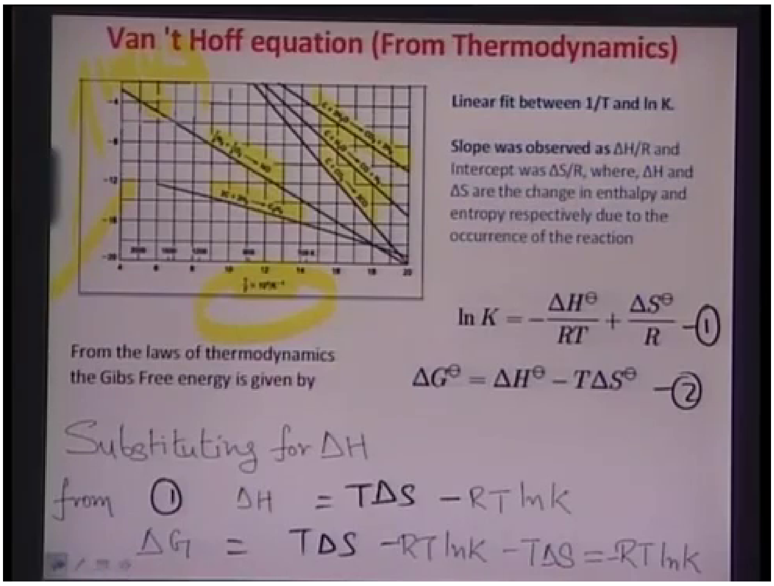

Van 't Hoff equation (From Thermodynamics)

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

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

Subgtituting for ΔH

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

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

This can be illustrated more in this particular curve as we are looking at. So, this is essentially the access which represents the natural log of K; where, K is the equilibrium constant. And, you are plotting this with respect to the inverse of temperature. And so, for different gas systems, he found out systems of gases. And, these all these – these are equilibrium processes essentially. He found out that there is a linear relationship between the inverse of temperature and the log of K. So, what is really the equilibrium constant? This comes from another illustration called the Le Chatlier’s principle; the rate constant of any equilibrium process is of really any forward reaction is propositional to the product of the activity of the product totally created – the activity of the products totally, which are created by a reaction raised to the power there – stoichiometric coefficients.

So, in this particular case, alpha moles of A is reacting to beta moles of B to generate let us a sigma moles of S and tau moles of T. So, 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 A to the power alpha into activity of B to the power of beta. So, we would like to actually continue this and some other illustrations probably in the next lecture.

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

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

Thank you.